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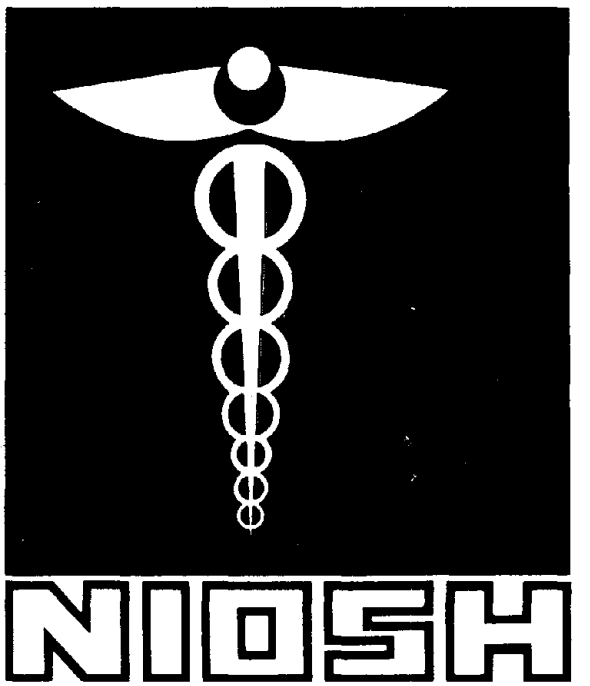

NIOSH MANUAL of ANALYTICAL METHODS

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health

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16. Abstract (Limit: 200 words)

Analytical methods were presented for determining about 135 chemicals in the atmosphere, in the workplace, and in biological materials. Specifically, methods were given for determining lead (7439921), mercury (7439976), antimony (7440360), arsenic (7440382), and fluoride (16984488) in urine; lead and mercury in blood; nitrogen-dioxide (10102440), carbon-monoxide (630080), cyanide (57125), acrolein (107028), beryllium (7440417), formaldehyde (50000), organic solvents, hydrogen-sulfide (7783064), arsenic, 2,4-toluenediisocyanate (584849), sulfur-dioxide (7446095), p,p'-diphenylmethanediisocyanate (101688), vinyl-chloride (75014), cadmium (7440439), chromium (7440473), ozone (10028156), lead, parathion (56382), oil mists, aromatic amines, chromic-acid (1333820) mist, fluoride, hydrogen-fluoride (7664393), and mercury in air; free silica (7631869) in atmospheric dust; and quartz (14808607) in coal dust. For each analytical procedure described the principle of the method was presented followed by the range and sensitivity, possible interferences, precision and accuracy, advantages and disadvantages of the method, apparatus used, reagents, procedure, collection and shipping of samples, analysis of samples, calibration and standards, calculations, and citations to additional references of interest.

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MANUAL OF ANALYTICAL METHODS

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health
Division of Laboratories and Criteria Development

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Mr. John V. Crable and Dr. David G. Taylor, Chief and Assistant Chief respectively, of the Physical and Chemical Analysis Branch were responsible for the development and preparation of the manual.

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DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
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Dear Manual Recipient:

Thank you for inquiring about the NIOSH Manual of Analytical Methods. This compilation of 39 procedures covering about 135 different chemicals is in its 1974 edition.

These are the methods that chemists in the Physical and Chemical Analysis Branch have used for industrial hygiene analyses. Many are adapted from procedures found in the literature. Some of the methods were developed by NIOSH through contracts or interagency agreements. Others were totally developed and evaluated by our research staff.

The NIOSH classification of the analytical methods, found in the front of the Manual, gives the user a guide as to the confidence one should place in the reliability of the method.

We invite your critical comments and suggestions about either typographical or substantive errors found in the Manual so that we may upgrade and enlarge a future edition.

Sincerely yours,

John V. Crable, Chief
Physical & Chemical Analysis Branch

David G. Taylor, Ph.D., Assistant Chief
Physical & Chemical Analysis Branch

Enclosures

NIOSH CLASSIFICATION OF ANALYTICAL METHODS

Physical and Chemical Analysis Branch
Division of Laboratories and Criteria Development

Class A--Recommended---A method which has been fully evaluated and successfully collaboratively tested by a selected group of laboratories.

Class B--Accepted---A method which has been subjected to a thorough evaluation procedure in the NIOSH laboratory and found to be acceptable.

Class C--Tentative---A method which is in wide use and which has been adopted as a standard method or recommended by another Government agency or one of several professional societies such as ACGIH, AOAC, AIHA, ASTM or ISC.

Class D--Operational---A method in general use or approved by most professional industrial hygiene analysts but has not been thoroughly evaluated by NIOSH or any professional societies.

Class E--Proposed---A new, unproved or suggested method not previously used by industrial hygiene analysts but which gives promise of being suitable for the determination of a given substance.

December 17, 1973

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LEAD IN BLOOD AND URINE

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Lead	**Method No.:**	P&CAM 101
Matix:	Blood, Urine	**Range, Blood:**	2 – >200 μg/100 mℓ
Procedure:	Chelation, Extraction, AA	**Range, Urine:**	8 – >500 μg/liter
Date Issued:	3/13/72	**Precision:**	Unknown
Date Revised:	1/15/74	**Classification:**	D (Operational)

1. **Principle of the Method**

   1.1 Whole blood or urine samples are ashed with a mixture of nitric and perchloric acids to destroy the organic matrix.

   1.2 The sample ash is dissolved by the addition of a weak nitric acid solution and the pH of the solution is adjusted to 2.6 – 3.0.

   1.3 The lead is chelated with ammonium pyrrolidine dithiocarbamate (APDC) and extracted from the aqueous phase into methyl isobutyl ketone (MIBK).

   1.4 An aliquot of the MIBK containing the lead-APDC complex is placed in the sampling boat of an atomic absorption spectrophotometer and its absorbance is determined at 2170 A.

2. **Range and Sensitivity**

   2.1 For a 2-mℓ blood sample, the analytical range extends from 2 μg to 200μg per 100 mℓ blood.

   2.2 For a 5-mℓ urine sample, the analytical range extends from 8 μg to 500 μg per liter of urine.

   2.3 The range in both blood and urine can be extended significantly by taking smaller aliquots.

3. **Interferences**

   There are no known interferences for this method.

4. **Precision and Accuracy**

The accuracy and precision of this method have not been completely determined at this time. No collaborative tests have been performed on this method.

5. **Advantages and Disadvantages of the Method**

This method is fast and does not require a high level of technical skill. A trained technician can do 25 – 30 samples per day. The only known disadvantage of this method is the need for special equipment. A sampling boat system for an atomic absorption spectrophotometer, together with the proper facilities for the handling and use of perchloric acid, is required. The MIBK solvent layer *cannot* be aspirated in the normal fashion because of the large amount of precipitate formed by the addition of the APDC. This precipitate can clog the capillary aspiration tubes. The small volume of MIBK is also detrimental to the successful aspiration of the organic phase.

6. **Apparatus**

6.1 15-mℓ pyrex graduated centrifuge tubes

6.2 Atomic absorption spectrophotometer equipped with sampling boat (Perkin-Elmer) or solid phase sampler (Instrumentation Laboratory) and air-acetylene system.

6.3 Hood facilities capable of handling perchloric acid fumes

6.4 Vortex mixer

6.5 125-mℓ Phillips borosilicate glass beakers

6.6 Centrifuge

6.7 Eppendorf pipets

6.8 125-mℓ polyethylene bottles with Teflon lined caps.

6.9 5-mℓ lead-free, heparinized Vacutainers

7. **Reagents**

The reagents described must be made up using ACS reagent grade or a better grade of chemical.

7.1 Double distilled water

7.2 Redistilled concentrated nitric acid (16 N)

7.3 Lead-free perchloric acid, 70% (G. Frederick Smith Chemical Company, Columbus, Ohio/or equivalent)

7.4 High Purity Ammonium Hydroxide, Sp. Gr. 0.92, (G. Frederick Smith Chemical Company/or equivalent)

7.5 High Purity Glacial Acetic Acid (G. Frederick Smith Chemical Company/or equivalent)

7.6 Ammonium Pyrrolidine Dithicarbamate (APDC) (Fisher Reagent Grade or equivalent): 2% in double distilled water.

7.7 Methyl Isobutyl Ketone (MIBK): water saturated

7.8 Bromphenol blue solution: Dissolve 0.10 g in 7.45 mℓ 0.02 N NaOH and dilute with double distilled water to 250 mℓ.

7.9 Thymol – Reagent Grade

8. **Procedure**

8.1 **Cleaning of Equipment.** All glassware must be rendered lead-free before use. This can be accomplished by using the following three-step procedure:

8.1.1 Wash in detergent-tap water and follow with tap water and distilled water rinses.

8.1.2 Soak in hot chromic acid and follow with tap and distilled water rinses.

8.1.3 Soak in 1:1 or concentrated nitric acid for 30 minutes and follow with tap, distilled, and double distilled water rinses.

This entire procedure must be used only when glassware is being initially prepared for use in the lead analysis. For each following successive use of equipment which has previously been subjected to the entire cleaning procedure, it is necessary only to use the nitric cleaning procedure described in step 8.1.3. Polyethylene equipment can be effectively cleaned by subjecting it to steps 8.1.1 and 8.1.3.

Note: Chromic acid cannot be used on polyethylene.

8.2 Collection and Shipping of Samples

8.2.1 *Blood* must be collected in lead-free heparinized vacutainers equipped with sterilized stainless steel needles. The vacutainers should be heparinized before the collection of the blood. Heparinized vacutainers are available commercially from most laboratory supply houses. The addition of a preservative after the collection of the blood can result in error because of volume changes. Caution should be exercised during handling to prevent any external contamination. The samples should be kept as cool as possible (do not freeze) during storage and shipment and should be shipped to the laboratory as quickly as possible. Heparinized, refrigerated blood samples are stable for two weeks. Two milliliters (2 mℓ) of whole blood are adequate for this determination.

8.2.2 *Urine* samples must be collected in lead-free borosilicate or polyethylene bottles. At least 25 mℓ should be collected. The sample must be preserved by the addition of 5 mg of thymol per 100 mℓ of urine. The urine should be kept cool during shipment and storage. Urine treated with thymol and refrigerated is stable for one week.

8.2 Analysis of Samples

8.3.1 To a clean 125-mℓ Phillips borosilicate glass beaker add 2 mℓ of heparinized whole blood or 5 mℓ of urine followed by 4 mℓ of concentrated nitric acid, and 1 mℓ of perchloric acid. A reagent blank using 2 mℓ of double distilled water in place of the blood or urine should also be started at this point.

8.3.2 The samples are heated until nearly dry, at which point the dense white fumes of perchloric acid should be coming off the sample. The color of the residue should range from yellow to white. If the residue has not reached this color, the beaker should be allowed to cool briefly, and 1 mℓ of perchloric acid should be added and the procedure repeated. When all organic matter has been destroyed, 1 mℓ of HNO_3 and 5 mℓ of distilled H_2O are added to the beaker and heat is applied slowly. When the residue has dissolved, the solution is transferred to a clean 15-mℓ centrifuge tube and made up to 10 mℓ with distilled water.

8.3.3 Pipet 1 or 2 mℓ of this solution into a clean 15-mℓ centrifuge tube.

8.3.4 Add 2 drops of bromphenol blue solution and mix. At this point the solution should be some shade of yellow.

8.3.5 Add NH_4OH dropwise until the solution color turns pale blue and mix with Vortex.

8.3.6 Add 0.5 mℓ of glacial acetic acid and mix with Vortex.

8.3.7 Add 0.4 mℓ of 2% APDC solution and mix with Vortex.

8.3.8 Add 3 mℓ of water-saturated MIBK and mix for 2 minutes with Vortex.

8.3.9 Centrifuge samples for 2 – 3 minutes to separate layers.

8.3.10 Pipet 200 μℓ of MIBK layer into the sampling boat and move the sampling boat toward the flame until the solvent ignites. Let the solvent burn off completely and after the boat appears completely dry, insert it into the flame and measure the percent absorption with a recorder. The ignition of the MIBK does not result in a loss of lead.

Note: The Pb – APDC complex is unstable in the MIBK. If the analyses are to be run immediately, the MIBK layer can be left on the aqueous layer. If there is to be a time lag between the centrifugation and the analysis, the MIBK must be removed and placed in a sealed, clean tube. It is recommended that no more than 10 samples be carried through the procedure at one time. If more samples are prepared for analysis at one time, the loss of lead from the MIBK phase is significant in the last few samples analyzed because of the time lag from the first sample analyzed to the last.

9. Calibration and Standards

9.1 A 1-mg/mℓ Pb stock standard is first made up by drying lead nitrate at 100°C for two hours, cooling, weighing out 1.5980 g, dissolving in 1:10 HNO_3, and making up to a 1-liter volume with additional 1:10 HNO_3. From this 1-mg/mℓ standard, working standards of 0.1, 0.2, 0.3, and 0.5 μg of Pb per mℓ of solution can be made up by appropriate dilutions with 1:10 HNO_3. The stock standard is stable for six months. The working standards should be made up fresh weekly.

9.2 A calibration curve is constructed by pipetting 0.5 mℓ of each working standard into a graduated centrifuge tube and then proceeding from step 8.3.4 of the procedure. A calibration curve of percent absorption versus micrograms of Pb on the sampling boat is then drawn up.

10. Calculations

10.1 The calculations for determining the concentration of Pb per 100 mℓ of blood would be as follows:

$$\frac{2\ \text{mℓ MIBK}}{0.2\ \text{mℓ MIBK}} \times \frac{\text{mℓ sample ash solution}}{\text{mℓ removed for extraction}} \times \frac{100\ \text{mℓ blood}}{\text{mℓ ashed}} \times \text{microgram reading from cal. curve}$$

= μg Pb/100 mℓ blood

10.2 The calculations for determining the concentration of Pb per liter of urine are similar.

$$\frac{2\ \text{mℓ MIBK}}{0.2\ \text{mℓ MIBK}} \times \frac{\text{mℓ sample ash solution}}{\text{mℓ removed for extraction}} \times \frac{1000\ \text{mℓ urine}}{\text{mℓ ashed}} \times \text{microgram reading from curve}$$

= μg Pb/liter of urine

11. References

11.1 Farrelly, R.O. and J. Pybus, "Measurement of Blood and Urine by Atomic Absorption Spectrophotometry," *Clinical Chemistry*, 15:566 (1969).

11.2 Hwang, J.Y., P. Ullucci, and A. Malenfant, "Atomic Absorption Spectrometric Determination of Lead in Blood by the Solid Phase Sampler Technique," Instrumentation Laboratory, Inc., Applications Report, 1971.

LEAD IN BLOOD AND URINE

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Lead	**Method No:**	P&CAM 102
Matrix:	Blood, Urine	**Range, Blood:**	3- > 250μg/100 mℓ
Procedure:	Dithizone	**Range, Urine:**	12- > 1000μg/100 mℓ
Date Issued:	3/23/72	**Precision:**	Average Coefficient of variation is 6%
Date Revised:	1/15/74	**Classification:**	A (Recommended)

1. **Principle of the Method**

   1.1 Whole blood or urine samples are ashed with nitric acid to destroy the organic matrix.

   1.2 The sample ash is dissolved in concentrated nitric acid and the solution diluted by the addition of double-distilled water.

   1.3 Diphenylthiocarbazone, which reacts with lead at pH 6 to 11.5, is added and lead dithizonate is formed. The dithizonate is then quantitatively extracted into chloroform at a pH of 9 to 11.

   1.4 The color of the lead dithizonate follows Beer's Law. Its absorbance is measured in a spectrophotometer at 510 nanometers.

2. **Range and Sensitivity**

   2.1 For a 10-mℓ blood sample, the analytical range extends from 3 μg to 250 μg per 100 mℓ of blood.

   2.2 For a 25-mℓ urine sample, the analytical range extends from 12 μg to 1000 μg per liter of urine.

   2.3 If the amount of lead in a given sample is found to exceed these ranges, a smaller aliquot may be taken for analysis.

3. Interferences

This procedure is subject to interference from stannous tin, bismuth, and thallium. However, these elements are found in biological samples so infrequently, that they do not present a significant problem.

4. Precision and Accuracy

This method has a reported accuracy of 97 ± 2% and coefficient of variation of 6% (Reference 11.1). These values are attainable by an experienced analyst.

5. Advantages and Disadvantages of the Method

5.1 The principal advantage of this method is that it has been thoroughly tested and evaluated. There are no other significant advantages.

5.2 On the other hand there are several significant disadvantages. Large quantities of glassware must be cleaned and kept clean. Large quantities of difficult-to-make reagents are required. This procedure is highly susceptible to contamination from outside sources. Finally, the procedure is tedious and time consuming and requires an analyst with a relatively high level of proficiency.

6. Apparatus

6.1 125-mℓ or 250-mℓ Phillips borosilicate glass beakers.

6.2 Squibb-type 125-mℓ separatory funnels with Teflon stopcocks.

6.3 A spectrophotometer capable of absorbance measurements at 510 nanometers and the appropriate sample cells.

6.4 Burettes with Teflon stopcocks for dispersing reagents.

6.5 Electric shakers capable of holding 8 separatory funnels.

7. Reagents

Analytical grade reagents are used. Purification is essential when biological tissues and fluids are being analyzed, because of the very low levels of lead in these materials. A reagent blank sample is carried through the entire procedure with each set of unknown samples and its analyzed lead content is subtracted from each analytical result to calculate the net quantity of lead in each unknown sample.

A boiling rod is used to prevent bumping in the flasks when the reagents are distilled. This rod is prepared by cutting 3- or 4-mm O.D. glass tubing to a length 1 cm greater than the height of the flask. The tubing is sealed at a spot about 1 cm above the bottom end which is firepolished but left open. Before each use, the liquid is shaken

out of the bottom section and the rod inserted in the flask. As the flask is heated a steady stream of air and vapor bubbles issues from the open space, thus providing nuclei for smooth boiling.

7.1 **Double-distilled Water.** To distilled water in an all-borosilicate glass still add a crystal each of potassium permanganate and barium hydroxide and redistill. Use for reagent and biological sample solutions unless tests indicate that single-distilled water is satisfactory; single-distilled water is usually adequate for air sample determinations.

7.2 **Nitric Acid, Concentrated.** Redistill in an all borosilicate-glass still the ACS reagent grade acid, 69.0% minimum, specific gravity 1.42. Use an electric heating jacket on the boiling flask to minimize danger of its breakage, and a boiling rod to prevent bumping, which otherwise would be severe. Discard the first 50 mℓ of distillate; this may be combined with the acid allowed to remain in the flask at the end of the distillation and used for washing glassware. The reagent is conveniently dispensed from a small automatic burette. No grease should be used on the stopcock.

7.3 **Nitric Acid,** 1:99. Dilute 10 mℓ of the redistilled, concentrated acid to 1 liter with double-distilled water.

7.4 **Ammonium Hydroxide, Concentrated.** Distill, in an all borosilicate-glass still, 3 liters of the ACS reagent grade, 28.0% minimum, specific gravity, 0.8957 at 60°F, into 1.5 liters of double-distilled water, contained in a 2-liter reagent bottle which is chilled in an ice bath. Continue the distillation until the bottle is filled to the previously marked 2-liter level. Submerge the condenser tube deeply in the water in the receiver, but withdraw it before discontinuing the heat to avoid siphoning back of distillate. This reagent may be prepared more conveniently from tank ammonia, using a small wash bottle to scrub the gas and a sintered glass delivery tube which extends to the bottom of the reagent bottle. The ammonia gas is absorbed in double-distilled water until the solution reaches the desired specific gravity.

7.5 **Chloroform.** Use a brand with a statement on the label that the chloroform passes the American Chemical Society test for suitability for use in dithizone procedures. In addition, each batch of chloroform should be purchased in glass containers only and should be tested as follows in the laboratory to make sure it is satisfactory for preparing the dithizone solutions: Add a minute quantity of dithizone to a portion of the chloroform in a test tube; shake gently, and then stopper with a cork. The faint green color should be stable for one day. Our experience has indicated that the procedures for reclaiming used chloroform are tedious, time-consuming, sometimes unsuccessful, and no longer warranted in view of the commercial availability of acceptable reagent grades.

7.6 **Extraction Dithizone.** Dissolve 16 mg of diphenylthiocarbazone (dithizone), Eastman Kodak Co. No. 3092, or equivalent, in 1 liter of chloroform. Store in a brown bottle in the refrigerator.

7.7 **Standard Dithizone.** Dissolve 8 mg of diphenylthiocarbazone in 1 liter of chloroform. Store in a brown bottle in the refrigerator BUT ALLOW TO WARM TO ROOM TEMPERATURE BEFORE USING. Age for at least one day; then standardize as described in the procedure. Restandardize every few months.

7.8 **Sodium Citrate.** Dissolve 125 g of the 2 $Na_3C_6H_5O_7.11\ H_2O$ salt in sufficient distilled water to provide a solution nearly 500 mℓ in volume. Adjust the pH to 9-10, using a very small quantity of phenol red indicator solution (strong red color) and fresh, pHydrion test paper to check the pH. Extract in a large separatory funnel with a 100 mg per liter chloroform solution of dithizone and finally with the extraction dithizone reagent until a green extract is obtained with the latter reagent. Add a small volume of lead-free citric acid until an orange color (pH 7) appears. Extract the excess dithizone repeatedly with chloroform until a colorless extract is obtained. Remove the last traces of chloroform.

7.9 **Hydroxylamine Hydrochloride.** Dissolve 20 g of the salt in distilled water to provide a volume of 65 mℓ. Add a few drops of m-cresol purple indicator, and then add ammonia until the indicator turns yellow (pH 3). Add a sufficient quantity of a 4% solution of sodium diethyldithiocarbamate to combine with metallic impurities. Mix. After a few minutes extract repeatedly with chloroform until the excess carbamate has been removed, as indicated by the absence of a yellow color in the final chloroform extract tested with a dilute copper solution. To the aqueous solution of the hydroxylamine hydrochloride add redistilled, 6N hydrochloric acid until the indicator turns pink, and adjust the volume to 100 mℓ with double-distilled water.

7.10 **Potassium Cyanide. (DANGER! HIGHLY POISONOUS!!)** To 50 g of potassium cyanide in a beaker, add sufficient distilled water to make a sludge. Transfer the sludge to a separatory funnel previously marked to show a 100-mℓ volume. Add a small amount of distilled water to the beaker and warm. (Potassium cyanide cools the solution as it dissolves, thus retarding the solution process.) Add this warm water to the separatory funnel but do not permit contents to exceed the 100-mℓ mark. Shake. Let stand until the contents come to room temperature. A practically saturated solution results.

Extract the lead by shaking repeatedly with portions of the extraction dithizone solution until the lead has been removed. Part of the dithizone dissolves in the aqueous phase but enough remains in the chloroform to color it. A green extract indicates that the lead has been completely extracted. Most of the dithizone in the aqueous phase is then removed by repeated extractions with pure chloroform.

Dilute the concentrated solution of potassium cyanide to 500 mℓ with double-distilled water. It should not be necessary to filter the solution, if the directions are followed precisely. Extraction is carried out before dilution because the higher pH of the dilute solution is less favorable.

Note: A colorless solution usually results if the above directions are followed. Occasionally aging results in a brown color or precipitate because of polymerization of hydrogen cyanide. This does not interfere with use of the reagent if it is carefully decanted. Old potassium cyanide reagent may lose enough strength to cause insufficient complexing of large amounts of zinc.

7.11 **Ammonia-Cyanide Mixture.** Mix 200 mℓ of the purified 10% potassium cyanide reagent with 150 mℓ of distilled ammonium hydroxide (specific gravity 0.9, corresponding to 28.4% NH_3) and dilute to 1 liter with double distilled water. If the measured specific gravity of the ammonia is not 0.9, use the equivalent volume as calculated from a table of specific gravity vs percent ammonia.

8. Procedure

8.1 **Cleaning of Equipment.** All glassware must be rendered lead-free before use. This can be accomplished by using the following three-step procedure.

8.1.1 Wash in a detergent-tap water and follow with tap water and distilled water rinses.

8.1.2 Soak in hot chromic acid and follow with tap and distilled water rinses.

8.1.3 Soak in 1:1 or concentrated nitric acid for 30 minutes and follow with tap, distilled, and double distilled water rinses. This entire procedure must be used only when one is initially preparing glassware for use in the lead analysis. For each following successive use of equipment which has previously been subjected to the entire cleaning procedure, it is necessary only to use the nitric cleaning procedure described in step 8.1.3. Polyethylene equipment can be effectively cleaned by subjecting it to steps 8.1.1 and 8.1.3. Chromic acid cannot be used on polyethylene.

8.2 **Collection and Shipping of Samples**

8.2.1 **Blood** must be collected in lead-free, heparinized vacutainers equipped with sterilized stainless steel needles. The vacutainers should be heparinized before the collection of the blood. Heparinized vacutainers are available commercially from most laboratory supply houses. The addition of a preservative after the collection of the blood can result in error because of volume changes. Caution should be exercised during handling

to prevent any external contamination. The samples should be kept as cool as possible (do not freeze) during storage and shipment and should be shipped to the laboratory as quickly as possible. Heparinized, refrigerated blood samples are stable for two weeks. Two milliliters (2 mℓ) of whole blood are adequate for this determination.

8.2.2 **Urine** samples must be collected in lead-free borosilicate or polyethylene bottles. At least 25 mℓ should be collected. The sample must be preserved by the addition of 5 mg of thymol per 100 mℓ of urine. The urine should be kept cool during shipment and storage. Urine treated with thymol and refrigerated is stable for one week.

8.3 **Analysis of Sample**

8.3.1 Transfer 10 mℓ of heparinized blood or 25 mℓ of urine to a 125-mℓ Phillips borosilicate glass beaker and add 7 mℓ nitric acid.

8.3.2 Place the samples on a hotplate operating at about 130°C and evaporate just to dryness. After the water is driven off in the initial evaporation to dryness, keep the beaker covered with a lead-free watchglass to increase the reflux action of the concentrated acid.

8.3.3 Cool the beaker briefly and then add successive portions of nitric acid ranging from 2 mℓ down to 0.5 mℓ as the ashing proceeds. Do not remove the watchglass at any time but merely slide it back sufficiently to facilitate each new addition of the acid.

8.3.4 Each time, as soon as the residue becomes light colored, heat on a 400°C hotplate **just long enough to blacken the residue**; then remove and cool the sample. Throughout the remainder of the ashing procedure, alternately heat the sample with a few drops of nitric acid on the 130°C hotplate and bake the residue on the 400°C hotplate for the few minutes required to darken it. Finally, the residue will remain pale yellow or light brown (due to iron content) after it has been heated for 5-10 minutes at the high temperature. Avoid excess baking at this stage because the ash will become decomposed to a difficultly soluble form. It is now ready for solution and analysis.

8.3.5 Warm the sample ash with 2 mℓ of concentrated nitric acid for a few minutes. Then add 25 mℓ of distilled water and heat on the hotplate until a clear solution is obtained.

8.3.6 Cool to room temperature. Add to the solution in the beaker 1 mℓ of hydroxylamine hydrochloride, 4 mℓ of sodium citrate (10 mℓ is required

for a urine sample), and 1 drop of phenol red indicator, and titrate to a strong red color with concentrated ammonia reagent. Add a few drops excess of ammonia to make sure that the pH is between 9 and 10, using fresh pHydrion test paper to check the pH.

Note: Phenol red has a weak orange-red color in strong acid, yellow in weak acid, and a red color in alkaline solution. Do not mistake the first color for that produced in alkaline medium.

8.3.7 Transfer the sample quantitatively with double-distilled water rinsings to a 125-mℓ Squibb separatory funnel containing 5 mℓ of the potassium cyanide reagent.

8.3.8 Add 5 mℓ of the extraction dithizone and shake two minutes, after releasing the initial pressure by momentarily opening the stopcock of the inverted separatory funnel. Allow the chloroform layer to settle.

8.3.9 Draw off most of the extraction dithizone into a second funnel containing **exactly** 30 mℓ of 1:99 nitric acid.

8.3.10 Add a second 5-mℓ portion of extraction dithizone to the first funnel and shake as before. Allow the layers to separate and combine the extracts in the second funnel. Continue the process until the extraction dithizone reagent remains green. A rough estimate of the lead present in the sample may be made on the basis of 20 μg for each cherry red 5 mℓ extract.

8.3.11 Shake the second funnel for two minutes to transfer the lead to the 1:99 nitric acid layer. Allow the layers to separate. Discard the chloroform layer.

8.3.12 Shake the nitric acid solution with approximately 5 mℓ of reagent chloroform and let settle. Drain the settled chloroform through the stopcock bore as completely as possible without loss of the aqueous layer. Evaporate the last drop of chloroform clinging to the upper surface of the liquid.

Note 1: Start a zero lead standard at the beginning of this step by placing 30 mℓ of 1:99 nitric acid in a separatory funnel. This zero lead standard will be used to set the spectrophotometer at zero absorbance for each series of samples being analyzed.

Note 2: If the quantity of lead estimated for any sample exceeds the 25-μg range of the colorimetric determination, pipet an appropriate aliquot of the nitric acid solution at the end of Step 8.3.11 into a clean

separatory funnel that contains 5 mℓ of 1:99 nitric acid (to minimize errors by possible leakage of the stopcock). Add sufficient 1:99 nitric acid to make 30 mℓ total volume, and continue from the beginning of 8.3.12.

Note 3: Start lead standards at this point if required. Add 5 mℓ portions of 1:99 nitric acid to each of four separatory funnels, then 2.5-, 5.0-, 7.5-, and 12.5-mℓ portions of dilute standard lead solution (2 μg Pb/mℓ) from a burette, one to each separatory funnel. Finally, add the proper quantity of 1:99 nitric acid to make a total volume of 30 mℓ. Continue from the beginning of 8.3.12.

8.3.13 Add 6.0 mℓ of the ammonia-cyanide mixture, **exactly** 15.0 mℓ of the **standard** dithizone, and shake two minutes. Allow the layers to separate. Drain the chloroform layer containing the lead dithizonate into a clean, dry test tube, and cork the tube immediately.

8.3.14 Decant this solution carefully into a dry photometer tube leaving the water behind. If any water spots are visible in the optical light path, transfer again to another photometer tube.

8.3.15 Set the spectrophotometer at a wavelength of 510 mμ.

8.3.16 Set the instrument at zero absorbance using the zero lead standard solution.

8.3.17 Read the absorbances of the samples and of the reagent blank.

9. Calibration and Standards

9.1 **Standard Lead Solution.** Dissolve 1.5984 g of pure lead nitrate in 1 liter of 1:99 nitric acid to provide a strong stock solution that contains 1 mg Pb per mℓ. Pipet exactly 20-mℓ into a 500-mℓ volumetric flask and make to mark with 1:99 nitric acid to give a dilute stock solution containing 40 μg Pb per mℓ. (A standard lead solution, 10 μg Pb/mℓ, was stable in 1:99 nitric acid for three years.) Prepare a working solution, containing 2 μg Pb per mℓ, just before it is needed by pipetting 5 mℓ into a 100-mℓ volumetric flask and making to mark with 1:99 nitric acid.

9.2 **Standard Curve.** A standard curve is constructed (see 8.3.12, Note 3) using 5-, 10-, 15-, and 25-μg quantities of lead.

10. Calculations

Calculate the lead content of each sample by multiplying its absorbance by the standardization factor (the slope of the standard curve in micrograms of lead per unit

of absorbance). Subtract the blank value from the gross lead content of each sample to obtain the net amount of lead expressed in micrograms. Divide this value by the original sample volume to obtain the concentration of lead in the original sample.

11. References

11.1 Keenan, R.G., et al., "The 'USPHS' Method for Determining Lead in Air and in Biological Materials," *Amer. Ind. Hyg. Assoc. J., 24:* 481 (1963).

MERCURY IN URINE

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Mercury	**Method No.**	P&CAM 103
Matrix:	Urine	**Range, Urine:**	0.003-0.3 mg/liter
Procedure:	Flameless Atomic Absorption	**Precision:**	Unknown
Date Issued:	3/30/72		
Date Revised:	12/1/73	**Classification:**	D (Operational)

1. **Principle of the Method**

   1.1 The urine sample is decomposed by treatment with strong nitric acid.

   1.2 Stannous chloride is added to reduce the ionic mercury species to elemental mercury, which is then purged from the solution with a gas stream and passed through a photometric detector set to detect the absorption of 254-nanometer radiation by the mercury vapor.

   1.3 The mercury content of the sample is calculated from calibration data for the sparger photometer system obtained by carrying known amounts of ionic mercury standards through the analysis procedure.

2. **Range and Sensitivity**

   2.1 For typical sparger-photometer systems utilizing 15.5-cm photometer cells, the sensitivity for mercury is 6 nanograms or less (Reference 11.1). For the 2.0-mℓ urine sample used in this method, the corresponding concentration limit is 3 μg/liter.

   2.2 The linear range extends to 0.3 mg mercury per liter for a 2-mℓ urine sample, and can be carried further by using a smaller sample.

3. **Interferences**

   3.1 Metals such as copper, gold or platinum, if present, are negative interferences since they are reduced by $SnCl_2$, and will then alloy with the mercury before it can be measured.

3.2 Organic solvents that absorb 254-nanometer radiation can be positive interferences if present in significant amounts. Examples are benzene and toluene. These compounds should not be used as preservatives.

4. Precision and Accuracy

4.1 Known amounts of mercury were added in the 0.05-0.1 mg/liter range to previously analyzed urine samples and the theoretical percent recoveries were calculated for eight samples. Recoveries ranged from 96% to 104% with the mean value being 99.6% (Reference 11.1).

4.2 Results obtained by this method were compared with results obtained using the dithizone colorimetric procedure on a series of 10 urine samples containing 0.02 to 0.3 mg/liter mercury. Absolute deviations between the methods varied from 0.00 to 0.02 mg/liter with the average deviation being 0.007 mg/liter.

5. Advantages and Disadvantages of the Method

5.1 This method is quite rapid. A trained technician can do 20-40 samples a day.

5.2 One important disadvantage of this method is that the nitric acid treatment will not release organomercury compounds in the sample.

6. Apparatus

6.1 A mercury evolution train is used. It consists of a source of gas (generally an air pump), a sparger or bubble vessel and a photometer cell (generally 10- to 20-cm path length) connected in that order by tubing. Typical trains are shown in References 11.1 and 11.3.

6.2 The photometric detector system consists of a radiation source capable of isolating the 254-nanometer mercury emission line (a low pressure mercury lamp in virtually all cases), the photometer cell (in 6.1) and a photo-detector-amplifier system. Many commercial and laboratory constructed versions have been described (1) (3). Typical units are manufactured by Perkin-Elmer Corporation, Coleman Instrument Corporation and Laboratory Data Control, Inc.

During operation of the system the maximum signal (mercury vapor absorption) can be read by observing the maximum reading on the signal meter or digital display; however, the most convenient method is to record the signal on a laboratory recorder interfaced to the detector.

6.3 Miscellaneous analytical equipment; all glassware should be cleaned as in 8.1.

6.3.1 Pipets: 2, 5, 10 and 25 mℓ.

6.3.2 Volumetric flasks: 100, 500 and 1000 mℓ.

7. Reagents

All reagents described must be ACS reagent grade or equivalent.

7.1 Water, double distilled.

7.2 Nitric Acid, 68%.

7.3 Hydrochloric Acid, 36%.

7.4 **Stannous Chloride Solution,** 20% (w/v) in 6 NHCl. Dissolve 20 g stannous chloride in 50 mℓ hydrochloric acid, and dilute to 100 mℓ with double distilled water.

7.5 **Mercury Standard Solutions**

7.5.1 Stock solution, 1000 μg/mℓ. Suitable stock solutions are now available from several reputable laboratory supply houses. Alternatively, the stock solution can be prepared by dissolving exactly 1.353 g of mercuric chloride ($HgCl_2$) in 5 mℓ of hydrochloric acid and diluting to 100 mℓ with double distilled water.

7.5.2 Stock solution, 50 μg/mℓ. Pipet 25 mℓ of 1000 μg/mℓ stock solution (7.5.1) into a 500-mℓ volumetric flask. Add 10 mℓ of nitric acid (68%) and dilute to volume with double distilled water. This solution is reported to be stable for six months (Reference 11.1).

7.5.3 Working standard, 0.5 μg/mℓ. Pipet 10 mℓ of the 50 μg/mℓ stock solution (7.5.2) into a 1-liter volumetric flask. Add 20 mℓ of HNO_3 (68%) and dilute to volume with double distilled water. The final concentration is 0.5 μg/mℓ. This solution should be prepared fresh daily.

7.6 **Antifoam Solution** (Reference 1). Suspend 5 g of General Electric "antifoam 60" in 95 mℓ of double distilled water. Antifoam 60 is available from General Electric Company, Silicone Products Division, Waterford, New York.

8. Procedure

8.1 **Cleaning of Equipment.** All glassware must be acid-cleaned before use. This can be done by using the following procedure.

8.1.1 Wash in detergent-tap water solution and follow with tap water rinse.

8.1.2 Soak in chromic acid (sulfuric acid mixture) and follow with tap and distilled water rinse.

8.1.3 Soak in concentrated HNO_3 for 30 minutes and follow with tap, distilled, and double distilled water rinses.

Note: For each following successive use of equipment which has previously been acid cleaned, it is only necessary to use the nitric acid cleaning procedure given in Step 8.1.3 but for less soaking time (3 minutes).

8.2 **Collection and Storage of Samples.** Urine samples must be collected in acid cleaned borosilicate or polyethylene bottles. At least 25 mℓ should be collected. The samples must be preserved by the addition of 5 mg of thymol per 100 mℓ of urine. The urine should be kept cool during shipment and storage. Urine treated with thymol and refigerated is stable for one week.

8.3 **Analysis of Samples**

8.3.1 Transfer a 2.0 mℓ urine sample to the sparger/bubbler reaction vessel. If a sediment is present in the collection bottle, shake well immediately before removing the aliquot and continue to swirl the bottle gently while withdrawing the sample. Add 5 mℓ of concentrated HNO_3 to the sample aliquot and allow the mixture to stand at room temperature for 3 minutes.

Note: The water used to dilute the samples and standards should be at the same temperature (± 1°C) since variations in water temperature produce variations in peak height of nearly 1% per degree Centigrade (Reference 11.1).

8.3.2 Add 95 mℓ of distilled water (temperature known) blowing out any mist that may form above the liquid with gentle puffs of air or nitrogen. Add two drops antifoam solution. Add 5.0 mℓ of $SnCl_2$ solution and then immediately connect the flask to the bubbler tube in the generating train.

8.3.3 Observe or record the minimum percent transmittance or maximum absorbance. If the reading goes beyond calibration range, repeat the analysis using a smaller sample volume.

9. Calibration and Standards

9.1 Add 5 mℓ of concentrated nitric acid to the sparger/bubbler vessel and then add 95 mℓ of distilled water (same temperature as sample water). Gently blow out mist above the solution with a gentle purge of air or nitrogen.

9.2 With a 1-mℓ graduated pipet add a measured quantity (between 0 and 1 mℓ of the standard working solution (0.5 μg/mℓ) to the vessel. Immediately add two drops of antifoam solution and 5.0 mℓ $SnCl_2$ solution. Then connect the bottle quickly to the fritted bubbler tube in the generating train.

9.3 Observe or record the detector response as in 8.3.3.

9.4 Repeat the calibration with appropriate quantities of mercury to cover the entire working range (0.006-0.6 μg mercury).

9.5 Prepare a calibration curve by plotting percent transmittance versus μg mercury added (calculated from mℓ solution x 0.5 μg per mℓ).

9.6 Run a calibration series before beginning samples, then insert a standard between every 5th or 6th sample to maintain a check on method integrity.

10. Calculations

10.1 From the percent transmittance reading for each sample, read the micrograms of mercury in the sample from the calibration curve.

10.2 The mercury concentration in the urine sample is then calculated:

$$\text{Mercury Concentration (mg/liter)} = \frac{\mu\text{g mercury found}}{\text{m}\ell \text{ of sample taken}}$$

11. References

11.1 Rathje, Arnold O., "A Rapid Ultraviolet Absorption Method for the Determination of Mercury in Urine," Am. Ind. Hyg. Assoc. J., 30, 126-132 (1969).

11.2 Wall, H., and Rhodes, C., "The Effect of Bacterial Contamination and Aging on the Volatility of Mercury in Urine Specimens," Clin. Chem., 12, 837-43 (1966).

11.3 Hatch, W.R., and Ott, W.L., "Determination of Sub-Microgram Quantities of Mercury by Atomic Absorption Spectrophotometry," Anal. Chem., 40, 2085 (1968).

MERCURY IN BLOOD

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Mercury	**Method No.:**	P&CAM 105
Matrix:	Blood	**Range:**	0.005 – 4.5 μg/mℓ Not Verified
Procedure:	Flameless Atomic Absorption	**Precision:**	Unknown
Date Issued:	3/31/72	**Classification:**	D (Operational)
Date Revised:	1/15/74		

1.* **Principle of the Method**

1.1 Whole blood samples are cold digested with H_2SO_4.

1.2 Permanganate solution, HNO_3 and H_2SO_4 are added to oxidize the organic matter.

1.3 Mercury is liberated by reduction with a $SnCl_2$ solution, and the amount of Hg vapor produced is measured (percent transmittance) by an ultraviolet light Hg vapor meter.

2. **Range and Sensitivity**

No actual range or sensitivity is given. However, the Coleman MAS-50 employed is capable of detecting 0.01 μg absolute of Hg or below. The range (scale) is 0 to 9 μg Hg (without dilution). This range corresponds to mercury concentrations in the blood from 0.005 - 4.5 μg/mℓ. This range has not been verified with actual blood samples.

3. **Interferences**

Since Hg forms very stable organic compounds, adequate digestion of the blood is needed in order that any organic mercurials be decomposed.

4. **Precision and Accuracy**

The accuracy and precision of the method have not been reported up to this time. No collaborative tests have been performed on this method.

5. **Advantages and Disadvantages of the Method**

This method has never been tried in this laboratory.

6. **Apparatus**

6.1 5 mℓ mercury-free heparinized vacutainers

6.2 Coleman MAS-50 Mercury Analyzer System

6.3 **Mercury Evolution Train**

6.3.1 Bubbler Flask – 300 mℓ BOD bottle as supplied with MAS-50. The inlet tube of this is replaced with a coarse fritted glass bubbler tube extending to within 1/8" of the bottom of the flask.

6.3.2 All components are connected together by minimum lengths of tygon tubing.

6.4 Vortex mixer

6.5 Eppendorf pipets

6.6 Water bath at 50° to 60°C

7. **Reagents**

The reagents described must be made up using ACS Reagent Grade or better.

7.1 Double-distilled water or equivalent

7.2 Concentrated H_2SO_4

7.3 $KMnO_4$ crystals

7.4 Hydroxylamine-Hydrochloride crystals

7.5 H_2SO_4 (18N) (1:1)

7.6 HNO_3, 5.6 N (35% V/V)

7.7 $SnCl_2$ – 20% (W/V) in 6N HCl

7.8 **Standard stock mercury solution.** Add 0.1000 g metallic Hg into a clean, dry 100 mℓ volumetric flask. Add 5 mℓ concentrated HNO_3, dissolve the Hg, then dilute to the mark with distilled H_2O. With a buret transfer a volume containing exactly 50.0 mg of Hg to a liter volumetric flask. Add 20 mℓ concentrated HNO_3 and dilute to the mark with distilled H_2O. The final concentration is 50 μg/mℓ.

7.9 **Working standard mercury solution.** Transfer 10.0 mℓ of standard stock solution to a 1-liter volumetric flask. Add 20 mℓ concentrated HNO_3 and dilute to the mark with distilled water. The final concentration is 0.5 μg/mℓ.

7.10 **Hydroxylamine-Hydrochloride solution.** Dissolve 1.5 g of hydroxylamine hydrochloride with distilled H_2O and bring up to 1 liter with distilled H_2O.

8. **Procedure**

8.1 **Cleaning of Equipment.** All glassware must be rendered acid-clean before use. This can be accomplished by using the following three step procedure:

8.1.1 Wash in a detergent-tap water solution and follow with tap water and distilled water rinses.

8.1.2 Soak in chromic acid and follow with tap and distilled water rinses.

8.1.3 Soak in 1:1 or concentrated nitric acid for 30 minutes and follow with tap, distilled, and double distilled water rinses.

This entire procedure must be used only when initially preparing glassware for use in the mercury analysis. For each following successive use of equipment which has previously been subjected to the entire cleaning procedure, it is necessary only to use the nitric acid cleaning procedure described in step 8.1.3. Since chromic acid cannot be used on polyethylene, polyethylene equipment is effectively cleaned by subjecting it to steps 8.1.1 and 8.1.3 only.

8.2 **Collection and Shipping of Samples**

8.2.1 **Blood** must be collected in Hg-free heparinized vacutainers equipped with sterilized stainless steel needles. The vacutainers should be heparinized before the collection of the blood. Heparinized vacutainers are available commercially from most laboratory supply houses. The addition of a preservative after the collection of the blood can result in error due to volume changes. Caution should be exercised during handling to prevent any external contamination.

8.2.2 The samples should be kept as cool as possible (do not freeze) during storage and shipment and should be shipped to the laboratory as quickly as possible. Heparinized, refrigerated blood samples are stable for two weeks.

8.2.3 Two milliliters (2 mℓ) of whole blood are adequate for this determination.

8.3 **Analysis of Samples**

8.3.1 Pipet 2 mℓ of blood into a 300-mℓ BOD bottle.

Caution: BOD bottles are not made of "Pyrex" and should not be subjected to rapid temperature changes.

8.3.2 Add 18 mℓ of mercury-free distilled H_2O.

8.3.3 Slowly add 15 mℓ of concentrated H_2SO_4.

8.3.4 Heat at 50° to 60°C in a H_2O bath for 30 minutes.

8.3.5 Slowly add potassium permanganate crystals until the purple color persists.

8.3.6 Continue heating the sample at 50° to 60°C for 20 minutes. Keep adding potassium permanganate crystals as necessary so that the purple color persists.

8.3.7 Add 65 mℓ of Hg-free distilled water.

8.3.8 Add 5 mℓ of 5.6 N HNO_3 acid and swirl. Let stand for 15 seconds.

8.3.9 Add 5 mℓ of 18 N H_2SO_4 and swirl. Let stand for 45 seconds.

8.3.10 Add 5 mℓ of hydroxylamine-hydrochloride solution and swirl. Sample should turn clear. If not add hydroxylamine-hydrochloride crystals until clear solution is obtained.

8.3.11 Add 5 mℓ $SnCl_2$ solution and immediately insert the bubbler, making sure that stopper provides a good seal.

8.3.12 Record highest value (percent transmittance) indicated by the meter pointer.

8.3.13 Remove bubbler, place it on a clean surface, and allow the signal to return to zero.

9. Calibration and Standards

9.1 The working standard mercury solution (0.5 μg/mℓ) is stable for at least two months if stored in a tightly-stoppered Pyrex container. It is advisable, however, to prepare this solution fresh daily.

9.2 Add 5 mℓ concentrated HNO_3 to a 300 mℓ BOD bottle and dilute to 100 mℓ with 25°C distilled water. Gently blow out mist above the solution with a gentle purge of air or nitrogen.

9.3 With a 1 mℓ graduated pipet add a measured quantity (between 0 and 1 mℓ) of the working standard solution (0.5 μg/mℓ) to the BOD bottle. Immediately add 5.0 mℓ $SnCl_2$ solution and connect the bottle quickly to the fritted bubbler tube, making sure that the stopper provides a good seal.

9.4 Observe and record the minimum arbitrary scale reading (percent transmittance) of the meter pointer.

9.5 Repeat the calibration with appropriate quantities of the working standard solution so as to cover the entire scale of the meter or a convenient working range.

10. Calculations

10.1 Subtract background signal, if any, from the sample signal.

10.2 From the scale reading (percent transmittance) for each sample, read the micrograms of Hg in the sample from the calibration curve.

10.3 Divide by the sample volume (in mℓ) to obtain the Hg concentration in μg/mℓ.

11. References

11.1 Applications Data Sheet, Coleman Instruments Division January 22, 1971.

11.2 Coleman MAS-50 Manual, December 1970.

11.3 Jacobs, M.B. et al, "Ultramicrodetermination of Mercury in Blood" Am. Ind. Hyg. Assoc. J. 22, 276-79 (1961).

11.4 Jacobs, M.B. et al,"Determination of Hg in Blood" Am. Ind. Hyg. Assoc. J. 21, 475 (1960).

COLORIMETRIC METHOD FOR FREE SILICA

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Free Silica (Quartz)	**Method No:**	P&CAM 106
Matrix:	Biologic Tissue, Airborne Particulates, Dusts	**Range:**	10 μg to 2.5 mg
Procedure:	Acid Digestion, Filtration, Color Development		
Date Issued:	3/31/72	**Precision:**	Relative Stand. Dev. = 9.25%
Date Revised:	1/15/74	**Classification:**	B (Accepted)

1. **Principle of the Method**

   1.1 The sample is digested in phosphoric acid to remove the silicates.

   1.2 The remaining crystalline material is dissolved in hydrofluoric acid.

   1.3 Silica is determined colorimetrically as silicomolybdate (420 mμ) or as molybdenum blue (820 mμ).

2. **Range and Sensitivity**

   2.1 In the silicomolybdate range, concentrations from 0.1 mg to 2.5 mg can be detected.

   2.2 In the molybdenum blue range, concentrations from < 5 μg to 140 μg can be detected.

   2.3 The range can be extended by varying the 0.50-g sample size.

3. **Interferences**

   3.1 The phosphate ion reacts with molybdic acid to form a yellow phosphomolybdate complex. It can be eliminated by lowering the pH to 1.2-1.3 with 10N H_2SO_4.

3.2 The ferric ion may consume the reducing agent and cause low results. As much as 1.0 mg will not interfere. Iron in excess of 1.0 mg per sample must be removed by preliminary treatment with 10:1 HCl-HNO_3.

4. Precision and Accuracy

Relative standard deviation on a run of 10 replicate samples was 9.25%. The wide deviation is due to error introduced by solution of some of the quartz in the phosphoric acid or the resistance of some silicates to dissolve. The same 10 samples reflected a mean free silica analysis of 3.36% on a sample with a concentration of 3.33% as determined gravimetrically. The error is less than 1%.

5. Advantages and Disadvantages of the Method

5.1 The major advantage lies in the versatility and wide range of the method. With facile pretreatment, dusts, airborne particulates and tissues can be analyzed by this method. If the SiO_2 concentration falls below the silicomolybdate detection limit, the simple addition of another reagent increases the sensitivity twentyfold.

5.2 The major disadvantage is the loss of free silica by solution during the phosphoric acid digestion. Quartz solubility is a function of the particle size, so the small, fine samples are vulnerable to this source of error. Some silicates may be resistant to phosphoric acid.

6. Apparatus

6.1 **Sampling Equipment.** The sampling unit for the filter-collection method has the following components:

6.1.1 The filter unit, consisting of the filter media and appropriate cassette filter holder, either a 2 or 3 piece filter cassette.

6.1.2 A vacuum pump such as a personal sampling pump. This pump must be properly calibrated so the volume of air sampled can be measured as accurately as possible. The pump must be calibrated with a representative filter unit in the line. Flow rate, time, and/or volume must be known.

6.1.3 Thermometer.

6.1.4 Manometer.

6.1.5 Stopwatch.

6.2 Membrane filters, 47 mm diameter, mean pore size, 0.45μ.

6.3 550-watt, 115-volt, Type RH, Precision heater (Precision Scientific Company).

6.4 750-watt variable transformer with built-in voltmeter.

6.5 Serological Rotator.

6.6 250-mℓ borosilicate glass Phillips beakers.

6.7 Short-stemmed glass funnels, with stems bent.

6.8 Crucible tongs padded with rubber or Tygon tubing.

6.9 Spectrophotometer with capacity of readings at 420 mμ and 820 mμ.

6.10 Filter funnel, membrane mount, and flask assembly.

6.11 125 mℓ polyethylene beakers, polyethylene watch glasses, stirring rods, 50 mm discs.

6.12 Polyethylene reagent bottles to store water, boric acid and standard solutions.

6.13 Bakelite or Nalgene buret (10 mℓ).

6.14 Constant temperature water bath.

7. **Reagents**

All reagents used should be ACS Reagent Grade or better.

7.1 Silica-free water for all solutions and dilutions. Use distilled deionized water and store in polyethylene carboy.

7.2 Hydrofluoric acid, 48%.

7.3 Orthophosphoric acid, 85%.

7.4 Hydrochloric acid, 1:10.

7.5 **Boric Acid Solution, 5%.** Dissolve 200 grams of boric acid crystals in 4 liters of warm, silica-free water. Cool. Filter with vacuum through a 0.45 micron membrane filter. Store in a polyethylene container.

7.6 **Molybdate Reagent.** Dissolve 50 g of ammonium molybdate tetrahydrate in about 400 mℓ of silica-free water. Acidify with 40 mℓ of concentrated sulfuric acid. Cool. Dilute to 500 mℓ. Store in dark.

7.7 **Sulfuric Acid, 10N.** Cautiously add 555 mℓ of concentrated H_2SO_4 to about 1.3 liters of water. Cool. Dilute to 2 liters.

7.8 **Reducing Solution.**

(A) Dissolve 9 grams of sodium bisulfite in 80 mℓ of water.

(B) In 10 mℓ of water dissolve 0.7 gram of anhydrous sodium sulfite and 0.15 gram of 1-amino-2-naphthol-4-sulfonic acid, in that order.

Combine solutions A and B and dilute to 100 mℓ. Reagent stored in refrigerator is stable for about one month.

7.9 Quartz – finely ground and acid-washed.

8. **Procedure**

8.1 **Cleaning of Equipment.** All glass and polyethylene ware used should be washed thoroughly and subjected to a final rinse in silica-free water.

8.2 **Collection and Shipping of Samples**

8.2.1 **Tissue samples** are usually those collected at the time of autopsy; 500 mg or more should be submitted. They should be frozen, if possible and placed in plastic containers. Whirlpacks for small specimens are convenient. Bags, bottles or jars of plastic materials may be used.

8.2.2 **Air samples** should be collected on standard 37 or 47 mm cellulose membrane filters as follows:

(1) Assemble the filter unit by mounting the filter disc in the filter casette.

(2) Connect the exit end of the filter unit to the pump with a short piece of flexible tubing.

(3) Turn on pump to begin sample collection. The flow rate, times, and/or volume must be measured as accurately as possible. The sample should be taken at a flow rate of 2 liters per minute. A minimum sample of 100 liters should be collected. Larger sample

volumes are encouraged provided the filters do not become loaded with dust to the point that loose material might fall off or the filter become plugged.

(4) The sample cassettes should be shipped in a suitable container designed by NIOSH to minimize contamination and to prevent damage in transit. Care must be taken during storage and shipping that no part of the sample is dislodged from the filter nor that the sample surface be disturbed in any way. Loss of sample from heavy deposits on the filter may be prevented by mounting a clean filter in the cassettes on top of the sample filter.

(5) With each batch of samples, one filter, labelled as a blank, must be submitted. No air should be drawn through this filter.

8.2.3 Bulk or rafter samples should be submitted in quantities equaling or exceeding 0.5 gram.

8.3 **Analysis of Samples**

8.3.1 A weighed sample containing no more than 2.5 mg SiO_2 or a filter membrane on which airborne particulates have been collected is placed in a clean 250-mℓ Phillips borosilicate glass beaker. Redistilled nitric acid (3 to 4 mℓ) is added and the sample heated to absence of brown fumes and dryness. The process is repeated until a white residue remains. (The filter should be consumed.) A blank should be carried through all steps of the analysis. If the sample is received on a membrane filter, an untreated membrane of the same type should be ashed. If a bulk sample is used, a beaker containing only the nitric or perchloric acid is started.

8.3.2 When polyvinyl chloride membranes have been used for sampling, nitric acid ashing is inadequate. Two mℓ of $HClO_4$ are added and heated slowly to just short of dryness. Ashing should be complete at this point. If necessary a second portion of $HClO_4$ can be added.

8.3.3 Add 25 mℓ of 85% phosphoric acid to the beaker. Start a reagent blank from this point, using only phosphoric acid. Cover the beaker with a bent-stem funnel.

8.3.4 In a hood preheat the Precision Heater for at least 45 minutes at 70 volts (about 240°C). Heat the sample for exactly 8 minutes, swirling it by the action of the serological rotator.

8.3.5 Remove the beaker from the heater by grasping it with padded crucible tongs and swirl it vigorously for one minute.

8.3.6 Allow the beaker to cool and add approximately 125 mℓ of water at 60° to 70°C. Swirl to mix the syrupy phosphoric mixture with the water.

8.3.7 Filter the sample with suction through a membrane filter. A Millipore disc, 47 mm in diameter with mean pore size of 0.45μ, is suitable. Wash thoroughly with 1:10 HCl.

8.3.8 Place the membrane flat in the bottom of a 150-mℓ polyethylene beaker and add 0.5 mℓ of 48% HF to the membrane surface. Float a thin polyethylene disc of about 50 mm diameter over the membrane and cover the beaker. Allow it to stand for 30 minutes.

8.3.9 Add 25 mℓ of water and 50 mℓ of boric acid solution. Stir well, cover.

8.3.10 Heat the solution in a 40°C water bath for at least 10 minutes.

8.3.11 Add 4 mℓ of molybdic acid reagent while stirring, staggering the addition at 2 minute intervals between samples. Time with a stopwatch from the beginning of the addition to the first sample.

8.3.12 Twenty minutes after the first addition, add 20 mℓ of 10N sulfuric acid, and stir thoroughly.

8.3.13 If any yellow color persists, read within two minutes after acidification in a spectrophotometer at 420 mμ against distilled water. Subtract blank.

8.3.14 If a colorless solution results, allow it to stand for 2 to 5 minutes and add 1 mℓ of 1-amino-2-naphthol-4-sulfonic acid reagent.

8.3.15 Mix and read after 20 minutes at 820 mμ against distilled water. Subtract blank. This color is stable for several hours.

9. **Calibration and Standards**

9.1 A 0.5 mg/mℓ SiO_2 stock standard is made by dissolving 250 mg of finely ground, acid-washed quartz in 10 mℓ of 48% hydrofluoric acid. Solution rate is slow and it may need to stand overnight. Dilute to 500 mℓ. This standard is stable indefinitely if stored in a polyethylene container.

9.2 A calibration curve in the silicomolybdate color range is made by diluting 1-, 2-, 3-, 4-, 5-, and 6-mℓ aliquots of the stock standard to 25 mℓ in polyethylene beakers and proceeding from step 8.3.9. Absorbance against mg of SiO_2 is plotted.

9.3 A standard usable in the molybdenum blue range is made by preparing a 1:25 dilution of the stock standard described in 9.1. This standard will contain 20μg SiO_2 per mℓ.

9.4 Dilute standards similar to those described in 9.2 are prepared for use in plotting the calibration curve. The upper limit for this curve is 140 μg.

10. Calculations

10.1 Milligrams of SiO_2 per sample is read from the appropriate calibration curve.

$$\text{mg } SiO_2/\text{gram of sample} = \frac{\text{mg } SiO_2 \text{ in sample}}{\text{sample weight in grams}}$$

$$\%\ SiO_2 = \frac{\text{mg } SiO_2}{\text{g of sample}} \times 0.1$$

10.2 Micrograms SiO_2 per sample is read from the appropriate calibration curve.

$$\mu\text{g } SiO_2/\text{gram of sample} = \frac{\mu\text{g } SiO_2 \text{ in sample}}{\text{sample weight in grams}}$$

$$\%\ SiO_2 = \frac{\mu\text{g } SiO_2}{\text{g of sample}} \times 0.0001$$

11. References

11.1 Talvitie, N.A., "Determination of Quartz in the presence of Silicates Using Phosphoric Acid," *Anal. Chem.*, 23, 623 (1951).

11.2 Talvitie, N.A., and Frances Hyslop, "Colorimetric Determination of Siliceous Atmospheric Contaminants," *Amer. Ind. Hyg. Assoc. J.*, 19:54 (1958).

11.3 Talvitie, N.A., "Determination of Free Silica: Gravimetric and Spectrophotometric Procedure Applicable to Air-Borne and Settled Dust," *Amer. Ind. Hyg. J.*, 25, 169, March-April, 1964.

ANTIMONY IN URINE

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Antimony	**Method No:**	P&CAM 107
Matrix:	Urine	**Range:**	1-10μg/samples
Procedure:	Colorimetric – Rhodamine B	**Precision:**	±5%
		Classification:	A (Recommended)
Date Issued:	4/13/73		
Date Revised:	1/15/74		

1. **Principle of the Method**

   1.1 Urine samples are ashed with a mixture of sulfuric and nitric acids to obtain a clear digest.

   1.2 The sample ash is treated with perchloric acid to oxidize any antimony present to the pentavalent state.

   1.3 Rhodamine B dye is added to form a colored complex with the pentavalent antimony.

   1.4 The colored complex is extracted with benzene and its absorbance at 565 nanometers is measured in a spectrophotometer or colorimeter.

2. **Range and Sensitivity**

   2.1 One microgram of antimony is detectable per determination. For 50 mℓ of urine sample, this should correspond to 0.02 mg/liter of urine.

   2.2 No range is given.

3. **Interferences**

   3.1 Iron is the only commonly encountered ion likely to interfere. Iron interference can be eliminated by extracting with isopropyl ether instead of benzene but this solvent causes troublesome emulsion formation. In the presented method 750 μg Fe/mℓ showed no significant interference. This is well above the normal iron content in urine of 7 μg/Kg body weight per day.

3.2 Gallium and thallium can also interfere.

4. **Precision and Accuracy**

4.1 Three standard unknowns containing 3.0, 5.0 and 8.0 μg Sb/mℓ were analyzed in triplicate by ten collaborating laboratories plus a referee. Mean standard deviations from the amount of antimony present were ±0.113, ±0.237, and ±0.245 μg/mℓ on each of the three unknowns. This corresponds to mean coefficients of variation of 3.8, 4.7, and 3.1 per cent respectively.

4.2 For these same samples, the mean recoveries were 101, 104, and 107 per cent respectively.

5. **Advantages and Disadvantages of the Method**

5.1 This method requires no special equipment except a good spectrophotometer.

5.2 Unless all antimony present is pentavalent, recoveries cannot be complete. Digestions must be arranged to minimize the formation of antimony (IV), which is difficult to convert to antimony (V). Ten drops of perchloric acid is sufficient to oxidize the antimony, but less than this may give low results.

5.3 Also it is imperative to operate at low temperatures throughout the determinations. Samples, reagents, and apparatus should all be kept cold in a refrigerator prior to use.

5.4 Although benzene was used in this method, due to its toxicity, toluene or xylene might be better solvents for the extraction.

5.5 This method has not been performed in this laboratory.

6. **Apparatus**

6.1 125 mℓ Erlenmeyer flasks.

6.2 125 mℓ Squibb separatory funnels with Teflon stopcocks.

6.3 1 cm light path cuvettes for spectrophotometer.

6.4 Pipettes, test tubes, ice bath.

6.5 Polyethylene bottles with Teflon lined caps for sample collection.

6.6 Spectrophotometer

7. Reagents

The reagents described should be made up using C.P. grade or a better grade of chemical.

7.1 Double distilled water

7.2 Sulfuric acid, sp. gr. 1.84

7.3 Nitric acid, sp. gr. 1.42

7.4 Perchloric acid, redistilled 70%

7.5 Benzene or toluene

7.6 **Hydrochloric acid, 6N**: This reagent is prepared from concentrated hydrochloric acid (sp. gr. = 1.19) by mixing with an equal volume of double distilled water.

7.7 **Orthophosphoric acid, 3N**: Dilute 70 mℓ of 85% phosphoric acid to 1 liter with double distilled water.

7.8 **Rhodamine B**: 0.02% w/v in double distilled water.

7.9 **Antimony standard stock solution,** 100 μg/mℓ: Dissolve 0.1000 g antimony in 25 mℓ conc. sulfuric acid with heat and dilute to 1 liter with double distilled water.

7.10 Thymol – Reagent Grade

8. Procedure

8.1 **Cleaning of Equipment**: All glassware should be thoroughly cleaned; the following procedure is recommended:

8.1.1 Wash with a detergent and tap water solution followed by tap water and distilled water rinses.

8.1.2 Soak in chromic acid for 30 minutes and follow with tap and distilled water rinses.

8.1.3 Soak in 1:1 or concentrated nitric acid for 30 minutes and then follow with tap, distilled, and double distilled water rinses.

This entire procedure should be used only initially. Any glassware re-used need only be nitric acid cleaned as in Section 8.1.3. Polyethylene equipment can be cleaned by subjecting it to Sections 8.1.1 and 8.1.3 only.

8.2 Collection and Shipping of Samples

Urine samples should be collected in clear borosilicate or polyethylene bottles. At least 100 mℓ should be collected. The sample must be preserved by the addition of 5 mg of thymol per 100 mℓ of urine. The urine should be kept cool during shipment and storage. Urine samples treated with thymol and refrigerated, are stable for 1 week.

8.3 Analysis of Samples

8.3.1 Specific gravities of the urine samples are determined after the samples have been allowed to warm to room temperature. This may be done using a specific gravity meter or a *reliable* hydrometer.

8.3.2 Precool in an ice bath or refrigerate all reagents and glassware to be used for the analysis.

8.3.3 Transfer 50 mℓ of urine into a 125 mℓ Erlenmeyer flask. The sample is wet ashed with 5 mℓ concentrated sulfuric acid and 5 mℓ concentrated nitric acid. It may be found necessary to add nitric acid in 1 mℓ increments up to 5-10 mℓ in order to obtain a clear digest.

8.3.4 The sample is heated to white fumes of sulfur trioxide and then cooled slightly.

8.3.5 Ten drops of 70% perchloric acid are added and the sample is again heated to white fumes. The resulting digest is cooled in a melting ice bath until temperature equilibrium is reached (at least 30 minutes).

Note: All operations after the addition of phosphoric acid should be carried out quickly. Thus, it would seem best to handle the color development (Sections 8.3.6 to 8.3.9) of each sample individually and then read the absorbances collectively. Color development should be carried out in subdued light.

8.3.6 5 mℓ of *precooled* 6N hydrochloric acid is added *slowly* by pipette and the solution is allowed to stand in the ice bath an additional 15 minutes.

8.3.7 8 mℓ of *precooled* 3N phosphoric acid is added, followed immediately by the addition of 5 mℓ Rhodamine B solution.

8.3.8 *Without delay*, the flask is stoppered, shaken vigorously, and transferred to a *precooled* 125 mℓ, Squibb separatory funnel with Teflon stopcock.

8.3.9 10.0 mℓ of *precooled* benzene is added and the contents are shaken vigorously for one minute. The aqueous layer is discarded.

8.3.10 The benzene phase (red if antimony is present) is collected in a test tube and allowed to stand a few minutes for any water to settle out.

8.3.11 A 1 cm light path cuvette is rinsed 3 times with 1-2 mℓ of the extract, then filled and the absorbance read at 565 nanometers against a benzene blank.

9. Calibration and Standards

The calibration curve is prepared by carrying 1-10 micrograms of antimony through the complete oxidation, extraction, and analysis procedures (Sections 8.3.1 to 8.3.11) and then plotting absorbance vs. micrograms per total sample.

10. Calculations

10.1 Determine the concentration of antimony in the sample in μg Sb per mℓ or mg per liter of urine.

$$\text{mg Sb}/\ell = \mu\text{g Sb}/\text{m}\ell_{\mu}$$

where:

μg Sb = micrograms Sb determined from the calibration curve. (Section 9)

$\text{m}\ell_{\mu}$ = mℓ of urine sample ashed

10.2 The use of a specific gravity correction factor to normalize values to 1.024, the average specific gravity of urine, has been proposed. There are two ways of using this correction.

10.2.1 One way is to use a straightforward gravity correction, in which case the magnitude of the factor is small.

$$\text{Corrected (mg Sb/}\ell\text{)} = \text{(mg Sb/}\ell\text{)} \times \frac{1.024}{\text{specific gravity}}$$

10.2.2 The other method corrects for differences in total solids or salt content of various urine specimens, whereby the specific gravity of water is initially subtracted from the urine specific gravities. Because of the wide range of reported urine specific gravities, 1.002 to 1.040, the use of such a correction factor can lead to unusually or erroneously high results.

$$\text{Corrected (mg Sb/}\ell\text{)} = \text{(mg Sb/}\ell\text{)} \times \frac{(1.024 - 1.000)}{(\text{specific gravity} - 1.000)}$$

11. References

11.1 Amer. Conf. of Govt. Ind. Hyg.: "Recommended Method for Antimony in Air Samples and Biological Materials" (1963).

11.2 Maren, Thomas H.: "Colorimetric Microdetermination of Antimony with Rhodamine B." Anal. Chem 19, 487-91 (1947).

NITROGEN DIOXIDE IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Nitrogen Dioxide	**Method No.:**	P&CAM 108
Matrix:	Air	**Range:**	.01 to 10 μg/liter
Procedure:	Colorimetric	**Precision:**	< 5% RSD
Date Issued:	12/11/72		
Date Revised:	January 10, 1974	**Classification:**	C (Tentative)

1. **Principle of the Method**

The nitrogen dioxide is absorbed in an azo dye forming reagent (Reference 1). A stable pink color is produced within 15 minutes which may be read visually or in an appropriate instrument at 550 nm.

2. **Range and Sensitivity**

2.1 This method is intended for the manual determination of nitrogen dioxide in the atmosphere in the range of 0.005 to about 5 parts per million (ppm) by volume or 0.01 to 10 μg/liter, when sampling is conducted in fritted bubblers. The method is preferred when high sensitivity is needed.

2.2 Concentrations of 5 to 100 ppm in industrial atmospheres and in gas burner stacks also may be sampled by employing evacuated bottles or glass syringes. For higher concentrations, for automotive exhaust, and/or for samples relatively high in sulfur dioxide content, other methods should be applied.

3. **Interferences**

3.1 A tenfold ratio of sulfur dioxide to nitrogen dioxide produces no effect. A 30-fold ratio slowly bleaches the color to a slight extent. The addition of 1 percent acetone to the reagent before use retards the fading by forming another temporary product with sulfur dioxide. This permits reading within 4 to 5 hours (instead of the 45 minutes required when acetone is not added) without appreciable interferences. Interference from sulfur dioxide may be a problem in some stack gas samples (Section 2.2).

3.2 A fivefold ratio of ozone to nitrogen dioxide will cause a small interference, the maximal effect occurring in 3 hours. The reagent assumes a slightly orange tint.

3.3 Peroxyacylnitrate (PAN) can give a response of approximately 15 to 35 percent of an equivalent molar concentration of nitrogen dioxide (Reference 2). In ordinary ambient air the concentrations of PAN are too low to cause any significant error.

3.4 The interferences from other nitrogen oxides and other gases which might be found in polluted air are negligible. However, if the evacuated bottle or syringe method is used to sample concentrations above 5 ppm, interference from NO (due to oxidation to NO_2) is possible (Section 8.2.3).

3.5 If strong oxidizing or reducing agents are present, the colors should be determined within 1 hour, if possible, to minimize any loss.

4. Precision and Accuracy

4.1 A precision of 1 percent of the mean can be achieved with careful work (Reference 3); the limiting factors are the measurements of the volume of the sample and of the absorbance of the color.

4.2 At present, accuracy data are not available.

5. Advantages and Disadvantages of the Method

This is a simple method with direct coloration of absorbing reagent, which can be put directly into cuvettes and read, or diluted with absorbing reagent and read.

6. Apparatus

6.1 **Absorber.** The sample is absorbed in an all-glass bubbler with a 60 μ maximum pore diameter frit.

6.1.1 The porosity of the fritted bubbler, as well as the sampling flow rate, affect absorption efficiency. An efficiency of over 95 percent may be expected with a flow rate of 0.4 liter/minute or less and a maximum pore diameter of 60 μ. Frits having a maximum pore diameter less than 60 μ will have a higher efficiency but will require an inconvenient pressure drop for sampling (see formula in Section 6.1.2). Considerably lower efficiencies are obtained with coarser frits, but these may be utilized if the flow rate is reduced.

6.1.2 Since the quality control by some manufacturers is rather poor, it is desirable to measure periodically the porosity of an absorber as follows: Carefully clean the apparatus with dichromate-concentrated sulfuric acid solution and then rinse it thoroughly with distilled water. Assemble the bubbler, add sufficient distilled water to barely cover the fritted portion, and measure the vacuum required to draw the first perceptible stream of air bubbles through the frit. Then calculate the maximum pore diameter as follows:

$$\text{Maximum pore diameter } (\mu) = \frac{30\,s}{P}$$

where:

s = surface tension of water at the test temperature in dynes/cm (73 at 18°C, 72 at 25°C, and 71 at 31°C),

P = measured vacuum, mm Hg.

6.1.3 Rinse the bubbler thoroughly with water and allow to dry before using. A rinsed and reproducibly drained bubbler may be used if the volume (r) of retained water is added to that of the absorbing reagent for the calculation of results. This correction may be determined as follows: Pipet into a drained bubbler exactly 10 mℓ of a colored solution (such as previously exposed absorbing reagent) of absorbance A_1. Assemble the bubbler and rotate to rinse the inside with the solution. Rinse the fritted portion by pumping gently with a rubber bulb. Read the new absorbance, A_2, of the solution. Then:

$$10A_1 = (10 + r)\,A_2$$

or:

$$r = 10\frac{A_1}{A_2} - 1$$

6.2 **Air Metering Device.** A glass rotameter capable of accurately measuring a flow of 0.4 liter/minute is suitable. A wet test meter is convenient to check the calibration.

6.3 **Sampling Probe.** A glass or stainless steel tube 6 to 10 mm in diameter provided with a downward-facing intake (funnel or tip) is suitable. A small loosely fitting plug of glass wool may be inserted, when desirable, in the probe to exclude water droplets and particulate matter. The dead volume of the system should be kept minimal to permit rapid flushing during sampling to avoid losses of nitrogen dioxide on the surfaces.

6.4 **Grab-Sample Bottles.** Ordinary glass-stoppered borosilicate glass bottles of 30 to 250 mℓ sizes are suitable if provided with a mating ground joint attached to a stopcock for evacuation. Calibrate the volume by weighing with connecting piece, first empty, then filled to the stopcock with distilled water.

6.5 **Glass Syringes.** 50 or 100 mℓ syringes are convenient (although less accurate than bottles) for sampling.

6.6 **Air Pump.** A vacuum pump capable of drawing the required sample flow for intervals of up to 30 minutes is suitable. A tee connection at the intake is desirable. The inlet connected to the sampling train should have an appropriate trap and needle valve, preferably of stainless steel. The second inlet should have a valve for bleeding in a large excess flow of clean air to prevent condensation of acetic acid vapors from the absorbing reagent, with consequent corrosion of the pump. Alternatively, soda lime may be used in the trap. A filter and critical orifice may be substituted for the needle valve (Reference 4).

6.7 **Spectrophotometer or Colorimeter.** A laboratory instrument suitable for measuring the pink color at 550 nm, with stoppered tubes or cuvettes. The wavelength band width is not critical for this determination.

6.8 Assorted laboratory glassware.

7. Reagents

All chemicals used should be analytical reagent grade (Reference 5).

7.1 **Nitrite-Free Water.** All solutions are made in nitrite-free water. If available distilled or deionized water contains nitrite impurities (produces a pink color when added to absorbing reagent), redistill it in an all-glass still after adding a crystal each of potassium permanganate and of barium hydroxide.

7.2 **N-(1-Naphthyl) -Ethylenediamine Dihydrochloride, Stock Solution** (0.1%). Dissolve 0.1 g of the reagent in 100 mℓ of water. Solution is stable for several months if kept well stoppered in a brown bottle in the refrigerator. (Alternatively, weighed small amounts of the solid reagent may be stored.)

7.3 **Absorbing Reagent.** Dissolve 5 g of anhydrous sulfanilic acid (or 5.5 g of $NH_2C_6H_4SO_3H \cdot H_2O$) in almost a liter of water containing 140 mℓ of glacial acetic acid. Gentle heating is permissible to speed up the process. To the cooled mixture, add 20 mℓ of the 0.1% stock solution of N-(1-naphthyl) -ethylenediamine dihydrochloride, and dilute to 1 liter. Avoid lengthy contact with air during both preparation and use, since discoloration of reagent will result because of absorption of nitrogen dioxide. The solution is stable for several months if kept

well-stoppered in a brown bottle in the refrigerator. The absorbing reagent should be allowed to warm to room temperature before use.

7.4 **Standard Sodium Nitrite Solution** (0.0203 g/liter). One mℓ of this working solution of sodium nitrite ($NaNO_2$) produces a color equivalent to that of 10 $\mu\ell$ of nitrogen dioxide (10 ppm in 1 liter of air at 760 mm of mercury and 25°C: see Section 10.2.1). Prepare fresh just before use by dilution from a stronger stock solution containing 2.03 g of the reagent grade granular solid (calculated as 100 percent) per liter. It is desirable to assay (Reference 5), the solid reagent, especially if it is old. The stock solution is stable for 90 days at room temperature, and for a year in a brown bottle under refrigeration.

8. Procedure

8.1 **Cleaning of Glassware**. All washed glassware should be allowed to stand awhile in chromic acid solution, and then thoroughly rinsed with single and then double distilled water.

8.2 **Collection and Storage of Samples**. Three methods are described below. Concentrations below 5 ppm are sampled by the bubbler method. Higher concentrations may be sampled by the evacuated bottle method, or more conveniently (but less accurately) by the glass syringe method. The latter method is more useful when appreciable concentrations (e.g., 20 ppm) of nitric oxide are expected.

8.2.1 Bubbler Method

1. Assemble, *in order*, a sampling probe (optional), a glass rotameter, fritted absorber, and pump. Use ground-glass connections upstream from the absorber. Butt-to-butt glass connections with slightly greased vinyl or pure gum rubber tubing also may be used for connections without losses if lengths are kept minimal. The sampling rotameter may be used upstream from the bubbler provided occasional checks are made to show that no nitrogen dioxide is lost. The rotameter must be kept free from spray or dust.

2. Pipet 10.0 mℓ of absorbing reagent into a dry fritted bubbler (Section 6.1.3).

3. Draw an air sample through it at the rate of 0.4 liter/minute (or less) long enough to develop sufficient final color (about 10 to 30 minutes). Note the total volume of air sampled.

4. Measure and record the sample air temperature and pressure.

8.2.2 Evacuated Bottle Method

1. Sample in bottles of appropriate size containing 10.0 mℓ (or other convenient volume) of absorbing reagent. For 1 cm spectrophotometer cells, a 5:1 ratio of air sample volume to reagent volume will cover a concentration range up to 100 ppm; a 25:1 ratio suffices to measure down to 2 ppm.

2. Wrap a wire screen or glass-fiber-reinforced tape around the bottle for safety purposes.

3. Grease the joint lightly with silicone or fluorocarbon grease.

4. If a source of vacuum is available at the place of sampling, it is best to evacuate just before sampling to eliminate any uncertainty about loss of vacuum. A three-way Y stopcock connection is convenient. Connect one leg to the sample source, one to the vacuum pump, and the third to a tee attached to the bottle and to a mercury manometer or accurate gauge. In the first position of the Y stopcock, the bottle is evacuated to the vapor pressure of the absorbing reagent. In the second position of the Y stopcock the vacuum pump draws air through the sampling line to flush it thoroughly. The actual vacuum in the sample bottle is read on the manometer. In the third position of the Y stopcock the sampling line is connected to the evacuated bottle and the sample is collected.

5. The stopcock on the bottle is then closed. Allow 15 minutes with occasional shaking for complete absorption and color development.

6. For calculation of the standard volume of the sample, record the temperature and the pressure. The pressure is the difference between the filled and evacuated conditions. The uncorrected volume is that of the bottle plus that of the connection up to the stopcock minus the volume of absorbing reagent.

8.2.3 Glass Syringe Method

1. Ten mℓ of absorbing reagent is kept in a capped 50 (or 100) mℓ glass syringe, and 40 (or 90) mℓ of air is drawn in at the time of sampling.

2. The absorption of nitrogen dioxide is completed by capping and shaking vigorously for 1 minute, after which the air is expelled. (When appreciable concentrations – e.g., 20 ppm – of nitric oxide are suspected, interference caused by the oxidation of nitric oxide to nitrogen dioxide is minimized by expelling the air sample immediately after the absorption period.)

3. Additional air may be drawn in and the process repeated several times, if necessary, to develop sufficient final color.

8.2.4 **Effects of Storage.** Colors may be preserved, if well stoppered, with only 3 to 4% loss in absorbance per day; however, if strong oxidizing or reducing gases are present in the sample in concentrations considerably exceeding that of the nitrogen dioxide, the colors should be determined as soon as possible to minimize any loss. (See Section 3 for effects of interfering gases.)

8.3 Analysis of Samples

8.3.1 After collection or absorption of the sample, a red-violet color appears. Color development is complete within 15 minutes at room temperature.

8.3.2 Compare with standards visually or transfer to stoppered cuvettes and read in a spectrophotometer at 550 mμ, using unexposed reagent as a reference. Alternatively, distilled water may be used as a reference and the absorbance of the reagent blank deducted from that of the sample.

8.3.3 Colors too dark to read may be quantitatively diluted with unexposed absorbing reagent. The measured absorbance is then multiplied by the dilution factor.

9. Calibration and Standardization

Either of two methods of calibration may be employed. The most convenient is standardizing with nitrite solution. Greater accuracy is achieved by standardizing with accurately known gas samples in a precision flow dilution system (References 3,6,7). The recently developed permeation tube technique (Reference 8) appears promising. If the gaseous method is used, the stoichiometric factor is eliminated from the calculations. Concentrations of the standards should cover the expected range of sample concentrations.

9.1 Nitrite Solution Method

9.1.1 Add graduated amounts of the $NaNO_2$ solution up to 1 mℓ (measured accurately in a graduated pipet or small buret) to a series of 25 mℓ volumetric flasks, and dilute to the mark with absorbing reagent.

9.1.2 Mix, allow 15 minutes for complete color development and read the colors (Section 8.3).

9.1.3 Good results can be obtained with these small volumes of standard solution if they are carefully measured. Making the calibration solutions up to 25 mℓ total volume, rather than the 10 mℓ volume used for samples, facilitates accuracy. If preferred, even larger volumes may be used with correspondingly larger volumetric flasks.

9.1.4 Plot the absorbances of the standard colors against the μℓ of nitrogen dioxide per mℓ of absorbing reagent. The latter values are equal to the corresponding mℓ of standard nitrite solution times 0.4 (Section 10.2.2). If preferred, transmittance may be plotted instead of absorbance, using semilogarithmic graph paper. The plot follows Beer's law. Draw the straight line through the origin giving the best fit, and determine the slope, K, which is μℓ of NO_2 intercepted at absorbance of exactly 1.0 or at 10 percent transmittance. For 1 cm cells, the value of K is about 0.73.

9.2 **Gaseous Standard Methods.** Two techniques are outlined below. Consult the original references for complete details, and Section 10.3 for calculations.

9.2.1 Method 1 (Reference 3) for gaseous standardization is as follows:

1. About 5 mℓ of pure liquid nitrogen dioxide is placed in a small glass bubbler (10 mm in diameter and 100 mm in length) provided with ground glass stopcocks and spherical joints on both intake and outlet tubes.

2. The bubbler is immersed in a thermos bottle ice bath and connected to an air line. A small pump with flowmeter delivers a steady stream of a few mℓ/min of air to the bubbler, thence through two flowmeters which permit the discarding of up to 90 percent of the NO_2 and finally to a large stream of carbon filtered air (1000 to 1500 liters/min) from a small blower. All this air passes through a 10 cm Biram anemometer mounted on the end of a pipe 10 cm in diameter. It has been found empirically with this arrangement that the anemometer reading in ft/min times 1.64 is equivalent to liters/min.

3. The bubbler is weighed to 0.1 mg at the beginning and end of an accurately measured time period. The stopcocks are closed each time before the bubbler is removed from the ice bath and wiped dry for weighing.

9.2.2 Method 2 (References 6,7) for preparing known dilutions of nitrogen dioxide consists in making a preliminary dilution (about 0.4%) of nitrogen dioxide in air in a stainless steel tank at 1000 lbs pressure. Subsequent dilution, by air in a flow system at atmospheric pressure, of the analyzed

tank mixture controlled by an asbestos plug and manometer yields concentrations of 0.1 to 10 ppm NO_2

9.2.3 Sample the gas mixtures by the bubbler method (Section 8.2.1), and read the colors (Section 8.3). Select concentrations and sample volumes to produce colors covering the accurate absorbance range of the spectrophotometer.

9.2.4 Standardization by gaseous samples can be based either upon a weight-volume relationship if the source of nitrogen dioxide is weighed, or a volume-volume relationship if the source is an analyzed tank mixture.

9.2.5 Calculate the concentration of the sample air stream, C, in ppm by volume ($\mu\ell$ NO_2/ℓ of air).

$$C = \frac{10^6\ (W_1 - W_2)}{t} \times \frac{0.532}{F_1} \times \frac{F_2}{F_3}$$

or: $$C = C_t \times \frac{F_2}{F_3}$$

where:

C = concentration of sample air stream in ppm.

$(W_1 - W_2)$ = difference between initial and final weights, in grams, of nitrogen dioxide bubbler (or of permeation tube); weight loss is usually 0.01 to 0.05 g.

t = time interval in minutes, between the weighings.

0.532 = (24.47/46.0), ideal volume in ℓ at 25°C and 760 mm Hg of 1.0 g of nitrogen dioxide.

F_1 = flow rate, in ℓpm, of air passed through nitrogen dioxide bubbler (or over permeation tube), corrected to 25°C and 760 mm Hg.

F_2 = flow rate, in ℓpm, of concentrated gas mixture injected into sample air stream.

F_3 = total flow rate, in ℓpm, of sample air stream

C_t = analyzed concentration of the tank mixture, in ppm by volume on an ideal gas basis.

9.2.6 For each standard color, calculate the $\mu\ell$ of nitrogen dioxide/mℓ of absorbing reagent:

$$\mu\ell\ NO_2/m\ell = C\ V$$

where:

C = ppm concentration (Section 9.2.5)

V = volume of air sample at 25°C and 760 mm Hg, in ℓ/mℓ of absorbing reagent.

9.2.7 Plot the absorbances of the colors against the μℓ of gaseous nitrogen dioxide/mℓ of absorbing reagent. Draw the straight line through the origin giving the best fit, and determine the slope, K (the value of μℓ/mℓ intercepted at absorbance of exactly 1.0).

10. Calculations

10.1 For convenience, standard conditions are taken as 760 mm Hg and 25°C, at which the molar gas volume is 24.47 liters. (This is identical with standard conditions for Threshold Limit Values of the American Conference of Governmental Industrial Hygienists; it is very close to the standard conditions used (Reference 9) for air-handling equipment, of 29.92 in. Hg, 70°F, and 50 percent relative humidity, at which the molar gas volume is 24.76 liters, of 1.2 percent greater.)

Ordinarily the correction of the sample volume to these standard conditions is slight and may be omitted; however, for greater accuracy, it may be made by means of the perfect gas equation.

10.2 Standardization by nitrite solution is based upon the empirical observation (References 1,6) that 0.72 mole of sodium nitrite produces the same color as 1 mole of nitrogen dioxide.

10.2.1 This factor is applied to calculate the equivalence of the nitrite solution to the volume of NO_2 absorbed as follows: One mℓ of the working standard solution contains 2.03×10^{-5} g $NaNO_2$. Since the molecular weight of $NaNO_2$ is 69.00, this is equivalent to:

$$\frac{2.03 \times 10^{-5}}{69.00} \times \frac{24.47}{0.72} = 1 \times 10^{-5}\ \ell \text{ of } NO_2, \text{ or}$$

$$= 10\ \mu\ell \text{ of } NO_2$$

10.2.2 In Section 9.1, the calibration standard containing 1 mℓ of nitrite solution (10 μℓ NO_2) per 25 mℓ total volume is equivalent to 10/25 or 0.4 μℓ of NO_2 per mℓ.

10.3 Compute the concentration of nitrogen dioxide in the sample as follows:

$$\text{Nitrogen dioxide, ppm} = AK/V$$

where:

A = measured absorbance

K = standardization factor from Section 9.1.4 or 9.2.7

V = volume of air sample, at 25°C and 760 mm Hg, in liters/mℓ of absorbing reagent.

10.4 If preferred, the graph from Section 9.1.4 or 9.2.7 may be used instead as follows:

$$\text{Nitrogen dioxide, ppm} = \mu\ell\ NO_2 \text{ per } m\ell/V$$

10.4.1 If V is a simple multiple of K, calculations are simplified. Thus, for the K value of 0.73 previously cited, if exactly 7.3 liters of air are sampled through a bubbler containing 10 mℓ of absorbing reagent, K/V = 1, and the absorbance is also ppm directly.

10.4.2 For exact work, an allowance may be made in the calculations for sampling efficiency and for fading of the color using the following equation:

$$\text{Nitrogen dioxide, ppm} = A_c K/VE$$

where:

A_c = corrected absorbance; the absorbance is corrected for fading of the color as indicated in Section 8.2.4 when there is a prolonged interval between sampling and measurement of the absorbance.

E = sampling efficiency; for a bubbler, E is estimated from prior tests using two absorbers in series (Reference 7 and Section 6.1.1); for a bottle or syringe, E = 1.0.

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FREE SILICA (QUARTZ, CRISTOBALITE, TRIDYMITE) IN ATMOSPHERIC DUST

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Quartz, Cristobalite, Tridymite	**Method No.:**	P&CAM 109
Matrix:	Atmospheric Dust	**Range:**	5 – 200 $\mu g/cm^2$
Procedure:	X-ray Diffraction		
Date Issued:	4/7/72	**Precision:**	± 5 μg
Date Revised:	1/15/74	**Classification:**	D (Operational)

1. **Principle of Method**

   1.1 Atmospheric dust samples are collected on membrane filters.

   1.2 The filters are ashed and the residues along with an internal calibration standard are redistributed onto silver membrane filters.

   1.3 Each sample is scanned by X-ray diffraction to determine the presence of free silica (quartz, cristobalite, and/or tridymite).

   1.4 If present, the mass of each free silica species is determined by measuring the ratio of the diffraction peak intensities of the free silica species and the internal standard (fluorite) and comparing this ratio to a calibration curve.

2. **Range and Sensitivity**

   2.1 The analytical range extends from 5 $\mu g/cm^2$ to 200 $\mu g/cm^2$ for each free silica species; the total atmospheric dust loading on the filter must not exceed 1 mg/cm^2.

   2.2 The sensitivity is 5 μg for each free silica species.

3. **Interferences**

   3.1 Several minerals have diffraction peaks that correspond in position to the major peak for quartz; these include micas (biolite, muscovite), potash, feldspars (microcline, plagioclase), sillimanite, graphite, iron carbide (FeC), and zircon. The

presence of these interferences is usually encountered in specific, recognizable situations and can be verified by X-ray diffraction analysis. Analytical measurements can be carried out at a secondary quartz peak with a commensurate decrease in sensitivity.

3.2 Comparable interference may occur for cristobalite and tridymite. This can be determined by X-ray diffraction analysis. If interference occurs, secondary cristobalite and tridymite peaks must be used.

3.3 Diffraction peak interference may also occur for the fluorite (CaF_2) internal calibration standard. Compensation must be made for increased peak intensity from the interfering species or an alternate standard must be employed.

3.4 The presence of specific elements in the sample (iron, in particular) may result in appreciable X-ray fluorescence, leading to high background intensity. This situation may be circumvented by employing a diffracted beam monochromator.

4. Precision and Accuracy

4.1 Bumstead (Reference 11.1) has reported eleven replicate measurements of quartz in 2 mg of coal dust as having an average of 0.63% (12.6 μg), a range of 0.51-0.91% and a standard deviation of 0.114% (2.3μg); he reports an accuracy of ± 30% (3.8 μg) of the quartz present in the sample.

4.2 No information is available regarding the accuracy for cristobalite or tridymite.

5. Advantages and Disadvantages

5.1 The X-ray diffraction method offers sensitivity equivalent to or greater than other methods (infrared or colorimetric), is non-destructive to the sample, is rapidly performed and may be automated.

5.2 The X-ray diffraction method is limited to a sample size of a few milligrams. Application of the method requires a rather high degree of technical skill and expensive equipment.

6. Apparatus

6.1 **Sampling Equipment**. The sampling unit for the filter-collection method has the following components:

6.1.1 The filter unit consisting of the filter media (Section 6.1.4) and a two-piece filter cassette holder.

6.1.2 A personal sampling pump. This pump must be properly calibrated (with a representative filter unit in the line) so the volume of air sampled can be measured accurately.

6.1.3 Ten-mm nylon cyclone.

6.1.4 Polyvinyl chloride membrane filters (or equivalent), 37 mm and 5.0 μm pore size. (Gelman VM-1 filters are unacceptable because of the high background produced by the ash.)

6.2 **X-ray diffraction equipment**, including copper and/or molybdenum target X-ray tubes.

6.3 **Low temperature radiofrequency asher**: Tracerlab Model LTA 600 or equivalent, or muffle furnace.

6.4 Ultrasonic bath.

6.5 Filtration apparatus.

6.6 **Silver membrane filters**, 25 mm diameter having an 0.45 μm pore size: Selas Flotronics.

6.7 Aluminum weighing pans.

6.8 Porcelain crucibles with covers.

6.9 100 mℓ Pyrex beakers.

6.10 Glass microscope slides.

6.11 Non-serrated, non-magnetic forceps.

6.12 Metal spatula.

7. **Reagents**

7.1 **Quartz, cristobalite** and **tridymite** powders: Acid-washed and wet-sieved through 10 μm sieve.

7.2 Fluorite (CaF_2): 400 mesh powder. Analytical Grade.

7.3 Wetting agent: Aerosol OT.

7.4 Petroleum jelly.

7.5 **Standard Solutions** of fluorite, quartz, cristobalite and tridymite. (Refer to Section 9.1.)

8. **Procedure**

8.1 **Cleaning of Equipment.** It is important that all equipment be kept as free of contaminant dust as possible.

8.1.1 The spatula, forceps, etc., may be satisfactorily cleaned using ethyl alcohol and disposable non-linting tissues.

8.1.2 The aluminum weighing pans are cleaned by rinsing twice with distilled water and twice with ethyl alcohol, and allowing to dry in a dust-free environment.

8.2 **Collection and Shipping of Samples**

8.2.1 Samples are collected on 5.0μm pore size, PVC (or equivalent) membrane filters. The quantity of dust collected on the filter should be 5 mg or less. The filters are held in plastic cassettes that permit the attachment of a 10 mm nylon cyclone to the inlet side of the cassette to collect a respirable sample. The filter is kept in the cassette for shipment.

8.2.2 Whenever an air sample or series of air samples is collected, a bulk sample of the suspected parent material of the atmospheric contaminant should be obtained and shipped back to the laboratory with the air samples.

8.3 **Analysis of Samples**

8.3.1 Either of these **two described methods** may be used to ash the sample.

1. Using forceps and spatula, place the filter samples in aluminum weighing pans and situate within the sample compartments of the low-temperature asher so that the sample exposure to the radiofrequency-excited oxygen plasma is optimized. The samples are ashed for one hour at 100 watts RF power and at an oxygen flow rate of 75 mℓ/min., using the techniques recommended in the instrument manual.

2. Using forceps and spatula, place the filter samples in porcelain crucibles, loosely cover and place in muffle furnace. Hold for two hours at 600°C (800°C if graphite is present in the sample).

8.3.2 Carefully scrape the ash residue into a 100 mℓ beaker. Rinse the weighing pan (or crucible) several times with about 5 mℓ of water and pour the rinse water into the beaker. Add 1 mℓ of the CaF_2 standard solution, a few drops of wetting agent, and distilled water to bring volume up to about 50 mℓ.

8.3.3 Ultrasonically agitate the beaker and its contents for 30 minutes at maximum setting.

8.3.4 Filter solution through a 25 mm diameter, 0.45 μm pore size silver membrane filter under suction. Thoroughly wash down the filter holder with distilled water to ensure that all dust particles have been transferred to the filter.

8.3.5 Using forceps, remove the filter, place in a Petri dish and dry at 105°C for 15 minutes.

8.3.6 The silver filter is then attached to a glass microscope slide with petroleum jelly, and inserted into the X-ray diffractometer. A portion of the filter should be inserted beneath the clamping surface of the diffractometer.

8.3.7 The diffractometer is then scanned over the 2 θ-range corresponding to d = 4.5 to 2.3Å (For a copper tube, 2 θ = 18° to 39° and for a molybdenum tube, 2 θ = 9° to 18°). The presence of crystalline forms of silica is determined by the occurrence of diffraction peak, as follows:

Mineral	d (Most Intense)	d (Second Most Intense)
Quartz	3.34 Å	4.26
Cristobalite	4.05	2.49
Tridymite	3.80	4.07
Fluorite Standard	3.15	

The presence of interfering compounds can be determined by the presence and identification of other X-ray diffraction peaks.

8.3.8 The intensity of the most intense diffraction peak for quartz, cristobalite and tridymite (as given in Section 8.3.7) is determined by measuring peak height or peak area from the diffraction scan or by scaler (fixed time or fixed count) measurement at peak position. All measurements must be corrected for background. Comparable measurements are made for the fluorite standard at d = 3.15Å. If diffraction peaks from other compounds interfere with the most intense quartz, cristobalite or tridymite peak, the second most intense peak for these silica compounds must be employed.

8.3.9 The free silica to fluorite intensity ratios are determined, and the mass of quartz, cristobalite and/or tridymite is determined from the appropriate calibration curve.

9. Calibration and Standards

9.1 Standards

9.1.1 A standard solution of fluorite is prepared by adding 20 mg of fluorite to 100 mℓ of distilled water containing a few drops of wetting agent and agitation.

9.1.2 Known amounts of quartz, cristobalite and tridymite are weighed to the nearest 0.1 mg and are added to 100 mℓ distilled water containing a few drops of wetting agent to provide five standard solutions of each mineral covering a concentration range of 0.01 – 0.3 mg/mℓ.

9.2 Standard Curve

9.2.1 One mℓ each of the standard fluorite solution (Section 9.1.1) and one of the crystalline free silica solutions (Section 9.1.2) are added to 50 mℓ distilled water and are analyzed according to steps 8.3.4 through 8.3.8. Similar data are collected for each of the free silica solutions (Section 9.1.2).

9.2.2 Standard curves are prepared for quartz, cristobalite and tridymite in which the intensity ratio of the free silica standard to fluorite is plotted against free silica mass in mg. This plot should give a nearly straight line that passes through the origin.

10. Calculations

The concentration of free silica in air can be expressed as milligrams silica per cubic meter of air sampled.

$$\text{mg } SiO_2/m^3 = \frac{\text{mg Q} + \text{mg C} + \text{mg T}}{V_s}$$

where:

$\text{mg } SiO_2/m^3$ = total milligrams of free silica per cubic meter of air sampled.

mg Q, mg C, mg T = milligrams of quartz, cristobalite and tridymite, respectively, determined from the appropriate calibration curve.

V_s = volume of air sampled in cubic meters (1000ℓ = $1 m^3$) at standard conditions of 25°C and 760 mm Hg.

11. References

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QUARTZ IN COAL DUST BY INFRARED SPECTROSCOPY

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Quartz	**Method No:**	P&CAM 110
Matrix:	Coal Dust	**Range:**	10-100 μg quartz
Procedure:	Infrared Spectroscopy	**Precision:**	Relative standard deviation $< 15\%$ at 30 μg quartz
Date Issued:	4/17/72	**Classification:**	B (Accepted)
Date Revised:	1/15/74		

1. Principle of the Method

1.1 Airborne coal dust samples (respirable fraction) are collected on mixed cellulose ester membrane filters.

1.2 The filter samples are ashed in a low-temperature radiofrequency asher to destroy the organic matrix.

1.3 The ash is incorporated into a potassium bromide (KBr) pellet of which an infrared spectrum from 900 cm^{-1} to 700 cm^{-1} is obtained.

1.4 The absorbance at 800 cm^{-1} is calculated and the weight of quartz is determined by reference to a standard curve.

2. Range and Sensitivity

2.1 For a 1- to 2-mg sample of coal dust, the analytical range extends from 10 to 100 μg of quartz.

2.2 The sensitivity is 5 μg of quartz.

3. Interferences

3.1 Cristobalite and tridymite both absorb in the area of the 800 cm^{-1} quartz analytical peak of the spectrum. The presence of significant amounts of cristobalite and tridymite can be ascertained by x-ray diffraction on a bulk sample.

3.2 No interference in the 800 cm^{-1} area of the spectrum is produced by the low-temperature ashing of kaolin ($Al_2O_3 \cdot 2\,SiO_2 \cdot 2H_2O$), which may be present in the coal sample.

3.3 Infrared spectra of water, calcite or limestone ($CaCO_3$), lime (CaO), and slaked lime [$Ca(OH)_2$] show no interference at 800 cm^{-1}.

3.4 Infrared spectra of the low-temperature ash of blank Millipore MF filters show no interference at 800 cm^{-1}

3.5 Amorphous silica does not interfere in the infrared analysis.

4. Precision and Accuracy

4.1 The relative standard deviation (computed from the results of 23 samples) is less than 15% at 30 μg quartz.

4.2 The accuracy has not been determined. No collaborative tests have been performed on this method.

5. Advantages and Disadvantages of the Method

5.1 This method offers greater sensitivity than does the x-ray diffraction method (Reference 11.1). The differential thermal analysis method requires a larger sample size than the infrared method, and in addition is not well suited to analysis of respirable-size ($<10\mu$) particles because thermal response decreases with decreasing particle size (Reference 11.2). The colorimetric method of Talvitie (References 11.3 and 11.4), offers comparable sensitivity, but fails to distinguish between the crystalline forms of free silica and also requires more dexterity of the analyst. In addition, quartz may be lost during the colorimetric analysis, causing an erroneously low result, or silicates may be retained, causing an erroneously high result.

5.2 The infrared method thus offers good sensitivity, does not require a large sample size, is ideally suited to the analysis of the respirable fraction of coal dust, and requires less dexterity of the analyst than do some other methods. A trained technician can perform 5-10 analyses per day.

5.3 The method, however, does require some expensive equipment.

6. Apparatus

6.1 Double beam, grating infrared spectrophotometer: Perkin-Elmer Model 621/or equivalent.

6.2 Low-temperature, radiofrequency asher: Tracerlab Model LTA600/or equivalent.

6.3 Microbalance: Cahn Model G-2 Electrobalance/or equivalent.

6.4 Analytical balance: Mettler Model H20/or equivalent.

6.5 13-mm evacuable pellet die.

6.6 30-ton laboratory press.

6.7 2-inch diameter agate mortar and pestle.

6.8 Aluminum weighing pans: Fisher Scientific/or equivalent.

6.9 Membrane filters: Millipore MF filters, 5-micron pore size, 37-mm diameter, white, plain, with filter backing.

6.10 Non-serrated, non-magnetic forceps.

6.11 Metal spatula.

6.12 Sampling apparatus:

6.12.1 Dorr-Oliver cyclones, 10-cm/or equivalent.

6.12.2 Unico Micronair personal sampling pumps/or equivalent.

6.12.3 Plastic cassettes (sample holders for 37-mm filters).

6.12.4 Cabinet with tight-sealing door (desiccator).

6.12.5 Saturated solution of zinc nitrate.

7. Reagents

7.1 Potassium bromide: Harshaw Chemical Company, infrared quality/or equivalent.

7.2 Quartz: Acid-washed, sieved to 10-micron size.

7.3 Ethyl alcohol: U.S.P. grade, 95%.

8. **Procedure**

8.1 **Cleaning of Equipment.** It is important that all equipment be kept as free of contaminant dust as possible.

8.1.1 The spatula, forceps, LTA sample compartments, mortar and pestle, and pellet die may be satisfactorily cleaned using ethyl alcohol and disposable non-linting tissues.

8.1.2 The aluminum weighing pans are cleaned by rinsing twice with distilled water and twice with ethyl alcohol, and allowing to dry in a dust-free environment.

8.2 **Collection and Shipping of Samples.** The coal dust samples (1-2 mg) are obtained and shipped and the sample weights (to 0.01 mg) are obtained by the procedure outlined in "Coal Dust in Air," Tentative Method of the Physical and Chemical Analysis Branch and Engineering Branch. (See, also, References 11.1 and 11.7.)

8.3 **Analysis of Samples**

8.3.1 Using forceps and spatula, carefully place the weighed filter samples in aluminum weighing pans, and situate within the sample compartments of the low-temperature asher so that sample exposure to the radiofrequency-excited oxygen plasma is optimized.

8.3.2 The samples are ashed for one hour at 100 watts RF power and at an oxygen flow rate of 75 cc/min., using the techniques recommended in the instrument manual.

8.3.3 Approximately 300 mg of KBr, dried overnight at 110-120°C, are weighed to 0.1 mg and added directly to the weighing pan containing the ash. The KBr and the ash are thoroughly mixed in the aluminum pan with an agate pestle. The KBr is weighed and mixed in a 25% or less relative humidity environment to facilitate sample handling.

8.3.4 The sample mixture is transferred to a 13-mm evacuable pellet die, and a pellet is made using standard technique. The finished pellet, about 0.85 mm thick, is weighed to 0.1 mg. The value of (weight finished pellet ÷ weight KBr initially added) is computed. This value usually is about 0.98.

8.3.5 The pellet is scanned in a Perkin-Elmer Model 621 double-beam grating infrared spectrophotometer. The standard settings described in the instrument manual are used. No mechanical reference beam attenuation is used.

Before each scan, the 100% transmittance and scale position adjustments are made at the 800 cm^{-1} frequency.

The pellet is scanned from 900 cm^{-1} to 700 cm^{-1} (11 to 14 microns) over a period of about 2 minutes. When the quartz peak at 800 cm^{-1} is small, an ordinate expansion of 5X is used to enhance the peak height. The pellet is scanned through each of 4 pellet diameters spaced 45° apart. The resulting 4 absorbance values at 800 cm^{-1} are averaged to obtain the value for the pellet. The range of absorbance values for a single pellet is usually 0.005 absorbance units or less, which corresponds to a range of 5 μg or less of quartz.

8.3.6 Absorbances are computed from the transmittance values for the peak and baseline, which are read to 0.1% transmittance.

The baseline is chosen to be the horizontal tangent to the maximum of the trace on the higher-frequency side of the quartz peak. Such a horizontal baseline is concentration-independent. The value of the baseline transittance is I_0. The value of the peak transmittance is I. The absorbance of the peak equals the common logarithm of I_0/I. When the absorbance value at the 800 cm^{-1} quartz peak has been determined for the pellet, the weight in micrograms of quartz is obtained by reference to the standard curve.

9. Calibration and Standards

9.1 **Standards.** Known amounts of quartz, between 10 and 100 μg, are weighed out to 0.001 mg, as a 0.5% dilution in KBr, on a microelectrobalance in a 25% or less relative humidity environment. Approximately 300 mg of KBr, dried overnight at 110-120°C, are weighed to 0.1 mg, added to the quartz mixture in an agate mortar, and ground with an agate pestle. Pellets are prepared as in 8.3.4 and weighed to 0.1 mg. The value of (weight of finished pellet ÷ weight of constituent solids) is computed. Again, this value usually is about 0.98.

9.2 **Standard Curve.** A plot is made of the pellet absorbances at 800 cm^{-1} (obtained as in 8.3.5) vs. weight in micrograms of quartz (corrected as in 10.2) in the pellets. This plot should give a straight line approximately passing through the origin.

10. Calculations

10.1 A correction factor is applied to the original weight of coal dust in the sample to account for loss of coal ash during the pellet-making process. The original weight of coal dust is multiplied by the value computed in 8.3.4. This corrected weight of coal dust is used when the percent quartz in the dust is computed.

10.2 A correction factor is applied to the amount of quartz weighed out in 9.1 to account for loss of quartz during the pellet-making process. The measured weight of quartz is multiplied by the value computed in 9.1. This corrected weight of quartz is used when the standard curve is plotted.

10.3 After the weight, in micrograms of quartz in the sample, has been determined as in 8.3.6, the percent quartz is computed:

$$\frac{\mu g \text{ of quartz in sample}}{\text{corrected wgt in mg of coal dust sample} \times 1000} \times 100 = \% \text{ quartz}$$

11. References

11.1 Morse, K.M., H.E. Bumsted, and W.C. Janes, "The Validity of Gravimetric Measurements of Respirable Coal Mine Dust," *Amer. Ind. Hyg. Assoc. J.*, 32:104 (1971).

11.2 Weiss, B., E.A. Boettner, and M. Stenning, "Determination of Quartz: Evaluation of the Differential Thermal Analysis Method," *Arch. Environ. Health*, 20: 37 (1970).

11.3 Talvitie, N.A., "Determination of Free Silica: Gravimetric and Spectrophotometric Procedures Applicable to Air-Borne and Settled Dust," *Amer. Ind. Hyg. Assoc. J.*, 25:169 (1964).

11.4 Talvitie, N.A., and F. Hyslop, "Colorimetric Determination of Siliceous Atmospheric Contaminants," *Amer. Ind. Hyg. Assoc. J.*, 19:54 (1958).

11.5 Standard Method No. 19, United States Bureau of Mines, 4800 Forbes Avenue, Pittsburgh, Pennsylvania 15213.

11.6 Dixon, K., and T.S. Fretwell, "The Determination of Quartz in the Airborne Dust of Coal Mines and in Coal Measure Minerals by Infrared Spectroscopy," Report No. SNT/55/68, Scientific Department, South Nottinghamshire Area, National Coal Board, Great Britain.

11.7 Larsen, D.J., L.J. von Doenhoff, and J.V. Crable, "The Quantitative Determination of Quartz in Coal Dust by Infrared Spectroscopy," *Amer. Ind. Hyg. Assoc. J.*, 33:367 (1972).

CARBON MONOXIDE IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Carbon Monoxide	**Method No:**	P&CAM 112
Matrix:	Air	**Range:**	10-500 ppm
Procedure:	Infrared Absorption Spectrophotometry		
Date Issued:	4/7/72	**Precision:**	±10%
Date Revised:	1/12/74	**Classification:**	C (Tentative)

1. **Principle of the Method**

Air samples are obtained in 5-liter or larger inert plastic bags and analyzed by infrared spectrophotometry in a 10-meter-path-length gas cell. Compressed air tanks (scuba tanks) may also be analyzed.

2. **Range and Sensitivity**

The analytical range extends from 10 ppm to 500 ppm. The upper limit may be extended by using an aliquot of the sample.

3. **Interferences**

Any gas that absorbs infrared radiation at the analytical wavelength will interfere. Possible interferences include: acetylene, aldehyde, cyanogen, diazomethane, hydrogen sulfide, nitrosylchloride, nitrous oxide, olefins and propyne. These gases are not usually present in significant concentration in normal atmospheres, but they can readily be ruled out by reference to the complete spectrum of the gas sample scanned from 2-14 microns. Each of the interfering gases has additional absorption lines in other areas of the spectrum which readily denote its presence. Carbon dioxide in concentrations as high as 3% does not interfere. Water vapor is eliminated by the use of drying agent traps on the inlet of the IR cell.

4. **Precision and Accuracy**

4.1 The analytical method has a precision of ± 10%.

4.2 No collaborative testing has been done with this method.

5. **Advantages and Disadvantages**

5.1 The major advantage of the method over CO meters and detector tubes is that the analysis is more accurate. Approved detector tubes are accurate to only ± 25%.

5.2 The disadvantage is that samples must be returned to the laboratory for analysis whereas immediate results are available with CO meters and detector tubes.

6. **Apparatus**

6.1 Peristaltic sampling pump, diaphragm pump, or vacuum pump with filtered outlet to remove oil.

6.2 Tedlar bags (5-liter or larger).

6.3 Infrared spectrometer, 2- to 15-micron range, wavelength accuracy ± 0.015μ, resolving power 0.01μ, wavelength reproducibility 0.005μ, transmission accuracy ± 0.5%.

6.4 10-meter-path-length gas cell.

6.5 Manometer

6.6 Vacuum pump (capable of reducing pressure to 1 mm).

6.7 Gas-tight syringes (100 $\mu\ell$, 500 $\mu\ell$, 1000 $\mu\ell$).

6.8 Gas tank regulators, connections, and needle valves for introducing dilution gas, CO, and samples.

7. **Reagents**

7.1 Anhydrous calcium chloride or indicating drierite.

7.2 Carbon monoxide.

7.3 Tank or dry nitrogen or CO-free air. (CO-free air can be obtained by using cylinder air known to be free of CO, or by allowing dilution air to enter the cell via a Hopcalite absorption trap connected to the inlet of the cell.)

7.4 Hopcalite (used to remove CO if room air is used for dilution).

8. Procedure

8.1 **Cleaning of Equipment.** Equipments must be properly evacuated or flushed to minimize any background interference.

8.2 **Collection and Shipping of Samples**

8.2.1 The sampling containers, Tedlar and Mylar bags, are flushed or evacuated prior to use.

8.2.2 Samples are obtained by filling the sampling containers with air either by using a sampling pump to push air in or by simply opening the valve on an evacuated container and allowing it to reach atmospheric pressure.

8.2.3 After the sample has been taken, all parts are sealed to minimize leakage in or out of the containers.

8.2.4 Care must be taken in transporting the samples to the laboratory, so as not to damage or alter the existing sample.

8.2.5 CO samples do not deteriorate on standing. If samples collected for analysis are under reduced pressure, care should be taken to see that dilution does not occur because of leaks in the container. Atmospheric samples can generally be stored at atmospheric pressure to avoid dilution.

8.2.6 Compressed air tanks (scuba tanks) may also be analyzed for CO content.

8.3 **Analysis of Samples**

8.3.1 The 10-meter path-length gas cell is connected to a manometer via a T connection.

8.3.2 The cell is then evacuated to approximately 1.0 mm Hg.

8.3.3 The Tedlar bag sample is introduced into the cell through a calcium chloride or drierite tube. If a rigid sample container is used, the equilibrium pressure (Pe) must be noted and the cell filled to atmospheric pressure with CO-free air or dry nitrogen. A 15-minute waiting period before analysis is necessary for equilibrium to be established.

If the sample is a compressed air tank, fill the evacuated gas cell to atmospheric pressure with air from the tank.

8.3.4 The spectrum is scanned from 4-6μ (2500-1670 cm^{-1}) and the absorbance at 4.67μ (2143 cm^{-1}) is measured by the baseline technique.

9. Calibration and Standards

9.1 The volume of the 10-meter cell is determined by standard techniques. The simplest procedure is to evacuate the cell, and then bring to atmospheric pressure by permitting air to enter via a calibrated wet-test meter. The volume of the cell is the volume of air shown on the meter. After the volume has been ascertained, the cell is again evacuated, and known volumes of CO added with the aid of standard gas-tight syringes, through a rubber serum bottle cap attached to the inlet of the cell, or through the rubber tubing which connects the gas cell with the tank of dilution gas.[1] The pressure in the cell is then brought to atmospheric pressure with CO-free dry air or nitrogen. The absorbance at 4.67μ (2143 cm^{-1}) is measured as described in the procedure.

9.2 The CO concentration is calculated from the quantity of CO added, and the volume of the cell. For example, 1.0 mℓ CO in a 3.85-liter cell gives a concentration of 260 ppm CO. A calibration curve relating absorbance and concentration is prepared for a series of known volumes of CO introduced into the IR cell.

10. Calculations

10.1 The concentration of the unknown is read from the calibration curve. To calculate the standard curve concentrations in parts per million (ppm), one may use the following equation.

$$\text{Sample concentration (ppm)} = \frac{V_{std}}{V_c}$$

where:

V_{std} = Volume of CO added ($\mu\ell$)
V_c = Volume of IR cell (liter)

10.2 The observed concentration from the calibration curve is corrected for the volume of sample actually introduced into the cell. For samples introduced into the cell with syringes, the volume is readily known and the correction applied using the following equation:

$$\text{Sample concentration (ppm)} = C_{obs} \times \frac{V_c}{V_s}$$

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1. An alternative is to use CO "span gases" of known concentration. These standards may be obtained from Mathieson.

where:

C_{obs} = Observed concentration from the calibration curve (ppm)

V_c = Volume of IR cell (liter)

V_s = Volume of sample (liter)

For samples introduced from non-rigid Tedlar bags with volumes greater than the volume of the IR cell, $V_s = V_c$ and the sample concentration = C_{obs}.

10.3 For samples introduced by pressure measurements, the sample concentration is calculated as follows:

$$\text{Sample concentration (ppm)} = C_{obs} \times \frac{(Pa)}{(Pa-Pe)}$$

where:

C_{obs} = Observed concentration from the calibration curve (ppm)

Pe = Equilibrium pressure after connecting the sample container to the IR cell.

Pa = Atmospheric pressure.

11. References

Intersociety Tentative Method, *Health Laboratory Science*, 7, 78 (January, Supplement, 1970).

FLUORIDE IN URINE

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Fluoride	**Method No.**	P&CAM 114
Matrix:	Urine	**Range:**	Lower Limit Urine 0.19 mg/liter
Procedure:	Ion Specific Electrode		
Date Issued:	8/28/72	**Precision:**	Unknown
Date Revised:	12/1/73	**Classification:**	D (Operational)

1. **Principle of the Method**

   1.1 Urine samples are diluted with an equal volume of a pH-activity coefficient buffer solution.

   1.2 A fluoride sensitive specific ion electrode and a reference electrode are inserted into the buffered sample. The observed potential difference between the electrodes can then be related to the fluoride concentration in the sample via calibration curves prepared with the same buffer and electrodes.

2. **Range and Sensitivity**

   The range and sensitivity of this method have not been established at this time. The electrode recommended range is 0.19-1900 mg/ℓ urine.

3. **Interferences**

   Hydroxide, the only positive interference in the measurement, is eliminated by use of the pH buffer. Negative interferences, which may result from complexion of fluoride by cations such as a calcium, are minimized by the buffer and EDTA added as a stabilizer. The buffer also yields a solution of high ionic strength in which the activity coefficient of fluoride is relatively constant.

4. **Precision and Accuracy**

   The accuracy and precision of this method have not been completely determined at this time. No collaborative tests have been performed on this method.

5. **Advantages and Disadvantages of the Method**

5.1 Advantages over previous methods include simplicity, accuracy, speed, specificity, and elimination of ashing, distillation or diffusion steps. Interfering ions are complexed.

5.2 No significant disadvantages are known.

6. **Apparatus**

6.1 Fluoride sensitive specific ion electrode, Model 94-09, Orion Research Corporation (Cambridge, Massachusetts) or equivalent.

6.2 Reference electrode, calomel or silver/silver chloride, sleeve junction preferable but not necessary.

6.3 pH/Millivolt meter, capable of measuring to within 0.5 millivolt.

6.4 Magnetic stirrer, equipped with small stirring bars which can spin freely in the sample beakers.

6.5 Plastic beakers (50 mℓ) and sample collection bottles (100-mℓ capacity), polyethylene or polypropylene.

6.6 Laboratory glassware.

7. **Reagents**

All chemicals used should be ACS Reagent grade or equivalent. After being prepared in clean glassware, all fluoride-containing solutions should be stored in plastic beakers and bottles.

7.1 Double Distilled Water.

7.2 Sodium Citrate.

7.3 Ethylenedinitrilotetracetic Acid (EDTA), disodium salt.

7.4 Glacial Acetic Acid.

7.5 Sodium Chloride

7.6 **Sodium Hydroxide, 5 M Solution.** Dissolve 20 g sodium hydroxide pellets in sufficient distilled water to give 100 mℓ of solution.

7.7 **Total Ionization Activity Buffer (TISAB).** Place 500 mℓ of double distilled water in a 1-liter beaker. Add 57 mℓ of glacial acetic acid, 85 g of sodium chloride, and 0.30 g of sodium citrate. Stir to dissolve. Place beaker in a water bath (for cooling). Slowly add 5M sodium hydroxide until the pH is between 5.0 and 5.5. Cool to room temperature and pour into a 1-liter volumetric flask and add double distilled water to the mark.

7.8 Sodium Fluoride, for preparation of standards.

7.9 **Standard Fluoride Solutions.** All solutions should be stored in plastic bottles. The 0.1M fluoride standard is reported to be stable at least two months. All other dilutions should be prepared fresh weekly.

7.9.1 0.1M Fluoride (1900 μg F/mℓ) – Dissolve 4.20 g of sodium fluoride in water and dilute to 1000 mℓ. This solution can also be purchased from Orion Research, Inc., Cambridge, Massachusetts.

7.9.2 10^{-2} M Fluoride (190 μg F/mℓ)– Dilute 10 mℓ of 7.9.1 to 100 mℓ with water.

7.9.3 10^{-3} M Fluoride (19 μg F/mℓ) – Dilute 10 mℓ of 7.9.2 to 100 mℓ with water.

7.9.4 10^{-4} M Fluoride (1.9 μg F/mℓ) – Dilute 10 mℓ of 7.9.3 to 100 mℓ with water.

7.9.5 10^{-5} M Fluoride (0.19 μg F/mℓ) – Dilute 10 mℓ of 7.9.4 to 100 mℓ with water.

8. **Procedure**

8.1 **Cleaning of Equipment.** All plastic and glassware must be rendered free of any fluoride before use.

8.2 **Collection and Shipping of Samples**

8.2.1 Urine samples representing pre-exposure (early morning) and after-exposure (end of working day) conditions should be taken. To minimize bacterial contamination, one should collect the mid-stream urine sample of a single voiding.

8.2.2 The urine samples are collected in chemically clean bottles containing 0.2 g of EDTA (ethylenedinitrilotetracetic acid).

8.2.3 Upon receipt at the laboratory, the volume of the urine sample should be determined. If the volume is greater than 100 mℓ, an amount of EDTA equivalent to 0.2 g per 100 mℓ in excess of the first 100 mℓ should be added.

8.2.4 Samples that cannot be analyzed within 48 hours should be refrigerated.

8.3 **Analysis of Urine Samples**

8.3.1 Transfer 10 mℓ of well mixed urine sample and 10 mℓ of TISAB buffer solution into a 50 mℓ plastic buffer, and add a magnetic stirring bar.

8.3.2 Immerse the electrodes in the solution. Adjust stirring speed and stirrer position to avoid splashing and hitting the electrodes.

8.3.3 After the EMF (voltage) reading stabilizes (that is, EMF drift less than 0.5 millivolt per minute) record the EMF to the nearest millivolt.

For most samples, the EMF will stabilize in a minute or two if the fluoride concentration is 2 μg/mℓ or more. Stabilization may take slightly longer at lower concentrations.

8.3.4 Rinse the electrodes with double distilled water and wipe dry with clean tissue before proceeding with next step.

9. **Calibration and Standards**

9.1 Use the standard fluoride solutions prepared in 7.9 and treat them in the same way as the samples, Section 8.2 start with the most dilute solution (7.9.5) and proceed to 7.9.2 (10^{-2} M fluoride).

9.2 Prepare a calibration curve by plotting the concentration – EMF data on semi-log paper with the fluoride concentration on the log axis.

9.3 Calibrations should be repeated at least twice daily.

10. **Calculations**

10.1 The concentration of fluoride is obtained by converting the millivolt readings into concentrations using the calibration curve.

10.2 The concentration is reported as mgF per liter (numerically equivalent to μg per mℓ) of urine.

11. References

11.1 *Instruction Manual for Fluoride Electrode Model 94-09*, Orion Research Incorporated, Cambridge, Massachusetts.

11.2 Sun, Mu-Wan, "Fluoride Ion Activity Electrode for Determination of Urinary Fluoride," *Amer. Inc. Hyg. Assoc. J.*, 30, 133 (1969).

CYANIDE IN AIR

Physical and Chemical Analysis Branch
Analytical Method

Analyte:	Cyanide	**Method No.**	P&CAM 116
Matrix:	Air	**Range:**	0.013 -13 mg/m^3
Procedure:	Collection via Impinger/ Ion Specific Electrode		
Date Issued:	9/8/72	**Precision:**	Unknown
Date Revised:	12/1/73	**Classification:**	D (Operational)

1. **Principle of the Method**

   1.1 Atmospheric samples are taken using midget impingers that contain 10 mℓ of 0.1M NaOH.

   1.2 Samples are analyzed using the cyanide ion specific electrode.

2. **Range and Sensitivity**

   The range and sensitivity of the method have not been established at this time. The recommended range of the method is 0.013-13 mg/m^3 in air.

3. **Interferences**

   3.1 Sulfide ion irreversibly poisons the cyanide ion specific electrode and must be removed if found to be present in the sample. Check for the presence of sulfide ion by touching a drop of sample to a piece of lead acetate paper. The presence of sulfide is indicated by discoloration of the paper.

   3.2 Sulfide is removed by the addition of a small amount (spatula tip) of powdered cadmium carbonate to the pH 11-13 sample. Swirl to disperse the solid, and recheck the liquid by again touching a drop to a piece of lead acetate paper. If sulfide ion has not been removed completely, add more cadmium carbonate. Avoid a large excess of cadmium carbonate and long contact time with the solution.

3.3 When a drop of liquid no longer discolors a strip of lead acetate paper, remove the solid by filtering the sample through a small plug of glass wool contained in an eye dropper and proceed with the analysis.

4. **Precision and Accuracy**

The precision and accuracy of this method have not been completely determined at this time. No collaborative tests have been performed on this method.

5. **Advantages and Disadvantages of the Method**

Advantages are the simplicity, specificity, speed and accuracy of the method.

6. **Apparatus**

6.1 **Sampling Equipment.** The sampling unit for the impinger collection method consists of the following components:

6.1.1 A prefilter unit (if needed) which consists of the filter media and cassette filter holder.

6.1.2 A midget impinger containing the absorbing solution or reagent.

6.1.3 A pump suitable for delivering desired flow rates. The sampling pump is protected from splashover or water condensation by an adsorption tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump.

6.1.4 An integrating volume meter such as a dry gas or wet test meter.

6.1.5 Thermometer.

6.1.6 Manometer.

6.1.7 Stopwatch.

6.2 Orion 94-06 Cyanide ion specific electrode or equivalent.
6.3 Orion 90-01 Single junction reference electrode or equivalent.
6.4 Expanded scale millivolt – pH meter.
6.5 Associated Laboratory Glassware.
6.6 Plastic Bottles.
6.7 Magnetic Stirrer and Stirring Bars.

7. **Reagents**

The reagents described must be made up using ACS reagent grade or better grade of chemical.

7.1 Double distilled water.

7.2 Potassium Cyanide.

7.3 **Sodium Hydroxide 0.1M.** Dissolve 2.0 g NaOH in double distilled water and dilute to 500 mℓ.

7.4 **Potassium Cyanide Standards**

7.4.1 Dissolve 0.65 g KCN in 0.1M NaOH and dilute to 100 mℓ with additional 0.1M NaOH for 10^{-1} M[CN^-] (2600 μg/mℓ).

7.4.2 Dilute 10 mℓ of 10^{-1} M[CN^-] to 100 mℓ with 0.1M NaOH for 10^{-2} M[CN^-] (260 μg/mℓ).

7.4.3 Dilute 10 mℓ of 10^{-2} M[CN^-] to 100 mℓ with 0.1M NaOH for 10^{-3} M[CN^-] (26 μg/mℓ).

7.4.4 Dilute 10 mℓ of 10^{-3} M[CN^-] to 100 mℓ with 0.1M NaOH for 10^{-4} M[CN^-] (2.6 μg/mℓ).

7.4.5 Dilute 10 mℓ of 10^{-4} M[CN^-] to 100 mℓ with 0.1M NaOH for 10^{-5} M[CN^-] (0.26 μg/mℓ).

7.5 **Lead Acetate Paper.**

7.6 Cadmium Carbonate

8. **Procedure**

8.1 **Cleaning of Equipment.** All glassware is washed in detergent solution, rinsed in tap water and then rinsed with double distilled water.

8.2 **Collection and Shipping of Samples**

8.2.1 Pour 10 mℓ of the absorbing solution (Section 7) into the midget impinger, using a graduated cylinder to measure the volume.

8.2.2 Connect the impinger (via the adsorption tube) to the vacuum pump and the prefilter assembly (if needed) with a short piece of flexible tubing. The minimum amount of tubing necessary to make the joint between the prefilter and impinger should be used. The air being sampled should not be passed through any other tubing or other equipment before entering the impinger.

8.2.3 Turn on pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible. The sample should be taken at a flow rate of 2.5 ℓ pm. A sample size of not more than 200 liters and no less than 10 liters should be collected. The minimum volume of air sampled will allow the measurement at least 1/10 times the TLV, 0.5 mg/m^3 (760 mm Hg, 25°C).

8.2.4 After sampling, the impinger stem can be removed and cleaned. Tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Wash the stem with a small amount (1-2 mℓ) of unused absorbing solution and add the wash to the impinger. Then the impinger is sealed with a hard, non-reactive stopper (preferably Teflon). Do not seal with rubber. The stoppers on the impingers should be tightly sealed to prevent leakage during shipping. If it is preferred to ship the impingers with the stems in, the outlets of the stem should be sealed with Parafilm or other non-rubber covers, and the ground glass joints should be sealed (i.e., taped) to secure the top tightly.

8.2.5 Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within a day.

8.2.6 Whenever possible, hand delivery of the samples is recommended. Otherwise, special impinger shipping cases designed by NIOSH should be used to ship the samples.

8.2.7 A "blank" impinger should be handled as the other samples (fill, seal and transport) except that no air is sampled through this impinger.

8.2.8 Where a prefilter has been used, the filter cassettes are capped and placed in an appropriate cassette shipping container. One filter disc should be handled like the other samples (seal and transport) except that no air is sampled through, and this is labeled as a blank.

8.3 **Analysis of Samples**

8.3.1 The solution is quantitatively transferred from the impinger to a 50-cc beaker.

8.3.2 The cyanide ion electrode and the single junction reference electrode are placed in the solution and the resulting millivolt reading recorded. The reading should be taken after the meter has stabilized. Both the samples and standards should be stirred while the readings are being taken.

9. **Calibration and Standards**

9.1 Obtain the millivolt readings from each of the cyanide standards.

9.2 Plot the millivolt readings vs. the cyanide ion concentrations of the standards on semi-log paper. The cyanide ion concentration in $\mu g/m\ell$ is plotted on the log axis.

10. **Calculations**

10.1 The millivolt readings from the analysis of the sample are converted to $\mu gCN/m\ell$ of solution using the calibration curve.

10.2 The μg content of the sample is multipled by the sample volume to obtain the total μgCN in the sample.

10.3 Convert the volume of air sampled to standard conditions of 25°C and 760 mm Hg:

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

V_S = volume of air in liters at 25°C and 760 mm Hg
V = volume of air in liters as measured
P = Barometric Pressure in mm Hg
T = Temperature of air in degree centrigrade.

10.4 The concentration of CN in the air sampled can be expressed in μg CN per liter or mg CN per cubic meter.

$$mg/m^3 = \mu g/liter$$

$$mg/m^3 = \frac{\text{total } \mu g \text{ CN}}{V_s} \qquad \begin{matrix}\text{(Section 10.2)} \\ \text{(Section 10.3)}\end{matrix}$$

10.5 The concentration of CN can also be expressed in ppm, defined as $\mu\ell$ of component per liter of air.

$$\text{ppm} = \mu\ell\ CN/V_s = R/MW\ \mu g\ CN/V_s$$

$$= 0.94 \times \mu g\ CN/V_s$$

where:

$R = 24.45$ at 25°C, 760 mm Hg.
$MW = 26$

11. References

Orion, Cyanide Ion Specifications

FLUORIDES AND HYDROGEN FLUORIDE IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Total Fluoride	**Method No:**	P&CAM 117
Matrix:	Air	**Range:**	Lower Limit Air 0.009 mg/m^3
Procedure:	Collection via Impinger/ Ion Specific Electrode	**Precision:**	Unknown
Date Issued:	9/7/72		
Date Revised:	12/1/73	**Classification:**	D (Operational)

1. **Principle of the Method**

   1.1 Atmospheric samples are taken using midget impingers containing 10 mℓ of 0.1M NaOH.

   1.2 Samples are diluted 1:1 with Total Ionic Strength Activity Buffer (TISAB).

   1.3 The diluted samples are analyzed using the fluoride ion specific electrode.

2. **Range and Sensitivity**

   The range and sensitivity have not been established at this time. The recommended range of the method is 0.009-95 mg/m^3 air.

3. **Interferences**

   Hydroxide ion is the only significant electrode interference; however, addition of the TISAB eliminates this problem. Very large amounts of complexing metals such as aluminum may result in low readings even in the presence of TISAB.

4. **Precision and Accuracy**

   The accuracy and precision of this method have not been completely determined at this time. No collaborative tests have been performed on this method.

5. **Advantages and Disadvantages of the Method**

5.1 Advantages over previous methods include simplicity, accuracy, speed, specificity and elimination of distillation, diffusion and ashing of the samples.

5.2 No significant disadvantages are known at present.

6. **Apparatus**

6.1 **Sampling Equipment.** The sampling unit for the impinger collection method consists of the following components:

6.1.1 A prefilter unit (if needed) which consists of the filter media and cassette filter holder.

6.1.2 A midget impinger containing the absorbing solution or reagent.

6.1.3 A pump suitable for delivering desired flow rates. The sampling pump is protected from splashover or water condensation by an adsorption tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump.

6.1.4 An integrating volume meter such as a dry gas or wet test meter.

6.1.5 Thermometer.

6.1.6 Manometer.

6.1.7 Stopwatch.

6.2 Orion Model 94-09 Fluoride Specific Ion Electrode, or equivalent.

6.3 Reference Electrode, Orion 90-01 single junction, or equivalent calomel or silver/silver chloride electrode.

6.4 Expanded Scale Millivolt-pH Meter, capable of measuring to within 0.5 millivolt.

6.5 Polyethylene Beakers, 50-mℓ capacity.

6.6 Laboratory Glassware.

6.7 Magnetic Stirrer and Stirring bars for 50-mℓ Beakers.

7. Reagents

All chemicals must be ACS reagent grade or equivalent. Polyethylene beakers and bottles should be used for holding and storing all fluoride-containing solution.

7.1 Double Distilled Water.

7.2 Glacial Acetic Acid.

7.3 **Absorbing Solution: 0.1M Sodium Hydroxide Solution.** Dissolve 4 g sodium hydroxide pellets in 1 liter distilled water.

7.4 **Sodium Hydroxide, 5M Solution.** Dissolve 20 g sodium hydroxide pellets in sufficient distilled water to give 100 mℓ of solution.

7.5 Sodium Chloride.

7.6 Sodium Citrate.

7.7 **Total Ionic Strength Activity Buffer (TISAB).** Place 500 mℓ of double distilled water in a 1-liter beaker. Add 57 mℓ of glacial acetic acid, 58 g of sodium chloride and 0.30 g of sodium citrate. Stir to dissolve. Place beaker in a water bath (for cooling) and slowly add 5M sodium hydroxide until the pH is between 5.0 and 5.5. Cool to room temperature and pour into a 1-liter volumetric flask and add double distilled water to the mark.

7.8 Sodium Fluoride, for preparation of standards.

7.9 **Standard Fluoride Solution**

7.9.1 Dissolve 4.2 g of sodium fluoride in double distilled water and dilute to 1 liter. This solution contains 10^{-1} M[F^-] (1900 $\mu gF^-/m\ell$). The 0.1M fluoride solution may also be purchased from Orion Research, Inc., Cambridge, Mass.

7.9.2 Prepare 10^{-2} M[F^-] by diluting 10 mℓ of 10^{-1} M[F^-] to 100 mℓ with double distilled water (190 $\mu gF^-/m\ell$).

7.9.3 Prepare 10^{-3} M[F^-] by diluting 10 mℓ of 10^{-2} M[F^-] to 100 mℓ with double distilled water (19 $\mu gF^-/m\ell$).

7.9.4 Prepare 10^{-4} M[F^-] by diluting 10 mℓ of 10^{-3} M[F^-] to 100 mℓ with double distilled water (1.9 $\mu gF^-/m\ell$).

7.9.5 Prepare 10^{-5} M[F^-] by diluting 10 mℓ of 10^{-4} M[F^-] to 100 mℓ with doubled distilled water (0.19 μgF^-/mℓ).

8. **Procedure**

8.1 **Cleaning of Equipment.** All glassware and plastic ware are washed in detergent solution, rinsed in tap water, and then rinsed with double distilled water.

8.2 **Collection and Shipping of Samples**

8.2.1 Pour 10 mℓ of the absorbing solution (section 7) into the midget impinger, using a graduated cylinder to measure the volume.

8.2.2 Connect the impinger (via the adsorption tube) to the vacuum pump and the prefilter assembly (if needed) with a short piece of flexible tubing. The minimum amount of tubing necessary to make the joint between the prefilter and impinger should be used. The air being sampled should not be passed through any other tubing or other equipment before entering the impinger.

8.2.3 Turn on pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible. The sample should be taken at a flow rate of 2.5 ℓpm. A sample size of not more than 200 liters and no less than 10 liters should be collected. The minimum volume of air sampled will allow the measurement at least 1/10 times the TLV, 0.2 mg/m^3 (760 mm Hg, 25°C).

8.2.4 After sampling, the impinger stem can be removed and cleaned. Tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Wash the stem with a small amount (1-2 mℓ) of unused absorbing solution and add the wash to the impinger. Then the impinger is sealed with a hard, non-reactive stopper (preferably Teflon). Do not seal with rubber. The stoppers on the impingers should be tightly sealed to present leakage during shipping. If it is preferred to ship the impingers with the stems in, the outlets of the stem should be sealed with Parafilm or other non-rubber covers, and the ground glass joints should be sealed (i.e., taped) to secure the top tightly.

8.2.5 Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within a day.

8.2.6 Whenever possible, hand delivery of the samples is recommended. Otherwise, special impinger shipping cases designed by NIOSH should be used to ship the samples.

8.2.7 A "blank" impinger should be handled as the other samples (fill, seal and transport) except that no air is sampled through this impinger.

8.2.8 Where a prefilter has been used, the filter cassettes are capped and placed in an appropriate cassette shipping container. One filter disc should be handled as the other samples (seal and transport) except that no air is sampled through, and this is labeled as a blank.

8.3 **Analysis of Samples**

8.3.1 The sample is transferred from the impinger to a 50-cc plastic beaker; an equal volume of TISAB is added and the solution is stirred.

8.3.2 The fluoride ion electrode and the reference electrode are lowered into the stirred solution and the resulting millivolt reading recorded (to the nearest 0.5 millivolt) after it has stabilized (drift less than 0.5 millivolt per minute).

9. **Calibration and Standards**

Prepare a series of fluoride standard solutions by diluting equal volumes of each fluoride standard (7.9) and TISAB in a clear polyethylene beaker. Insert the fluoride ion electrode and the reference electrode into each of the stirred calibration solutions starting with the most dilute solution and record the resulting millivolt reading to the nearest 0.5 millivolt. Plot the millivolt readings vs the fluoride ion concentration of the standard of semi-log paper. The fluoride ion concentration in $\mu g/m\ell$ is plotted on the log axis. The calibration points should be repeated twice daily.

10. **Calculations**

10.1 The concentration ($\mu g/m\ell$) of fluoride in the sample solution is obtained from the calibration curve.

10.2 Total μg F^- in the sample = sample concentration ($\mu g/m\ell$) x sample solution volume ($m\ell$).

10.3 The total μg F^- is divided by the volume in liters, of air sampled to obtain concentration in μg F^-/liter or mg F^-/m^3.

$$mg\ F^-/m^3 = \mu g\ F^-/liter$$

$$mg\ F^-/m^3 = \frac{total\ \mu g\ F^-}{V_s} \qquad \text{(Section 10.4)}$$

10.4 Convert the volume of air sampled to standard conditions of 25°C and 760 mm Hg.

$$= V \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

V_s = volume of air in liters at 25°C and 760 mm Hg
V = volume of air in liters as measured
P = barometric pressure in mm Hg
T = temperature of air in degree centigrade

10.5 The concentration can also be expressed in ppm, defined as $\mu\ell$ of component per liter of air.

$$\text{ppm } F^- = \mu\ell\ F^-/V_s = \frac{24.45}{MW} \times \mu g\ F^-/V_s$$

$$= 1.29\ \mu g\ F^-/V_s$$

Where:

24.45 = molar volume at 25°C and 760 mm Hg
MW = 19, weight of fluoride ion,
(i.e., 19 μg F^- = 24.45 $\mu\ell$ at 25°C, 760 mm Hg)

10.6 To calculate the concentration of hydrogen fluoride as mg HF/m^3 or ppm HF, simply multiply the corresponding concentration of F^- (from 10.3 or 10.4) by 1.05.

11. References

11.1 Elfers, L.A., and C.E. Decker, "Determination of Fluoride in Air and Stack Gas Samples by Use of an Ion Specific Electrode," Anal. Chem., 40 (11), p. 1658 (1968).

ACROLEIN IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Acrolein	**Method No.:**	P&CAM 118
Matrix:	Air	**Range:**	1 – 30 μg/10 mℓ
Procedure:	Complexation, Colorimetric	**Precision:**	Unknown
Date Issued:	4/6/72		
Date Revised:	1/10/74	**Classification:**	C (Tentative)

1. **Principle of Method**

Acrolein reacts with 4-hexylresorcinol in an ethyl alcohol-trichloroacetic acid solvent medium in the presence of mercuric chloride and forms a blue colored product. The strong absorption maximum at 605 nm is used as a quantitative measure of acrolein.

2. **Range and Sensitivity**

2.1 The linear range of the absorbance at 605 nm is at least 1-30 μg of acrolein in the 10 mℓ portions of mixed reagent.

2.2 A concentration of 0.01 ppm of acrolein can be determined in a 50 liter air sample based on a difference of 0.05 absorbance unit from the blank using a 1 cm cell. Greater sensitivity could be obtained by use of a longer path length cell.

3. **Interferences**

There is no interference from ordinary quantities of sulfur dioxide, nitrogen dioxide, ozone and most organic air pollutants. A slight interference occurs from dienes: 1.5 percent for 1,3-butadiene and 2 percent for 1,3-pentadiene. The red color produced by some other aldehydes and undetermined materials does not interfere in the spectrophotometric measurement.

4. **Precision and Accuracy**

The available information is insufficient to determine the precision and accuracy of this method.

5. **Advantages and Disadvantages of the Method**

5.1 The major advantage of this method is the sensitivity. A concentration of 0.01 ppm of acrolein can be determined in a 50 liter air sample.

5.2 Both the solid trichloroacetic acid and the solution are corrosive to the skin. Mercuric chloride is highly toxic. This reagent and the former should be handled carefully. This method is not attractive as a field technique since the absorbing solution tends to evaporate upon collection of large volumes of air and the colored complex begins to fade after 2 hours upon completion of sampling.

6. **Apparatus**

6.1 **Sampling Equipment.** The sampling unit for the impinger collection method consists of the following components:

6.1.1 A train of two glass standard midget impingers with fritted glass inlets containing the absorbing solution or reagent (Section 7.5). The fritted end should have a porosity approximately equal to that of Corning EC (170-220 μ maximum pore diameter).

6.1.2 A pump suitable for delivering desired flow rates; at least 2 ℓ per minute for 60 minutes. The sampling pump is protected from splashover or water condensation by an adsorption tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump.

6.1.3 An integrating volume meter such as a dry gas or wet test meter.

6.1.4 Thermometer.

6.1.5 Manometer.

6.1.6 Stopwatch.

6.2 **Water Bath.** Any bath capable of maintaining a temperature of 58-60°C is acceptable.

6.3 **Spectrophotometer.** This instrument should be capable of measuring the developed color at 605 nm. The absorption band is rather narrow and thus a lower absorptivity may be expected in a broad-band instrument.

6.4 Matched glass cells or cuvettes, 1 cm path length.

6.5 Assorted laboratory glassware – pipettes, volumetric flasks, graduated cylinders of appropriate capacities.

7. Reagents

All reagents must be analytical reagent grade. An analytical grade of distilled water must be used.

7.1 Ethanol (96%).

7.2 **Trichloroacetic Acid Solution, Saturated.** Dissolve 100 g of the acid (reagent grade) in 10 mℓ of water by heating on a water bath. The resulting solution has a volume of approximately 70 mℓ. Even reagent grade trichloroacetic acid has an impurity which affects product intensities. Every new batch of solution should be standardized with acrolein. It is convenient to prepare a large quantity of solution from a single batch of trichloroacetic acid to maintain a uniformity of response.

7.3 **Mercuric Chloride Solution (3%).** Dissolve 3 g of mercuric chloride in 100 mℓ of ethanol.

7.4 **4-Hexylresorcinol Solution.** Dissolve 5 g of 4-hexylresorcinol (MP 68°-70°C) in 5.5 mℓ of ethanol. This makes about 10 mℓ of solution.

7.5 **Mixed Absorbing Reagent.** Mix, in the specified order, the reagents in the following proportions: 5 mℓ ethanol, 0.1 mℓ 4-hexylresorcinol solution, 0.2 mℓ mercuric chloride solution, and 5 mℓ saturated trichloroacetic acid solution. The mixed reagent may be stored for a day at room temperature. Prepare the needed quantity by selecting an appropriate multiple of these amounts. Protect from direct sunlight.

7.6 **Acrolein, Purified.** Freshly prepare a small quantity (less than 1 mℓ is sufficient) by distilling 10 mℓ of the purest grade of acrolein commercially available. Reject the first 2 mℓ of distillate. (The acrolein should be stored in a refrigerator to retard polymerization.) The distillation should be done in a hood because the vapors are irritating to the eyes.

7.7 **Acrolein, Standard Solution "A" (1 mg/mℓ).** Weigh 0.1000 g (approximately 0.12 mℓ) of freshly prepared, purified acrolein into a 100 mℓ volumetric flask and dilute to volume with ethanol. This solution may be kept for as long as a month if properly refrigerated.

7.8 **Acrolein, Standard Solution "B" (10 μg/mℓ).** Dilute 1 mℓ of standard solution "A" to 100 mℓ with ethanol. This solution may be kept for as long as a month if properly refrigerated.

8. Procedure

8.1 **Cleaning of Equipment.** No specialized cleaning of glassware is required, however, since known interferences occur with dienes, cleaning techniques should insure the absence of all organic materials.

8.2 **Collection and Shipping of Samples**

8.2.1 Draw through the assembled sampling unit measured volumes of the vapor laden air at a rate of either 1 ℓ/minute for no more than 60 minutes or 2 ℓ/minute for no more than 30 minutes through 2 bubblers in series, each containing 10 mℓ of mixed absorbing reagent. An extra bubbler containing water may be added as a trap to protect the pump. A maximum of 60 ℓ of air can be sampled before possible reagent decomposition may occur. Care should be taken to measure flow rate, time and/or volume as accurately as possible. Note also the atmospheric pressure and temperature.

8.2.2 This sampling system collects 70-80 percent of the acrolein in the first bubbler and 95 percent of the acrolein in the first 2 bubblers, using absorbers with EC fritted glass inlets. The absorption efficiency might be increased by use of a C porosity frit (60μ maximum pore diameter).

8.2.3 Because of the two hour time limit for color development, it is probably best to analyze the samples soon after completion of sampling. For this reason shipping of the sample involving time periods of as much as two hours should not be practiced with this method.

8.3 **Analysis of Sample**

8.3.1 If evaporation has occurred during sampling the absorbing solution is diluted to its original 10 mℓ volume with ethanol.

8.3.2 Transfer the samples from each bubbler and backup bubbler to separate glass stoppered test tubes.

8.3.3 Immerse the tubes in a 60°C water bath for 15 minutes to develop the colors. A test tube containing only 10 mℓ of mixed absorbing reagent must be run similarly and simultaneously. This serves as the reagent blank.

8.3.4 Cool the test tubes in running water immediately upon removal from the water bath.

8.3.5 After 15 minutes read the absorbances at 605 nm in a suitable spectrophotometer using 1 cm cells. There is no appreciable loss in accuracy if the samples are allowed to stand up to 2 hours before reading the absorbances. For very low acrolein concentrations it may be convenient to use a longer path length cell.

9. Calibration and Standards

9.1 Preparation of standard curve.

9.1.1 Pipette 0, 0.5, 1.0, 2.0, and 3.0 mℓ of standard solution "B" into glass stoppered test tubes.

9.1.2 Dilute each standard to exactly 5 mℓ with ethanol.

9.1.3 Add in order, to each tube, exactly 0.1 mℓ of 4-hexylresorcinol solution, 0.2 mℓ of mercuric chloride solution, and 5 mℓ of trichloroacetic acid solution.

9.1.4 Mix, develop and read the colors as described in the analytical procedure (Sections 8.3.3 to 8.3.5).

9.2 Construct a calibration curve by plotting absorbance against micrograms of acrolein in the color developed solution.

10. Calculations

10.1 Subtract blank values, if any, from each sample.

10.2 Determine from the calibration curve the concentration of the acrolein present in each of the two bubblers, and add the values to get the total μg of acrolein in the air sampled.

$$\mu g \text{ acrolein} = \mu g_1 + \mu g_2$$

where:

μg_1 = microgram concentration of acrolein in the first bubbler.

μg_2 = microgram concentration of acrolein in the back up bubbler.

10.3 The concentration of acrolein in the sampled atmosphere can be calculated in ppm, defined as $\mu\ell$ acrolein per liter of air.

$$\text{ppm} = \frac{\mu\text{g acrolein}}{V_s} \times \frac{24.45}{MW}$$

where:

μg acrolein = total μg concentration as determined in 10.1. (Probably 95% of the actual concentration as stipulated in Section 8.2.2. A correction for efficiency may be used accordingly if deemed necessary.)

V_s = volume of air sampled in ℓ at 25°C and 760 mm Hg.

24.45 = molar volume of an ideal gas at 25°C and 760 mm Hg.

MW = molecular weight of acrolein, 56.06.

11. References

11.1 Cohen, I.R., and Altshuller, A.P., "A New Spectrophotometric Method for the Determination of Acrolein in Combustion Gases and the Atmosphere." Anal. Chem. 33, 726 (1961).

11.2 Altshuller, A.P., and McPherson, S.P. "Spectrophotometric Analysis of Aldehydes in the Los Angeles Atmosphere," J. Air Poll. Control Assoc. 13, 109 (1963).

11.3 Cohen, Israel, R., and Bernard E. Saltzman, "Determination of Acrolein: 4-Hexylresorcinol Method," *Selected Methods for the Measurement of Air Pollutants,* Public Health Service Publication No. 999.AP-11, p. G-1, 1965.

11.4 Intersociety Committee, Methods for Ambient Air Sampling and Analysis, "Tentative Method of Analysis for Acrolein Content of Atmosphere," 435-05-01-70T. H.L.S. 7:179-181, 1970.

BERYLLIUM IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Beryllium	**Method No.:**	P&CAM 121
Matrix:	Air, Settled Dust, Ore & Swipe Samples	**Range:**	0.03-8.0 μg/mℓ
Procedure:	Atomic Absorption	**Precision:**	Unknown
Date Issued:	4/7/72		
Date Revised:	January 10, 1974	**Classification:**	D (Operational)

1. **Principle of the Method**

   1.1 The samples are ashed with nitric acid to destroy the organic matrix. The ash is treated with 1:1 hydrochloric acid and dissolved in a weak hydrochloric acid solution maintaining a pH between 1 and 2.

   1.2 The liquid sample is aspirated into the nitrous oxide-acetylene flame of the atomic absorption spectrophotometer and the absorbance of the 2348.6 Å line of beryllium is measured.

2. **Range and Sensitivity**

   2.1 For aqueous solutions, the working range for beryllium is linear up to concentrations of approximately 4 μg/mℓ, but is useful up to concentrations of 8 μg/mℓ.

   2.2 The sensitivity under the standard operating conditions is about 0.03 μg beryllium/mℓ. This sensitivity can be increased with chemical concentration by solvent extraction.

3. **Interferences**

   High concentrations of aluminum (>500 μg/mℓ), silicon and magnesium depress the sensitivity of the beryllium determination. The interference can be controlled by adding oxine (8-hydroxyquinoline) to the sample and standards.

4. Precision and Accuracy

The precision and accuracy of this method have not been completely determined at this time. However, most standard atomic absorption procedures will provide a coefficient of variation of about 0.5 to 2% depending on the instrument used and the absorbance of the samples.

5. Advantages and Disadvantages of the Method

5.1 This method is rapid and does not require a high degree of technical skill.

5.2 The method is virtually free from spectral interferences, and has very good precision and accuracy. It is almost as sensitive as the emission spectrographic method, and far more precise.

5.3 The method is limited in that samples must be in enough volume of solution for a suitable aspiration time. This is rarely a problem when analyzing air samples, since the samples are usually collected for long periods of time.

6. Apparatus

6.1 Atomic Absorption Spectrophotometer. The instrument must be equipped with a nitrous oxide burner head.

6.2 Be Hollow Cathode Lamp of high spectral purity and adequate sensitivity.

6.3 Acetylene Gas and Regulator.

6.4 Nitrous Oxide and Regulator. Heating tape, with the temperature controlled by a rheostat, can be wound around the second stage regulator and connecting hose to prevent freeze-up of the line during operation.

6.5 125 mℓ Phillips borosilicate glass beakers with watchglasses.

6.6 15 mℓ graduated borosilicate glass centrifuge tubes.

7. Reagents

All reagents must be analytical reagent grade or better. All solutions are prepared with deionized water.

7.1 Redistilled concentrated nitric acid (16N).

7.2 Redistilled hydrochloric acid (6N).

7.3 **Stock Beryllium Solution.** A solution containing 1000 μg of beryllium per milliliter is prepared by dissolving 1.000 g of beryllium metal in a minimum volume of 1:1 HCl. Dilute to 1 liter with 1% (V/V) HCl. (This stock solution can also be purchased from reputable laboratory supply firms.)

7.4 **Beryllium Standard Solutions.** These solutions are prepared by making appropriate dilutions from the stock beryllium solution, and acidifying with 0.5 mℓ of 1:1 redistilled HCl for each 10 mℓ of solution. These standard solutions are stable for at least several months.

8. Procedure

8.1 **Cleaning of Equipment.** Borosilicate glassware is recommended for this method. Glassware is soaked in a mild detergent solution immediately after use to remove any residual grease or chemicals and thus prevent the formation of an adsorptive surface. Before use, each piece is cleaned with a saturated solution of sodium dichromate in concentrated sulfuric acid and then rinsed thoroughly with warm tap water, concentrated nitric acid, tap water and deionized water.

8.2 **Collection and Handling of Samples**

8.2.1 **Air Samples** can be collected by:

1. A 0.45 μ cellulose membrane filter.
2. An electrostatic precipitator.
3. A chemically clean impinger containing a 10% HNO_3 solution.

The Hi-Vol sampler, which samples at a rate of about 1.5 m^3/min when operated 24 hours, will provide an adequate sample for the determination of beryllium in ambient air in concentrations as low as 0.002$\mu g/m^3$. Filters should not be overloaded with the sample to the point where the sample is falling off the filter. Each filter sample should be sealed in its own container for shipment. Plastic petri dishes are suitable for small membrane filters and cardboard file folders and large envelopes are suitable for hi-vol filters.

8.2.2 **Settled Dust and Ore Samples** can be collected directly in chemically clean jars.

8.2.3 **Swipe Samples** should be collected on Whatman filter paper by thoroughly wiping a *measured* area and placing the filter in a chemically clean jar.

8.3 Analysis of Samples

8.3.1 Ashing of Samples

a. **Air Samples.** The entire filter or impinger sample is transferred to a 125-mℓ Phillips beaker and ashed with nitric acid. If a fiberglass filter was used for sampling, it is necessary to first destroy the filter with hydrofluoric acid in a platinum or teflon dish prior to ashing with nitric acid in the Phillips beaker. When ashing is completed, as indicated by a white residue, convert the residue to the chloride form by three *successive* evaporations, just short of dryness, with 1:1 HCl. The residue is then dissolved in 0.1 mℓ of 1:1 HCl and deionized water and transferred with triplicate washings to a graduated centrifuge tube. The sample is evaporated to a volume of 2.0 mℓ for analysis. If a dilution is needed the solution is diluted with 0.3 N HCl to the appropriate volume for analysis.

b. **Ores and Settled Dusts.** Ore and settled dust samples are ground in a clean mill to pass a U.S. Standard 200-mesh sieve. The ground materials are shaken thoroughly in a mixer mill and a 0.2000g representative sample is weighed out. Dust samples are ashed with nitric acid and if insoluble beryllium minerals are suspected, a potassium fluoride-sodium pyrosulfate fusion is also performed. Ore samples are fused without prior nitric acid ashing. The resulting hydrochloric acid solution of the fused sample is diluted or concentrated to the volume required to place the anticipated beryllium concentration in the working range of the method, maintaining a final pH between 1 and 2.

8.3.2 Determination of Beryllium

The HCl solution of the ashed or fused sample is aspirated directly into the nitrous oxide – acetylene flame. A special nitrous oxide-acetylene burner head must be used. The 2349 Å resonance line of beryllium is used. The operating parameters vary according to the make of instrument being employed. Consult the instrument manufacturer's instructions for the particular instrument settings and procedure for lighting the nitrous oxide-acetylene flame. A reducing, fuel rich flame, is needed for the desired sensitivity in the beryllium analysis.

If the beryllium concentration falls between 0.2 and 8.0 μg/mℓ, the percent of absorption values of the samples are recorded on the 1X scale, or the absorbance or concentration values are read directly if these features are available on the instrument being employed. If the beryllium concentration is between 0 and 0.2 μg/mℓ, scale expansion can be used to

improve the readability of small signals and thereby improve the detection limit. However, longer aspiration time is needed when using scale expansion since higher noise suppression is required.

9. Calibration and Standards

9.1 Beryllium standards are prepared by appropriate dilutions of the stock solution to cover the range from 0 – 8 μg Be/mℓ. Each standard solution contains 0.5 mℓ of 1:1 redistilled HCl per every 10 mℓ of solution. Each standard solution is aspirated into the nitrous oxide-acetylene flame and either the % absorption is recorded or the absorbance or concentration are read directly. If the instrument records in % absorption, the readings of the standards and samples must be converted to absorbance.

9.2 The absorbance values are plotted against concentration to get the standard working curve. For low concentrations of beryllium, standards and samples can be run using scale expansion to improve the detection limit of the method. When scale expansion is used, it is not necessary to convert to absorbance before plotting.

10. Calculations

The concentration of Be in ambient air can be expressed as μg Be per cubic meter.

$$\mu g\ Be/m^3 = \frac{\mu g\ Be/m\ell}{V_s} \times m\ell\ soln$$

where:

μg Be/mℓ = the concentration of Be in the sample solution analyzed derived from the calibration curve (Section 9.2).

mℓ soln = final volume of sample solution analyzed including any dilution factor.

V_s = volume of air sampled in m^3 at 25°C and 760 mm Hg, (1000 ℓ = 1 m^3).

11. References

11.1 *Analytical Methods for Atomic Absorption Spectrophotometry.* The Perkin-Elmer Corporation, Norwalk, Connecticut (1971).

11.2 Sill, C.W. "Decomposition of Refractory Silicates in Ultramicro Analysis." Anal. Chem. 33; 1684 (1961).

11.3 Keenan, R.G., and J.L. Holtz. "Spectrographic Determination of Beryllium in Air, Biological Materials, and Ores Using the Sustaining A.C. Arc." American Ind. Hyg. Assoc. J, 25; 254 (1964).

11.4 Elwell, W.T., and J.A.F. Gidley. *Atomic Absorption Spectrophotometry*, 2nd Edition Pergamon Press, New York, 1966.

BERYLLIUM IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Beryllium	**Method No:**	P&CAM 123
Matrix:	Air, Settled Dust, Ore and Swipe Samples	**Range:**	0.001 – 0.05 μg Be/electrode
Procedure:	Emission Spectrography	**Precision:**	Unknown
Date Issued:	4/7/72		
		Classification:	D (Operational)
Date Revised:	1/15/74		

1. **Principle of the Method**

   1.1 The ashed or fused sample is quantitatively added to an electrode containing a chloride matrix composed of LiCl-graphite buffer and liver ash solution.

   1.2 The sustaining A.C. arc is used to excite the beryllium volatilized from the chloride matrix, and the resulting spectra are recorded photographically.

   1.3 The percent transmittance of the 2348.6 Å line of beryllium and the adjacent minimal background are measured with a microphotometer.

   1.4 The %T values for the Be line and background are converted to an intensity ratio by means of an emulsion calibration curve. This intensity ratio is related to beryllium concentration in the sample by comparing it to a series of beryllium standards prepared under the same conditions.

2. **Range & Sensitivity**

   2.1 The method has a sensitivity of 0.001 μg of beryllium. The standard working curve covers the range from 0.001 μg to 0.05 μg of beryllium on the electrode.

3. **Interferences**

   Spectrographic methods in general are very specific in the detection of any given element. However, spectral interferences do occur for many specific elemental lines. In the case of the 2348.6 Å line of beryllium, the only interference which occurs is when high concentrations of iron are present in the sample. The 2348.3 Å iron line casts additional background on the 2348.6 Å Be line.

4. **Precision and Accuracy**

The precision and accuracy of this method have not been completely established. However, the relative standard deviation obtained when analyzing four replicate sets of rabbit liver ash samples, containing known added 0.001 to 0.100 μg quantities of beryllium per 2 mg of ash on separate dates within a six month period was 14%.

5. **Advantages and Disadvantages of the Method**

5.1 This method is specific for beryllium and has very good sensitivity. It is the method of choice when analyzing very small samples or when a sensitivity greater than that obtained when using atomic absorption spectrophotometry is required.

5.2 This method is not nearly as fast as the atomic absorption method and requires a higher degree of skill on the part of the analyst.

5.3 Many laboratories do not have spectrographic instrumentation due to its high cost as compared to atomic absorption instrumentation.

6. **Apparatus**

6.1 **Excitation Source,** to provide a sustaining A.C. arc operating at 18 amperes with an analytical gap maintained at 4 mm.

6.2 **Spectrograph,** of the very large Littrow type with a 30° quartz prism and a condensing lens system. A 20 μ fixed slit and a 50% neutral filter in the optical path are used. The spectrograph should have a reciprocal linear dispersion of at least 5 Å/mm or less at 3200 Å, and be capable of operation from 2280 to 5000 Å.A 1:1.5 step sector is used for the spectroscopic emulsion calibration.

6.3 **Photographic Processing Equipment,** providing developing, fixing, washing and drying operations suitable for general spectrochemical analysis. D-19 developer, F-5 fixer.

6.4 **Microphotometer,** having a precision of ±1.0 percent for transmittance values between 5 and 90 percent.

6.5 **Photographic Plates** – Eastman SA No. 1 or equivalent.

6.6 **Calculating Equipment,** a calculating board which is used for preparing the emulsion calibration curve and converting microphotometer readings to intensity ratios.

6.7 **Micropipet** assembly for precise control (±1%) of the addition of standards and sample solutions to the electrodes.

6.8 **Electrodes** – Regular grade, spectroscopic graphite electrodes, 5/16 inch diameter. The sample electrodes are cut into 1.5-inch lengths and craters, 4.5 mm wide and 5.0 mm deep, are drilled into each, using an electrode shaper. The crater ends are immersed in the electrode waterproofing solution and then air-dried for one hour. The upper electrodes are clean, freshly pointed, 5/16-inch graphite rods.

6.9 125 mℓ Phillips borosilicate glass beakers with watchglasses.

6.10 15 mℓ graduated borosilicate glass centrifuge tubes.

6.11 Drying Oven for evaporation of liquids on electrodes – capable of operating at least to 110°C.

Reagents

7.1 All reagents are analytical reagent grade, except where otherwise indicated. Deionized water is used in the preparation of all reagents and solutions. Nitric and hydrochloric acids are redistilled in borosilicate glass stills.

7.2 **Electrode Waterproofing Solution** – Dissolve 2 g of Dow Corning DC-702 silicone in C.P. acetone and dilute to 100 mℓ with acetone. Store in a chemically clean, tightly capped jar.

7.3 **Beryllium Stock Solution** – A solution containing 1000 μg of beryllium per milliliter is prepared by dissolving 1.000 g of beryllium metal in a minimum volume of 1:1 redistilled HCl. Silute to 1 liter with 1% (v/v) HCl.

7.4 **Beryllium Standard Solutions** – These solutions should be prepared by making the appropriate dilutions from the stock solution. Suggested concentrations are 0.05, 0.02, 0.01, 0.005, 0.002 and 0.001 micrograms of beryllium per 0.05 mℓ. Maintain the pH of each solution between 1 and 2 to prevent the deposition of beryllium on the walls of the volumetric flasks.

7.5 **Liver Ash Solution** – Ash a suitable quantity of normal rabbit or beef liver using the nitric acid ashing procedure. Determine the ash weight. Convert the residue to the chloride form by three separate evaporations just to dryness with hydrochloric acid. Dissolve the residue in 1:1 redistilled HCl and dilute with water to provide a solution containing 40 mg ash per mℓ.

7.6 **Spectroscopic Buffer Mixture** – Mix and grind thoroughly in a mullite or agate mortar 1.000g of spectroscopically pure graphite and 0.400 g of C.P. lithium chloride (with labelled Mg and heavy metal contents of 0.000%) or lithium chloride which has been prepared from commercially available, spectroscopically pure lithium carbonate. Store in a loosely covered, screw cap jar in a desiccator over concentrated sulfuric acid.

8. Procedure

8.1 **Cleaning of Equipment.** Borosilicate glassware is recommended for this method. Glassware is soaked in a mild detergent solution immediately after use to remove any residual grease or chemicals and thus prevent the formation of an adsorptive surface. Before use, each piece is cleaned with a saturated solution of sodium dichromate in concentrated sulfuric acid and then rinsed thoroughly with warm tap water, concentrated nitric acid, tap water and deionized water.

8.2 Collection and Handling of Samples

8.2.1 **Air Samples**: Can be collected by

1) a 0.8 μ cellulose membrane filter.
2) a chemically clean impinger containing a 10% nitric acid solution.
3) an electrostatic precipitator.

The Hi-Vol sampler, which samples at a rate of about 1.5 m^3/min. when operated 24 hours, will provide an adequate sample for the determination of beryllium in ambient air in concentrations as low as 0.002 $\mu g/m^3$. Filters should not be overloaded with the sample to the point where the sample is falling off the filter. Each filter sample should be sealed in its own container for shipment. Plastic petri dishes are suitable for small membrane filters and cardboard file holders and large envelopes are suitable for Hi-Vol filters.

8.2.2 **Settled Dust and Ore Samples**: Can be collected directly in chemically clean jars.

8.2.3 **Swipe Samples**: Should be collected on Whatman filter paper by thoroughly wiping a *measured* area and placing the filter in a chemically clean jar.

8.3 Analysis of Samples

8.3.1 Ashing of Samples

1. **Air Samples**: The entire filter or impinger sample is transferred to a 125 mℓ Phillips beaker and ashed with nitric acid. If a fiberglass filter was used

for sampling, it is necessary to first destroy the filter with hydrofluoric acid in a platinum or Teflon dish prior to ashing with nitric acid in the Phillips beaker. When ashing is complete as indicated by a white residue, convert the residue to the chloride form by triple evaporations with 1:1 HCl. The residue is then dissolved in a minimal amount of hydrochloric acid and water, transferred to a graduated centrifuge tube, and evaporated in an oven to an appropriate volume for analysis. If the beryllium concentration, on analysis, is out of the range of the method, the volume must be adjusted accordingly to bring the concentration in range.

2. **Settled Dust and Ore Samples:** Ore and settled dust samples are ground in a clean mill to pass a U.S. Standard 200 mesh sieve. The ground materials are shaken thoroughly in a mixer mill and a 0.200 g representative sample is weighed out. Dust samples are ashed with nitric acid and if insoluble beryllium minerals are suspected, a potassium fluoride-sodium pyrosulfate fusion is also performed (See Ref. 11.2). Ore samples are fused without prior nitric acid ashing. The resulting hydrochloric acid solution of the fused sample is diluted or concentrated to the volume required to place the anticipated beryllium concentration in the working range of the method, maintaining a final pH between 1 and 2.

8.3.2 Determination of Beryllium

1. Prepare a series of 1.5 inch electrodes from regular grade, 5/16 inch graphite rods. Drill craters of 4.5 mm diameter and 5 mm deep. (If preferred, a commercially available electrode prepared from 1/4 inch stock may be employed, if its crater dimensions approximate those described and if standardization is performed with the type of electrode to be used routinely.) Support the electrodes in special blocks made from wood, aluminum, or other suitable material. Immerse the crater ends of each electrode briefly in the electrode waterproofing solution and then air-dry for one hour.

2. Transfer approximately 20 mg of the LiCl-graphite buffer mixture to each electrode, tapping the lower end of the electrode on the bench to produce a uniform settling in the crater. Using a micropipet, add exactly 0.05 mℓ of the liver ash solution to each prepared electrode. Dry in an oven operating at 65-75°C to evaporate the liquid slowly without causing creepage of salts to the top of the crater. This step requires about 20 minutes. Remove the blocks of electrodes and cool for 10 minutes.

3. Add exactly 0.05 mℓ of the prepared sample to each of three electrodes (use micropipet). Dry at 65-75°C, as before, and then for at least one hour at 105°C.

4. Prepare a set of counter electrodes from 1/4 or 5/16 inch graphite rods using a pencil sharpener reserved for this purpose. (If preferred, a hemispherically tipped counter electrode may be used exclusively.) A separate counter electrode is used with each sample electrode. After spectroscopic excitation of each group of samples, these counter electrodes are wiped clean of condensate and are resharpened before their next use.

5. Introduce each sample electrode, in turn, into the lower holder of the arc stand and a counter electrode into the upper holder. Burn each sample 90 seconds, operating the sustaining A.C. arc at 18 amperes. Use a 50% neutral filter in the optical path and maintain a steady arc gap of 4 mm throughout each exposure.

6. Develop the spectroscopic plate, using D-19 developer and F-5 fixer, at 68°F. The developing time is two minutes and the fixing period is 10 minutes. Wash the plate for 20 minutes and then dry.

7. Read the percent transmittance values of the Be 2348.6 Å line and of the minimal background on the higher wavelength side of the beryllium line. Determine the intensity ratio of Be 2348.6 to background, using the emulsion calibration curve prepared for this purpose by the step sector or other appropriate method. Calculate the mean I Be/I Bkgd for each sample. Subtract the mean I Be/I Bkgd for the zero beryllium standard from the mean intensity ratio of each sample to obtain the net ratio. The concentration of the beryllium in the analyzed aliquot portion of the sample is then determined using the standard curve.

9. Calibration and Standards

9.1 The standard beryllium curve is prepared by applying the "Determination of Beryllium" procedure (Section 8.3.2) to triplicate sets of electrodes containing 0.000 to 0.050 μg quantities of beryllium plus the lithium chloride graphite buffer and 0.05 mℓ liver ash solution.

9.2 The intensity ratio of each standard analyzed in triplicate is calculated using the emulsion calibration curve.

9.3 The mean intensity ratio of the zero beryllium standard is subtracted from the mean intensity ratio of the other standards containing increasing amounts of beryllium.

9.4 The net intensity ratio of each standard is then plotted on log-log paper against the various beryllium standard concentrations.

9.5 The beryllium analytical curve is then used to determine the concentration of beryllium in each sample aliquot.

10. Calculations

10.1 Subtract the mean intensity ratio of the blank or zero beryllium standard from the mean intensity ratio of each sample to obtain the net ratio.

10.2 Determine the beryllium concentration in the analyzed aliquot portion of the sample from the standard curve.

10.3 Calculate the total concentration of beryllium in the whole sample as μg Be per filter or μg Be per gram of sample.

$$\mu\text{g Be/filter or } \mu\text{g Be/g} = \frac{\mu\text{gBe}}{0.05} \times \frac{\text{vol. sample}}{x}$$

where:

μg Be = the microgram concentration of Be as determined from the calibration curve (Section 10.2)

0.05 = mℓ of solution on electrode

vol. sample = total volume in mℓ of sample

x = total filter or total weight of sample in grams.

10.4 For air samples, the beryllium concentration can also be expressed as μg Be per cubic meter of air.

$$\mu\text{g Be/m}^3 = \frac{\mu\text{g Be}}{0.05} \times \frac{\text{vol. sample}}{V_s}$$

where:

V_s = volume of air sampled in cubic meter at 25°C and 760 mm Hg.

11. References

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FORMALDEHYDE IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Formaldehyde	**Method No:**	P&CAM 125
Matrix:	Air	**Range:**	0.1 ppm – 2.0 ppm
Procedure:	Spectrophotometric	**Precision:**	±5%
Date Issued:	9/24/73	**Classification:**	C (Tentative)
Date Revised:	1/15/74		

1. **Principle of the Method**

   1.1 Formaldehyde reacts with chromotropic acid-sulfuric acid solution to form a purple monocationic chromogen. The absorbance of the colored solution is read in a spectrophotometer at 580 nm and is proportional to the quantity of formaldehyde in the solution (References 11.2, 11.6).

   1.2 The chemistry of this color reaction is not known with certainty (Reference 11.3).

2. **Range and Sensitivity**

   2.1 From 0.1 μg/mℓ to 2.0 μg/mℓ of formaldehyde can be measured in the color developed solution.

   2.2 A concentration of 0.1 ppm of formaldehyde can be determined in a 25 liter air sample based on an aliquot of 4 mℓ from 20 mℓ of absorbing solution and a difference of 0.05 absorbance unit from the blank.

3. **Interferences**

   3.1 The chromotropic acid procedure has very little interference from other aldehydes. Saturated aldehydes give less than 0.01 percent positive interference, and the unsaturated aldehyde acrolein results in a few percent positive interference. Ethanol and higher molecular weight alcohols and olefins in mixtures with formaldehyde are negative interferences. However, concentrations of alcohols in

air are usually much lower than formaldehyde concentrations and, therefore, are not a serious interference.

3.2 Phenols result in a 10 to 20 percent negative interference when present at an 8:1 excess over formaldehyde. They are, however, ordinarily present in the atmosphere at lesser concentrations than formaldehyde and, therefore, are not a serious interference.

3.3 Ethylene and propylene in a 10:1 excess over formaldehyde result in a 5 to 10 percent negative interference and 2-methyl-1,3-butadiene in a 15:1 excess over formaldehyde showed a 15 percent negative interference. Aromatic hydrocarbons also constitute a negative interference (Reference 11.6). It has recently been found that cyclohexanone causes a bleaching of the final color (Reference 11.4).

4. Precision and Accuracy

The method was checked for reproducibility by having three different analysts in three different laboratories analyze standard formaldehyde samples. The results listed in Table 1 agreed within ±5 percent.

TABLE 1

COMPARISON OF FORMALDEHYDE RESULTS FROM THREE LABORATORIES

Micrograms Formaldehyde	Absorbance		
	Lab. 1	Lab. 2	Lab. 3
1	0.057	0.063	0.061
3	0.183	0.175	0.189
5	0.269	0.279	0.262
7	0.398	0.381	0.392
10	0.566	0.547	0.537
20	1.02	0.980	1.07

5. Advantages and Disadvantages

5.1 Effect of Storage – Disadvantage

5.1.1 The absorbance of the reaction product increases slowly on standing. An increase of 3 percent in absorbance was noted after one day standing and an increase of 10 percent after eight days standing (11.6).

5.1.2 No information is available on the effect of storage on the collected air sample.

5.2 **Precision – Advantage.** Results checked for reproducibility agreed within ±5 percent (see Table 1).

6. Apparatus

6.1 **Sampling Equipment.** The sampling unit for the impinger collection method consists of the following components:

6.1.1 A graduated midget impinger containing the absorbing solution or reagent.

6.1.2 A pump suitable for delivering flow rates of 1 liter per minute for 24 hours. The sampling pump is protected from splashover or water condensation by an adsorption tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump.

6.1.3 An integrating volume meter such as a dry gas or wet test meter.

6.1.4 Thermometer.

6.1.5 Manometer.

6.1.6 Stopwatch.

6.2 **Spectrophotometer or Colorimeter.** An instrument capable of measuring the absorbance of the color developed solution at 580 nm.

6.3 Associated laboratory glassware.

7. Reagents

7.1 **Chromotropic Acid Reagent.** Dissolve 0.10 g of 4,5-dihydroxy-2,7-naphthalenedisulfonic acid disodium salt (Eastman Kodak Company, Rochester, New York, Cat. No. P230) in water and dilute to 10 mℓ. Filter if necessary and store in a brown bottle. Make up fresh weekly.

7.2 Concentrated sulfuric acid.

7.3 **Formaldehyde Standard Solution "A"** (1 mg/mℓ). Dilute 2.7 mℓ of 37 percent formalin solution to 1 liter with distilled water. This solution must be standardized as described in Section 9.1. The solution is stable for at least a 3-month period. Alternatively sodium formaldehyde bisulfite (Eastman Kodak Company, Cat. No. P6450) can be used as a primary standard (Reference 11.4). Dissolve 4.4703 g in distilled water and dilute to 1 liter.

7.4 **Formaldehyde Standard Solution "B"** (10 μg/mℓ). Dilute 1 mℓ of standard solution "A" to 100 mℓ with distilled water. Make up fresh daily.

7.5 **Iodine, 0.1 N** (approximate). Dissolve 25 g of potassium iodide in about 25 mℓ of water, add 12.7 g of iodine and dilute to 1 liter.

7.6 **Iodine, 0.01 N.** Dilute 100 mℓ of the 0.1 N iodine solution to 1 liter. Standardize against sodium thiosulfate.

7.7 **Starch Solution, 1 Percent.** Make a paste of 1 g of soluble starch and 2 mℓ of water and slowly add the paste to 100 mℓ of boiling water. Cool, add several mℓ of chloroform as a preservative, and store in a stoppered bottle. Discard when a mold growth is noticeable.

7.8 **Sodium Carbonate Buffer Solution.** Dissolve 80 g of anhydrous sodium carbonate in about 500 mℓ of water. Slowly add 20 mℓ of glacial acetic acid and dilute to 1 liter.

7.9 **Sodium Bisulfite, 1 Percent.** Dissolve 1 g of sodium bisulfite in 100 mℓ of water. It is best to prepare a fresh solution weekly.

8. **Procedure**

8.1 **Cleaning of Equipment.** Care must be exercised to ensure the absence of probable contaminants like organic materials that can be charred by concentrated sulfuric acid. Soaking glassware for one hour in a 1:1 mixture of nitric and sulfuric acids, followed by thorough rinsing with double-deionized water will remove all possible organic contaminants.

8.2 **Collection and Shipping of Samples**

8.2.1 Pour 20 mℓ of the absorbing solution (distilled water) into each graduated midget impinger.

8.2.2 Connect two impingers in series to the vacuum pump (via the absorption tube) and the prefilter assembly (if needed) with short pieces of flexible tubing. The minimum amount of tubing necessary to make the joint between the prefilter and impingers should be used. The air being sampled should not be passed through any other tubing or other equipment before entering the impingers.

8.2.3 It has been recommended that two impingers must be used in series because under conditions of sampling, the collection efficiency of only one impinger is approximately 80 percent. With two impingers in series the total collection efficiency is approximately 95 percent. The contents of each impinger should be analyzed separately.

8.2.4 Turn on pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible. The sample should be taken at a flow rate of 1 ℓpm for one hour. (References 11.1, 11.5). These conditions give a total of 60 liters of air that is drawn through the system. However, a shorter sampling time can be used providing enough formaldehyde is collected to be above the lower limit of sensitivity of the method.

8.2.5 After sampling, the impinger stem can be removed and cleaned. Tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Wash the stem with a small amount (1-2 mℓ) of unused absorbing solution and add the wash to the impinger. Then the impinger is sealed with a hard, non-reactive stopper (preferably Teflon). Do not seal with rubber. The stoppers on the impingers should be tightly sealed to prevent leakage during shipping. If it is preferred to ship the impingers with the stems in, the outlets of the stem should be sealed with Parafilm or other non-rubber covers, and the ground glass joints should be sealed (i.e., taped) to secure the top tightly.

8.2.6 Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within a day.

8.2.7 Whenever possible, hand delivery of the samples is recommended. Otherwise, special impinger shipping cases designed by NIOSH should be used to ship the samples.

8.2.8 A "blank" impinger should be handled as the other samples (fill, seal and transport) except that no air is sampled through this impinger.

8.3 **Analysis**

8.3.1 Transfer the sample from each impinger to either a 25 mℓ- or 50 mℓ-graduate. Note the volume of each solution.

8.3.2 Pipet a 4 mℓ aliquot from each of the sampling solutions into glass stoppered test tubes. A blank containing 4 mℓ of distilled water must also be run. If the formaldehyde content of the aliquot exceeds the limit of the method, a smaller aliquot diluted to 4 mℓ with distilled water is used.

8.3.3 Add 0.1 mℓ of 1 percent chromotropic acid reagent to the solution and mix.

8.3.4 To the solution pipette slowly and cautiously 6 mℓ of concentrated sulfuric acid. The solution becomes extremely hot during the addition of the sulfuric acid. If the acid is not added slowly, some loss of sample could occur due to spattering.

8.3.5 Allow to cool to room temperature. Read at 580 nm in a suitable spectrophotometer using a 1 cm cell. No change in absorbance was noted over a 3 hour period after color development. Determine the formaldehyde content of the sampling solution from a curve previously prepared from standard formaldehyde solutions.

8.3.6 During the analysis procedure, it is good practice to group together the two impingers from each sampling series and label them as "A" and "B." The formaldehyde content calculated in "A" is added to that calculated in "B" to give the total amount in the sampled atmosphere by the impingers in series.

9. Calibration and Standards

9.1 Standardization of Formaldehyde Solution

9.1.1 Pipette 1 mℓ of formaldehyde standard solution "A" into an iodine flask. Into another flask pipette 1 mℓ of distilled water. This solution serves as the blank.

9.1.2 Add 10 mℓ of 1 percent sodium bisulfite and 1 mℓ of 1 percent starch solution.

9.1.3 Titrate with 0.1 N iodine to a dark blue color.

9.1.4 Destroy the excess iodine with 0.05 N sodium thiosulfate.

9.1.5 Add 0.01 N iodine until a faint blue end point is reached.

9.1.6 The excess inorganic bisulfite is now completely oxidized to sulfate, and the solution is ready for the assay of the formaldehyde bisulfite addition product.

9.1.7 Chill the flask in an ice bath and add 25 mℓ of chilled sodium carbonate buffer. Titrate the liberated sulfite with 0.01 N iodine, using a microburette, to a faint blue end point. The amount of iodine added in this step must be accurately measured and recorded.

9.1.8 One mℓ of 0.0100 N iodine is equivalent to 0.15 mg of formaldehyde. Therefore, since 1 mℓ of formaldehyde standard solution was titrated, the mℓ of 0.01 N iodine used in the final titration multiplied by the factor, 0.15, gives the formaldehyde concentration of the standard solution in mg/mℓ.

9.1.9 The factor, 0.15, must be adjusted or determined accordingly on the basis of the exact normality of the iodine solution.

9.2 **Preparation of Standard Curve**

9.2.1 Pipet 0, 0.1, 0.3, 0.5, 0.7, 1.0, and 2.0 mℓ of standard solution "B" into glass stoppered test tubes.

9.2.2 Dilute each standard to 4 mℓ with distilled water.

9.2.3 Develop the color as described in the analysis procedure (Section 8.3).

9.2.4 Plot absorbance against micrograms of formaldehyde in the color developed solution. Note that the microgram concentration of the formaldehyde is determined based on the standardization value of solution A.

10. Calculations

10.1 Convert the volume of air sampled (V) to the volume of air at standard conditions (V_s) of 760 mm of mercury and 25°C, using the correction formula:

$$V_s = V \times \frac{P}{760} \times \frac{298}{(T + 273)}$$

where:

V_s = volume of air in liters at standard conditions
V = volume of air sampled in liters
P = barometric pressure in mm of mercury
T = temperature of sample air, °C

10.2 Determine the total concentration (C_t) of formaldehyde present in the two sample impingers in series, A and B.

$$C_t = C_A \times F_A + C_B \times F_B$$

where:

C_t = total μg of formaldehyde in the sample.

C_A and C_B = respective formaldehyde concentration in μg of the sample aliquots taken from impingers A and B as determined from the calibration curve

F_A and F_B = respective aliquot factor; $\frac{\text{sampling soln. vol. in m}\ell}{\text{m}\ell \text{ aliquot used}}$

10.3 The concentration of formaldehyde in the sampled atmosphere may be calculated by using the following equation, assuming standard conditions are taken as 760 mm of mercury and 25°C:

$$\text{ppm (volume)} = \frac{C_t \times 24.47}{V_s \times \text{M.W.}}$$

where:

V_s = liters of air sampled at standard conditions

M.W. = molecular weight of formaldehyde (30.03)

24.47 = $\mu\ell$ of formaldehyde gas in one micromole at 760 mm Hg and 25°C.

11. References

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11.7 Treadwell and Hall, Analytical Chemistry, Vol. II, Ninth English Edition. John Wiley & Sons, Inc., New York, p. 590, 1951.

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HYDROGEN SULFIDE IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Hydrogen Sulfide	**Method No.:**	P&CAM 126
Matrix:	Air	**Range:**	0.008 ppm – 50 ppm
Procedure:	Absorption – Methylene Blue – Spectrophotometric	**Precision:**	Unknown
		Classification:	C (Tentative)
Date Issued:	6/9/72		
Date Revised:	1/15/74		

1. **Principle of the Method**

1.1 Hydrogen sulfide is collected by aspirating a measured volume of air through an alkaline suspension of cadmium hydroxide (Reference 11.1). The sulfide is precipitated as cadmium sulfide to prevent air oxidation of the sulfide which occurs rapidly in an aqueous alkaline solution. STRactan 10® is added to the cadmium hydroxide slurry to minimize photo-decomposition of the precipitated cadmium sulfide (Reference 11.2). The collected sulfide is subsequently determined by spectrophotometric measurement of the methylene blue produced by the reaction of the sulfide with a strongly acid solution of N, N-dimethyl-p-phenylenediamine and ferric chloride (References 11.3, 11.4, 11.5). The analysis should be completed within 24-26 hours following collection of the sample.

1.2 Hydrogen sulfide may be present in the open atmosphere at concentrations of a few ppb or less. The reported odor detection threshold is in the 0.7-8.4 $\mu g/m^3$ (0.5-6.0 ppb) range (References 11.6, 11.7). Concentrations in excess of 140 $\mu g/m^3$ (100 ppb) are seldom encountered in the atmosphere.

1.3 Collection efficiency is variable below 10 $\mu g/m^3$ and is affected by the type of scrubber, the size of the gas bubbles and the contact time with the absorbing solution and the concentration of H_2S (References 11.8, 11.9, 11.10).

2. **Range and Sensitivity**

2.1 This method is intended to provide a measure of hydrogen sulfide in the range of 1.1-100 mg/m^3. For concentrations above 70 mg/m^3 the sampling period can be reduced or the liquid volume increased either before or after aspirating. (This

method is also useful for the mg/m^3 range of source emissions. For example, 100 mℓ cadmium $(OH)_2$-STRactan 10® media in Greenberg-Smith impingers and 5 minute sampling periods have been used successfully for source sampling.) The minimum detectable amount of sulfide is 0.008 μg/mℓ, which is equivalent to 0.2 μg/m^3 in an air sample of 1 m^3 and using a final liquid volume of 25 mℓ. When sampling air at the maximum recommended rate of 1.5 ℓ/minute for 2 hours, the minimum detectable sulfide concentration is 1.1 μg/m^3 at 760 mm Hg and 25°C.

2.2 Excellent results have been obtained by using this method for air samples having a hydrogen sulfide content in the range 5-50 ppm.

3. Interferences

3.1 The methylene blue reaction is highly specific for sulfide at the low concentrations usually encountered in ambient air. Strong reducing agents (e.g., SO_2) inhibit color development. Even sulfide solutions containing several micrograms sulfide/mℓ show this effect and must be diluted to eliminate color inhibition. If sulfur dioxide is absorbed to give a sulfite concentration in excess of 10 μg/mℓ, color formation is retarded. Up to 40 μg/mℓ,of this interference, however, can be overcome by adding 2-6 drops (0.5 mℓ/drop) of ferric chloride instead of a single drop for color development, and extending the reaction time to 50 minutes.

3.2 Nitrogen dioxide gives a pale yellow color with the sulfide reagents at 0.5 μg/mℓ or more. No interference is encountered when 0.3 ppm NO_2 is aspirated through a midget impinger containing a slurry of cadmium hydroxide-cadmium sulfide-STRactan 10®. If H_2S and NO_2 are simultaneously aspirated through cadmium hydroxide-STRactan 10® slurry, lower H_2S results are obtained, probably because of gas phase oxidation of the H_2S prior to precipitation as CdS (Reference 11.10).

3.3 Ozone at 57 ppb reduced the recovery of sulfide previously precipitated as CdS by 15 per cent (Reference 11.10).

3.4 Sulfides in solution are oxidized by oxygen from the atmosphere unless inhibitors such as cadmium and STRactan 10® are present.

3.5 Substitution of other cation precipitants for the cadmium in the absorbent (i.e., zinc, mercury, etc.) will shift or eliminate the absorbance maximum of the solution upon addition of the acid-amine reagent.

3.6 Cadmium sulfide decomposes significantly when exposed to light unless protected by the addition of 1 per cent STRactan® to the absorbing solution prior to sampling (Reference 11.2).

3.7 The choice of impinger used to trap H_2S with the $Cd(OH)_2$ slurry is very important when measuring concentration in the range 5-50 ppm. Impingers or bubblers having fritted-end gas delivery tubes are a problem source if the sulfide in solution is oxidized by oxygen from the atmosphere to free sulfur. The sulfur collects on the fritted-glass membrane and may significantly change the flow rate of the air sample through the system. One way of avoiding this problem is to use a midget impinger with standard, glass-tapered tips.

4. Precision and Accuracy

4.1 A relative standard deviation of 3.5 per cent and a recovery of 80 per cent has been established with hydrogen sulfide permeation tubes (Reference 11.2).

5. Advantages and Disadvantages of the Method

5.1 Effect of Light and Storage – Disadvantage

5.1.1 Hydrogen sulfide is readily volatilized from aqueous solution when the pH is below 7.0. Alkaline, aqueous sulfide solutions are very unstable because sulfide ion is rapidly oxidized by exposure to the air.

5.1.2 Cadmium sulfide is not appreciably oxidized even when aspirated with pure oxygen in the dark. However, exposure of an impinger containing cadmium sulfide to laboratory or to more intense light sources produces an immediate and variable photo-decomposition. Losses of 50-90 per cent of added sulfide have been routinely reported by a number of laboratories. Even though the addition of STRactan 10® to the absorbing solution controls the photo-decomposition (Reference 11.2), it is necessary to protect the impinger from light at all times. This is achieved by the use of low actinic glass impingers, paint on the exterior of the impingers, or an aluminum foil wrapping.

6. Apparatus

6.1 **Sampling Equipment.** The sampling unit for the impinger collection method consists of the following components:

6.1.1 A graduated 25 mℓ midget impinger with a standard glass-tapered gas delivery tube containing the absorbing solution or reagent.

6.1.2 A pump suitable for delivering desired flow rates with a minimum capacity of 2 ℓpm through the impinger. The sampling pump is protected from splashover or water condensation by an adsorption tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump.

6.1.3 An integrating volume meter such as a dry gas or wet test meter. The air meter must be capable of measuring the air flow within ±2 per cent. A wet or dry gas meter, with contacts on the 1-feet^3 or 10-l dial to record air volume, or a specially calibrated rotameter, is satisfactory. Instead of these, calibrated hypodermic needles may be used as critical orifices if the pump is capable of maintaining greater than 0.7 atmospheric pressure differential across the needle (Reference 11.11).

6.1.4 Thermometer.

6.1.5 Manometer.

6.1.6 Stopwatch.

6.2 Associated laboratory glassware.

6.3 Colorimeter with red filter or spectrophotometer at 670 nm.

6.4 Matched cells, 1 cm path length.

7. Reagents

All reagents must be ACS analytical reagent quality. Distilled water should conform to the ASTM Standards for Referee Reagent Water.

All reagents should be refrigerated when not in use.

7.1 **Amine-sulfuric Acid Stock Solution.** Add 50 mℓ concentrated sulfuric acid to 30 mℓ water and cool. Dissolve 12 g of N, N-dimethyl-p-phenylenediamine dihydrochloride (para-aminodimethylaniline) (redistilled if necessary) in the acid. Do not dilute. The stock solution may be stored indefinitely under refrigeration.

7.2 **Amine Test Solution.** Dilute 25 mℓ of the Stock Solution to 1 liter with 1:1 sulfuric acid.

7.3 **Ferric Chloride Solution.** Dissolve 100 g of ferric chloride, $FeCl_3 \cdot 6H_2O$, in water and dilute to 100 mℓ.

7.4 **Ammonium Phosphate Solution.** Dissolve 400 g of diammonium phosphate, $(NH_4)_2HPO_4$, in water and dilute to 1 liter.

7.5 **STRactan 10®**, (Arabinogalactan) Available from Stein-Hall and Company, Inc., 385 Madison Avenue, New York, New York.

7.6 **Absorbing Solution.** Dissolve 4.3 g of $3CdSO_4 . 8 H_2O$, and 0.3 g sodium hydroxide in separate portions of water. Mix and add 10 g STRactan 10® and dilute to 1 liter. Shake the resultant suspension vigorously before removing each aliquot. The STRactan®-cadmium hydroxide mixture should be freshly prepared. The solution is only stable for 3 to 5 days.

7.7 **H_2S Permeation Tube.** Prepare or purchase* a triple-walled or thick walled Teflon® permeation tube (References 11.10, 11.12, 11.13, 11.14, 11.15) which delivers hydrogen sulfide at a maximum rate of approximately 0.1 μg/minute at 25°C. This loss rate will produce a standard atmosphere containing 50 $\mu g/m^3$ (36 ppb H_2S when the tube is swept with a 2 ℓ/minute air flow. Tubes having H_2S permeation rates in the range of 0.004-0.33 μg/minute will produce standard air concentrations in the realistic range of 1-90 $\mu g/m^3$ H_2S with an air flow of 1.5 ℓ/min.

7.7.1 **Concentrated, Standard Sulfide Solution**

Transfer freshly boiled and cooled 0.1M NaOH to a liter volumetric flask. Flush with purified nitrogen to remove oxygen and adjust to volume. (Commercially available, compressed nitrogen contains trace quantities of oxygen in sufficient concentration to oxidize the small concentrations of sulfide contained in the standard and dilute standard sulfide standards. Trace quantities of oxygen should be removed by passing the stream of tank nitrogen through a Pyrex or quartz tube containing copper turnings heated to 400-450°C.) Immediately stopper the flask with a serum cap. Inject 300 mℓ of H_2S gas through the septum. Shake the flask. Withdraw measured volumes of standard solution with a 10 mℓ hypodermic syringe and fill the resulting void with an equal volume of nitrogen. Standardize with standard iodine and thiosulfate solution in an iodine flask under a nitrogen atmosphere to minimize air oxidation. The approximate concentration of the sulfide solution will be 440 μg sulfide/mℓ of solution. The exact concentration must be determined by iodine-thiosulfate standardization immediately prior to dilution.

For the most accurate results in the iodometric determination of sulfide in aqueous solution, the following general procedure is recommended:

1. Replace the oxygen from the flask by flushing with an inert gas such as carbon dioxide or nitrogen.

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*Available from Metronics, Inc., 3201 Porter Drive, Palo Alto, California 94304, or PolyScience Corp., 909 Pitner Avenue, Evanston, Illinois 60202.

2. Add an excess of standard iodine, acidify, and back titrate with standard thiosulfate and starch indicator (Reference 11.16).

7.7.2 **Diluted Standard Sulfide Solution**

Dilute 10 mℓ of the concentrated sulfide solution to 1 liter with freshly boiled, distilled water. Protect the boiled water under a nitrogen atmosphere while cooling. Transfer the deoxygenated water to a flask previously purged with nitrogen and immediately stopper the flask. This sulfide solution is unstable. Therefore, prepare this solution immediately prior to use. This test solution will contain approximately 4 μg sulfide/mℓ.

8. Procedure

8.1 **Cleaning of Equipment.** All glassware should be thoroughly cleaned; the following procedure is recommended:

8.1.1 Wash with a detergent and tap water solution followed by tap water and distilled water rinses.

8.1.2 Soak in 1:1 or concentrated nitric acid for 30 minutes and then follow with tap, distilled, and double distilled water rinses.

8.2 **Collection and Shipping of Samples**

8.2.1 Pipet 10 mℓ of the absorbing solution (Section 7.6) into the midget impinger. The addition of 5 mℓ of 95 per cent ethanol to the absorbing solution just prior to aspiration controls foaming for 2 hours (induced by the presence of STRactan 10®. In addition, 1 or 2 Teflon demister discs may be slipped up over the impinger air inlet tube to a height approximately 1-2" from the top of the tube.

8.2.2 Connect the impinger (via the absorption tube) to the vacuum pump with a short piece of flexible tubing. The minimum amount of tubing necessary to make the joint between the prefilter and impinger should be used. The air being sampled should not be passed through any other tubing or other equipment before entering the impinger.

8.2.3 Turn on pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible. The sample should be taken at a flow rate of 1.5 ℓpm.

8.2.4 After sampling, the impinger stem can be removed and cleaned. Tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Wash the stem with a small amount (1-2 mℓ) of unused absorbing solution and add the wash to the impinger. Then the impinger is sealed with a hard, non-reactive stopper (preferably Teflon). Do not seal with rubber. The stoppers on the impingers should be tightly sealed to prevent leakage during shipping. If it is preferred to ship the impingers with the stems in, the outlets of the stem should be sealed with Parafilm or other non-rubber covers, and the ground glass joints should be sealed (i.e., taped) to secure the top tightly.

8.2.5 Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within a day.

8.2.6 Whenever possible, hand delivery of the samples is recommended. Otherwise, special impinger shipping cases designed by NIOSH should be used to ship the samples.

8.2.7 A "blank" impinger should be handled as the other samples (fill, seal and transport) except that no air is sampled through this impinger.

8.3 **Analysis**

8.3.1 Add 1.5 mℓ of the amine-test solution to the midget impinger through the air inlet tube and mix.

8.3.2 Add 1 drop of ferric chloride solution and mix. (*Note:* See Section 3.1 if SO_2 exceeds 10 μg/mℓ in the absorbing media.)

8.3.3 Transfer the solution to a 25 mℓ volumetric flask. Discharge the color due to the ferric ion by adding 1 drop ammonium phosphate solution. If the yellow color is not destroyed by 1 drop ammonium phosphate solution, continue dropwise addition until solution is decolorized. Make up to volume with distilled water and allow to stand for 30 minutes.

8.3.4 Prepare a zero reference solution in the same manner using a 10 mℓ volume of absorbing solution, through which no air has been aspirated.

8.3.5 Measure the absorbance of the color at 670 nm in a spectrophotometer or colorimeter set at 100 per cent transmission against the zero reference.

9. Calibration and Standards

9.1 Aqueous Sulfide

9.1.1 Place 10 mℓ of the absorbing solution in each of a series of 25 mℓ volumetric flasks and add the diluted standard sulfide solution, equivalent to 1, 2, 3, 4, and 5 μg of hydrogen sulfide to the different flasks.

9.1.2 Add 1.5 mℓ of amine-acid test solution to each flask and mix.

9.1.3 Add 1 drop of ferric chloride solution to each flask. Mix, make up to volume and allow to stand for 30 minutes.

9.1.4 Determine the absorbance in a spectrophotometer at 670 nm, against the sulfide-free reference solution.

9.1.5 Prepare a standard curve of absorbance vs. μg H_2S/mℓ.

9.2 **Gaseous Sulfide.** Commercially available permeation tubes containing liquefied hydrogen sulfide may be used to prepare calibration curves for use at the upper range of atmospheric concentration. Triple-walled tubes, drilled rod and micro bottles which deliver hydrogen sulfide within a minimum range of 0.1-1.2 μg/minute at 25°C have been prepared by Thomas (Reference 11.10); O'Keeffe (References 11.12, 11.13); Scaringelli (References 11.14, 11.15). Preferably the tubes should deliver hydrogen sulfide within a loss rate range of 0.003-0.28 μg/minute to provide realistic concentrations of H_2S (1.5-140 μg/m^3, 1.1-100 ppb) without having to resort to a dilution system to prepare the concentration range required for determining the collection efficiency of midget impingers. Analyses of these known concentrations give calibration curves which simulate all of the operational conditions performed during the sampling and chemical procedure. This calibration curve includes the important correction for collection efficiency at various concentrations of hydrogen sulfide.

9.2.1 Prepare or obtain a Teflon® permeation tube that emits hydrogen sulfide at a rate of 0.1-0.2 μg/minute (0.07-0.14 μℓ/minute at standard conditions of 25°C and 1 atmosphere). A permeation tube with an effective length of 2-3 cm and a wall thickness of 0.318 cm will yield the desired permeation rate if held at a constant temperature of 25°C ± 0.1°C. Permeation tubes containing hydrogen sulfide are calibrated under a stream of dry nitrogen to prevent the precipitation of sulfur in the walls of the tube.

9.2.2 To prepare standard concentrations of hydrogen sulfide, assemble the apparatus consisting of a water-cooled condenser, constant temperature bath maintained at 25°C ±0.1°C cylinders containing pure dry nitrogen

and pure dry air with appropriate pressure regulators, needle valves and flow meters for the nitrogen and dry air, diluent-streams. The diluent gases are brought to temperature by passage through a 2-meter-long copper coil immersed in the water bath. Insert a calibrated permeation tube into the central tube of the condenser, maintained at the selected constant temperature by circulating water from the constant-temperature bath, and pass a stream of nitrogen over the tube at a fixed rate of approximately 50 mℓ/minute. Dilute this gas stream to obtain the desired concentration by varying the flow rate of the clean, dry air. This flow rate can normally be varied from 0.2-15 ℓ/minute. The flow rate of the sampling system determines the lower limit for the flow rate of the diluent gases. The flow rate of the nitrogen and the diluent air must be measured to an accuracy of 1-2 per cent. With a tube permeating hydrogen sulfide at a rate of 0.1 μℓ/minute, the range of concentration of hydrogen sulfide will be between 6-400 $\mu g/m^3$ (4-290 ppb), a generally satisfactory range for ambient air conditions. When higher concentrations are desired, calibrate and use longer permeation tubes.

9.2.3 Procedure for Preparing Simulated Calibration Curves

Obviously one can prepare a multitude of curves by selecting different combinations of sampling rate and sampling time. The following description represents a typical procedure for ambient air sampling of short duration, with a brief mention of a modification for 24 hour sampling.

1. The system is designed to provide an accurate measure of hydrogen sulfide in the 1.4-84 $\mu g/m^3$ (1-60 ppb) range. It can be easily modified to meet special needs.

2. The dynamic range of the colorimetric procedure fixes the total volume of the sample at 186 ℓ; then, to obtain linearity between the absorbance of the solution and the concentration of hydrogen sulfide in ppm, select a constant sampling time. This fixing of the sampling time is desirable also from a practical standpoint: In this case, select a sampling time of 120 minutes. Then to obtain a 186 ℓ sample of air requires a flow rate of 1.55 ℓ/minute. The concentration of standard H_2S in air is computed as follows:

$$C = \frac{P_r \times M}{(R + r)}$$

where:

C = Concentration of H_2S in ppm
P_r = Permeation rate in μg/minute
M = Reciprocal of vapor density, 0.719 $\mu\ell/\mu g$
R = Flow rate of diluent air, liter/minute
r = Flow rate of diluent nitrogen, liter/minute

3. The data for a typical calibration curve are listed in Table 1.

TABLE 1

TYPICAL CALIBRATION DATA

Concentrations H_2S, ppb	Amount of H_2S in μl/186 liters	Absorbance of Sample
1	.144	.010
5	.795	.056
10	1.44	.102
20	2.88	.205
30	4.32	.307
40	5.76	.410
50	7.95	.512
60	8.64	.615

4. A plot of the concentration of hydrogen sulfide in ppm (x – axis) against absorbance of the final solution (y – axis) will yield a straight line, the reciprocal of the slope of which is the factor for conversion of absorbance to ppm. This factor includes the correction for collection efficiency. Any deviation from the linearity at the lower concentration range indicates a change in collection efficiency of the sampling system. If the range of interest is below the dynamic range of the method the total volume of air collected should be increased to obtain sufficient color within the dynamic range of the colorimetric procedure. Also, once the calibration factor has been established under simulated conditions the conditions can be modified so that the concentration of H_2S is a simple multiple of the absorbance of the colored solution.

5. For long-term sampling of 24-hour duration, the conditions can be fixed to collect 1200 ℓ of sample in a larger volume of STRactan 10®-cadmium hydroxide. For example, for 24 hours at 0.83 ℓ/min, approximately 1200 ℓ of air are scrubbed. An aliquot representing 0.1 of the entire amount of sample is taken for the analysis.

6. The remainder of the analytical procedure is the same as described in the previous paragraph.

9.2.4 The permeation tubes must be stored in a wide-mouth glass bottle containing silica gel and solid sodium hydroxide to remove moisture and hydrogen sulfide. The storage bottle is immersed to two-thirds its depth in a constant temperature water bath in which the water is controlled at 25°C ±0.1°C.

Periodically, (every 2 weeks or less) the permeation tubes are removed and rapidly weighed on a semimicro balance (sensitivity ±0.01 mg) and then returned to the storage bottle. The weight loss is recorded. The tubes are ready for use when the rate of weight loss becomes constant (within ±2 per cent).

10. Calculations

10.1 Gaseous Sulfide

10.1.1 Determine the sample volume in liters from the gas meter or flow meter readings and time of sampling. Adjust volume to 760 mm mercury and 25°C (V_s).

10.1.2 Determine the concentration of H_2S in $\mu g/m^3$.

$$\mu g\ H_2S/m^3 = \mu g\ H_2S/V_s \times 10^{-3}$$

where:

$\mu g\ H_2S$ = micrograms hydrogen sulfide determined
10^{-3} = conversion factor, m^3/ℓ

10.2 Gaseous Sulfide from Aqueous Sulfide

10.2.1 Determine the sample volume (V) in liters from the gas meter or flow meter readings and time of sampling. Adjust volume to 760 mm mercury and 25°C (V_s), using the correction formula:

$$V_S = V \times \frac{P}{760} \times \frac{298}{(T + 273)}$$

where:

V_S = Volume of air in liters at standard conditions
V = Volume of air sampled in liters
P = Barometric pressure in mm Hg
T = Temperature of sample air in °C

10.2.2 Using the Beers-Law Standard curve of absorbance vs. $\mu g\ S^=$ ion, determine $\mu g\ S^=$ ion in the sampling impinger corresponding to its absorbance reading at 670 nm.

10.2.3 Calculate the concentration of H_2S in the aspirated volume of air using the formula:

$$\text{ppm, } H_2S = \frac{\mu g\ S^= \times 24.45}{V_S \times MW}$$

where:

$\mu g\ S^=$ = micrograms sulfide ion (Section 10.2.2)
24.45 = molar volume of an ideal gas at 25°C and 760 mm Hg
MW = mass of sulfide ion, 32.06

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ORGANIC SOLVENTS IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Organic Solvents (See Table 1)	Method No:	P&CAM 127
Matrix:	Air	Range:	For the specific compound, refer to Tables I&II
Procedure:	Adsorption on charcoal desorption with carbon disulfide, GC		
Date Issued:	9/15/72	Precision:	10.5% RSD
Date Revised:	7/15/74	Classification:	See Table 1

1. Principle of the Method

   1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

   1.2 The charcoal in the tube is transferred to a small, graduated test tube and desorbed with carbon disulfide.

   1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

   1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

   The lower limit in mg/sample for the specific compound at 16 x 1 attenuation on a gas chromatograph fitted with a 10:1 splitter is shown in Table 1. This value can be lowered by reducing the attenuation or by eliminating the 10:1 splitter.

3. Interferences

   3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

   3.2 When two or more solvents are known or suspected to be present in the air, such information including their suspected identities, should be transmitted with the sample; since with differences in polarity, one may displace another from the charcoal.

3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Hence, retention time data on a single column, or even on a number of columns, cannot be considered as proof of chemical identity. For this reason it is important that a sample of the bulk solvent(s) be submitted at the same time so that identity(ies) can be established by other means.

3.4 If the possibility of interference exists, separation conditions (column packing, temperatures, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The mean relative standard deviation of the analytical method is 8%. (Ref. 11.4).

4.2 The mean relative standard deviation of the analytical method plus field sampling using an approved personal sampling pump is 10% (Ref. 11.4). Part of the error associated with the method is related to uncertainties in the sample volume collected. If a more powerful vacuum pump with associated gas-volume integrating equipment is used, sampling precision can be improved.

4.3 The accuracy of the overall sampling and analytical method is 10% (NIOSH's unpublished data) when the personal sampling pump is calibrated with a charcoal tube in the line.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more solvents suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists. During sample storage the more volatile compounds will migrate throughout the tube until equilibrium is reached (33% of the sample on the backup section).

5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 An approved and calibrated personal-sampling pump for personal samples. For an area sample any vacuum pump whose flow can be determined accurately at 1 liter per minute or less.

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in frontof the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 ℓpm.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (20 ft x 1/8 in) with 10% FFAP stationary phase on 80/100 mesh, acid-washed DMCS Chromosorb W solid support. Other columns capable of performing the required separations may be used.

6.5 A mechanical or electronic integrator or a recorder and some method for determining peak area.

6.6 Glass stoppered micro tubes. The 2.5-mℓ graduated microcentrifuge tubes are recommended.

6.7 Hamilton syringes: 10 µl, and convenient sizes for making standards.

6.8 Pipets: 0.5 mℓ delivery pipets or 1.0 mℓ type graduated in 0.1 mℓ increments.

6.9 Volumetric flasks: 10 mℓ or convenient sizes for making standard solutions.

7. Reagents

7.1 Spectroquality carbon disulfide (Matheson Coleman and Bell)

7.2 Sample of the specific compound under study, preferably chromatoquality grade.

7.3 Bureau of Mines Grade A helium.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, the ends of the tube should be broken to provide an opening at least one-half the internal diameter of the tube (2mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be vertical during sampling.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 The flow, time, and/or volume must be measured as accurately as possible. The sample should be taken at a flow rate of 1 ℓpm or less to attain the total sample volume required. The minimum and maximum sample volumes that should be collected for each solvent are shown in Table 1. The minimum volume quoted must be collected if the desired sensitivity is to be achieved.

8.3.6 The temperature and pressure of the atmosphere being sampled should be measured and recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly before they are shipped to minimize tube breakage during shipping.

8.3.10 Samples of the suspected solvent(s) should be submitted to the laboratory in containers furnished by NIOSH for such purpose. These liquid bulk samples should not be transported in the same container as the samples or blank tube. If possible, a bulk air sample (at least 50ℓ air drawn through tube) should be shipped for qualitative identification purposes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In prepration for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a small stoppered test tube. The separating section of foam is removed and discarded; the second section is transferred to another test tube. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, one-half ml of carbon disulfide is pipetted into each test tube. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period. The use of graduated glass-stoppered, microcentrifuge tubes is recommended so that one can observe any apparent change in volume during the desorption process. Carbon disulfide is a very volatile solvent, so volume changes can occur during the desorption process depending on the surrounding temperature. The initial volume occupied by the charcoal plus the 0.5 mℓ CS_2 should be noted and corresponding volume adjustments should be made whenever necessary just before GC analysis.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 85 cc/min. (70 psig) helium carrier gas flow.
2. 65 cc/min. (24 psig) hydrogen gas flow to detector.
3. 500 cc/min. (50 psig) air flow to detector.
4. 200°C injector temperature.

5. 200°C manifold temperature (detector)
6. Isothermal oven or column temperature - refer to Table 1 for specific compounds.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blowback or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10 µℓ syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µℓ to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µℓ aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back a short distance to minimize evaporation of the sample from the tip of the needle. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process for a given compound, provided the same batch of charcoal is used. The Physical and Chemical Analysis Branch of NIOSH has found that the desorption efficiencies for the compounds in Table 1 are between 81% and 100% and vary with each batch of charcoal.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 5cm, 4-mm I.D. glass tube, flame-sealed at one end (similar to commercially available culture tubes). This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped

with Parafilm. A known amount of the compound is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. The amount injected is usually equivalent to that present in a 10-liter sample at a concentration equal to the federal standard.

At least five tubes are prepared in this manner and allowed to stand for at least overnight to assure complete abosrption of the specific compound onto the charcoal. These five tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.3.

Two or three standards are prepared by injecting the same volume of compound into 0.5 mℓ of CS_2 with the same syringe used in the preparation of the sample. These are analyzed with the samples.

The desorption efficiency equals the difference between the average peak area of the samples and the peak area of the blank divided by the average peak area of the standards, or

$$\text{desorption efficiency} = \frac{\text{Area sample - Area blank}}{\text{Area standard}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 mℓ CS_2 because samples are desorbed in this amount of CS_2. To minimize error due to the volatility of carbon disulfide, one can inject 20 times the weight into 10 mℓ of CS_2. For example, to prepare a 0.3 mg/0.5 mℓ standard, one would inject 6.0 mg into exactly 10 mℓ of CS_2 in a glass-stoppered flask. The density of the specific compound is used to convert 6.0 mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5mℓ versus peak area.

NOTE: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 The weight, in mg, corresponding to each peak area is read from the standard curve for the particular compound. No volume corrections are needed, because the standard curve is based on mg/0.5 mℓ CS_2 and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{Correct mg} = mg_s - mg_b$$

where:

mg_s = mg found in front section of sample tube

mg_b = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 The corrected amounts present in the front and backup sections of the same sample tube are added to determine the total measured amount in the sample.

10.4 This total weight is divided by the determined desorption efficiency to obtain the total mg per sample.

10.5 The volume of air sampled is converted to standard conditions of of 25°C and 760 mm Hg.

$$V_s = V \times \frac{P}{760} \quad \frac{298}{T+273}$$

where:

V_s = volume of air in liters at 25°C and 760 mm Hg

V = volume of air in liters as measured

P = Barometric pressure in mm Hg

T = Temperature of air in degree centigrade

10.6 The concentration of the organic solvent in the air sampled can be expressed in mg per m^3, which is numerically equal to µg per liter of air

$$mg/m^3 = \mu g/\ell = \frac{\text{total mg (Section 10.4) x 1000 (µg/mg)}}{V_s}$$

10.7 Another method of expressing concentration is ppm, defined as µℓ of compounds per liter of air

$$\text{ppm} = \mu\ell \text{ of compound}/V_s$$

$$\text{ppm} = \frac{\mu\ell \text{ of compound}}{V_s} \times \frac{24.45}{MW}$$

where:

24.45 = molar volume at 25°C and 760 mm Hg

MW = molecular weight of the compound (Table 1)

11. References

11.1 White, L.D., D.G. Taylor, P.A. Mauer, and R.E. Kupel, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," *Amer. Ind. Hyg. Assoc. J.*, 31:225 (1970).

11.2 Young, D.M. and A.D. Crowell, Physical Adsorption of Gases, Butterworths, London, 1962, pp. 137-146.

11.3 Federal Register, 37 (#202), 22139-22142 (October 18, 1972).

11.4 NIOSH Contract HSM-99-72-98, Scott Research Laboratories, Inc., "Collaborative Testing of Activated Charcoal Sampling Tubes for Seven Organic Solvents," pp. 4-22, 4-27 (1973).

TABLE I

PARAMETERS ASSOCIATED WITH P&CAB ANALYTICAL METHOD NO. 127

Organic Solvent	Method Classification	Detection limit (mg/sample)	Sample Volume (ℓ) Minimum[a]	Maximum[b]	GC Column Temperature(°C)	Molecular Weight
Acetone	D	-	0.5	7.7	60	58.1
Benzene	A	0.01	0.5	55	90	78.1
Carbon tetrachloride	A	0.20	10	60	60	154.0
Chloroform	A	0.10	0.5	13	80	119
Dichloromethane	D	0.05	0.5	3.8	85	84.9
p-Dioxane	A	0.05	1	18	100	88.1
Ethylene dichloride	D	0.05	1	12	90	99.0
Methyl ethyl ketone	B	0.01	0.5	13	80	72.1
Styrene	D	0.10	1.5	34	150	104
Tetrachloroethylene	B	0.06	1	25	130	166
1,1,2-trichloroethane	B	0.05	10	97	150	133
1,1,1-trichloroethane (Methyl Chloroform)	B	0.05	0.5	13	150	133
Trichloroethylene	A	0.05	1	17	90	131
Toluene	B	0.01	0.5	22	120	92.1
Xylene	A	0.02	0.5	31	100	106

(a) Minimum volume, in liters, required to measure 0.1 times the OSHA standard

(b) These are breakthrough volumes calculated with data derived from a potential plot (reference 11.2) for activated coconut charcoal. Concentrations of vapor in air at 5 times the OSHA standard (reference 11.3) or 500 ppm, whichever is lower, 25°C, and 760 torr were assumed. These values will be as much as 50% lower for atmospheres of high humidity. The effects of multiple contaminants have not been investigated, but it is suspected that less volatile compounds may displace more volatile compounds (See 3.1 and 3.2)

TABLE II

CHEMICALS WHICH HAVE GREATER THAN 80%
DESORPTION EFFICIENCY BUT HAVE NOT BEEN
THOROUGHLY TESTED BY NIOSH

Class E (Proposed)

Acrylonitrile
Allyl glycidyl ether
n-Amyl acetate
2-Butoxyethanol
n-Butyl acetate
n-Butyl alcohol
n-Butylglycidyl ether
Chlorobenzene
Cyclohexane
Cyclohexanone
o-Dichlorobenzene
p-Dichlorobenzene
Diethyl ether
N,N-Dimethyl aniline
Epichlorohydrin
2-Ethoxylethyl acetate
Ethyl acetate
Ethylbenzene
Ethyl butyl ketone
Fufural
Heptane
Hexane
Isoamyl acetate
Isobutyl acetate
Isobutyl alcohol
Isoctane
Isophorone
Isopropyl acetate
Isopropyl glycidyl ether
2,6-Lutidine
Methyl acetate
Methyl acrylate
Methyl n-butyl ketone
Methyl ethyl ketone
Methyl isobutyl ketone
Methyl methacrylate
α-Methyl styrene
p-Methyl styrene
n-Octane
3-Octanone
Pentane
2-Pentanone
α-pinene
n-Propyl acetate
1,1,2,2-Tetrachloroethane
Tetrahydrofuran
Trichlorotrifluoroethane (Freon 113)

Recommended Sample Size = 10ℓ

ARSENIC IN URINE AND AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Arsenic	**Method No.:**	P&CAM 139
Matrix:	Urine and Air	**Range:**	0.05 to 2.0 μg/sample
Procedure:	Arsenic generation – AA	**Precision:**	Unknown
Date Issued:	3/24/72		
Date Revised:	1/10/74	**Classification:**	D (Operational)

1. **Principle of Method**

   1.1 Samples are ashed with a mixture of nitric, perchloric, and sulfuric acids to destroy the organic matrix.

   1.2 The sample ash is treated with ammonium oxalate and taken to fumes of SO_3 to remove all traces of nitric acid.

   1.3 The sample is transferred to an arsine generator where the arsenic is converted to the trivalent form by the addition of KI, HCl, and $SnCl_2$.

   1.4 Arsine is generated either by the addition of metallic zinc or by the addition of $NaBH_4$ and is flushed through the burner of an atomic absorption spectrophotometer for the determination of arsenic content.

2. **Range and Sensitivity**

   2.1 For a 25 mℓ urine sample, the range extends from 0.001 mg/ℓ to 0.040 mg/ℓ.

   2.2 For a 30 liter air sample, the range extends from 0.001 mg/m^3 to 0.060 mg/m^3.

   2.3 The range can be extended by taking smaller (or larger) aliquots for analysis.

3. **Interferences**

   There are no known interferences for this method, providing that appropriate background correcting techniques are applied.

4. Precision and Accuracy

The accuracy and precision of this method have not been completely determined at this time.

5. Advantages and Disadvantages of the Method

5.1 This method has the advantage of being free of Sb interference. It is somewhat faster, and several times as sensitive as the colorimetric measurement of arsenic.

5.2 The disadvantages include the requirement of specialized equipment and the use of rather large volumes of expensive gases. The sampling method will not collect arsine gas.

6. Apparatus

6.1 **Sampling Equipment.** The sampling unit for the collection of personal air samples has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate cassette filter holder, either a 2- or 3-piece filter cassette (Millipore Filter Corporation, Bedford, Massachusetts).

6.1.2 A vacuum pump such as a personal sampling pump. This pump must be properly calibrated so the volume of air sampled can be measured as accurately as possible. The pump must be calibrated with a representative filter unit in the line. Flow rate, times, and/or volume must be known.

6.1.3 Thermometer.

6.1.4 Manometer.

6.1.5 Stopwatch.

6.1.6 Various clips, tubing, spring connectors, and belt for connecting sampling apparatus to worker being sampled.

6.2 Type HA millipore filter (or equivalent), 37 mm.

6.3 125 mℓ borosilicate Phillips beakers.

6.4 Atomic absorption spectrophotometer equipped with arsine generator and argon-hydrogen system. (Figure 1)

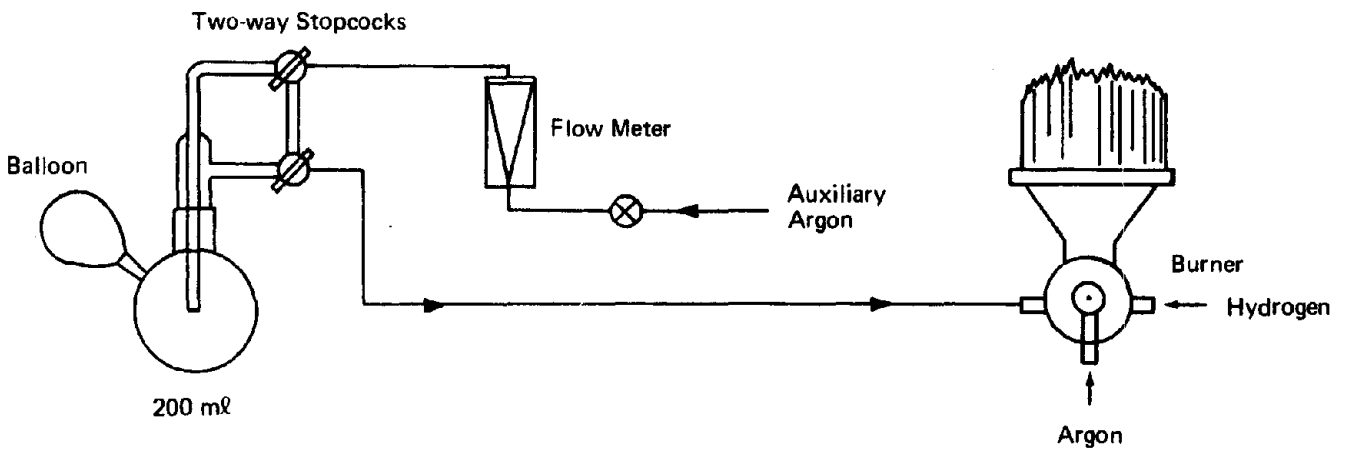


FIGURE 1 APPARATUS FOR ARSINE GENERATION

Instrument conditions to use for arsine measurement by atomic absorption.

wavelength – 1937 Å
slit – 7 Å
burner – three slot
Argon Flow – 8 scfh
H_2 Flow – 3 scfh
Recorder – fast response
Aspirate water continuously during analysis.

6.5 Hood facilities capable of handling perchloric acid fumes.

6.6 Specific gravity meter or hydrometer capable of measuring specific gravities in the range of 1.000 to 1.040 ± 0.001.

6.7 25 mℓ pyrex volumetric flasks.

7. **Reagents and Gases**

All chemicals must be ACS reagent grade or better.

7.1 Nitric acid, distilled reagent grade.

7.2 Perchloric acid, 72%.

7.3 Sulfuric acid, 90%.

7.4 **Ammonium Oxalate.** Prepare a saturated solution in double distilled water.

7.5 Hydrochloric acid, 36%.

7.6 **Potassium Iodide Solution.** Dissolve 20 g of potassium iodide in 100 mℓ double distilled water.

7.7 **Stannous Chloride Solution.** Dissolve 20 g of stannous chloride dihydrate in 100 mℓ of concentrated HCl.

7.8 Zinc, 20 mesh granular, low arsenic.

7.9 Sodium borohydride, 11/32 in. pellets.

7.10 **Arsenic Standards**

7.10.1 **Arsenic Standard Stock Solution, 1000 ppm.** Dissolve 0.4165 g of $Na_2HASO_4 \cdot 7H_2O$ in a mixture of double distilled water, 5 mℓ of concentrated H_2SO_4 and 20 mℓ of concentrated HCl and bring volume to 100 mℓ with double-distilled water.

7.10.2 **Working Standards.** Dilute stock solution with appropriate amounts of solution prepared by adding 100 mℓ concentrated HCl and 25 mℓ concentrated H_2SO_4 to 300 mℓ double distilled water and diluting to volume of 500 mℓ with double distilled water.

7.11 All water used is double distilled in pyrex.

7.12 **Gases**

7.12.1 Hydrogen – electrolytic grade.

7.12.2 Argon – high purity

8. **Procedure**

8.1 **Cleaning of Equipment.** All glassware must be cleaned with a detergent solution followed by both tap water and distilled water rinses. Then the glassware is cleaned with hot concentrated nitric acid and thoroughly rinsed with tap water followed by distilled water. (Arsine generators are rinsed with concentrated HCl following the nitric acid wash.)

8.2 **Collection and Shipping of Samples**

8.2.1 **Urine Samples** are collected in polyethylene bottles which are precleaned in nitric acid. About 0.1 g EDTA is added as a preservative. At least 75 mℓ should be collected. Care should be taken to prevent leaking of bottles in transit.

8.2.2 **Air Samples** are collected on 37 mm HA Millipore filter (or equivalent) as follows:

1. Assemble the filter unit by mounting the filter disc in the filter cassette.

2. Connect the exit end of the filter unit to the pump with a short piece of flexible tubing.

3. Turn on pump to begin sample collection. The flow rate, times, and/or volume must be measured as accurately as possible. Record atmospheric pressure and temperature. The sample should be taken at a flow rate of 1.7 liters per minute. A minimum sample of 30 liters should be collected. Larger sample volumes are encouraged, provided the filters do not become loaded with dust to the point that loose material might fall off or the filter become plugged.

4. The sample cassettes should be shipped in a suitable container designed by NIOSH to minimize contamination and to prevent damage in transit. Care must be taken during storage and shipping that no part of the sample is dislodged from the filter, nor that the sample surface be disturbed in any way. Loss of sample from heavy deposits on the filter may be prevented by mounting a clean filter in the cassette on top of the sample filter.

5. With each batch of samples, one filter, labeled as a blank, must be submitted. No air should be drawn through this filter.

8.3 **Analysis of Samples**

8.3.1 Determine the specific gravity of the urine sample at room temperature. This may be done with the use of a specific gravity meter or a reliable hydrometer.

8.3.2 Transfer 25 mℓ of the urine sample or the filter paper sample into a 125 mℓ Phillips beaker.

8.3.3 Wet-ash the sample by treating with 5 mℓ of a mixture of 3 parts HNO_3, 1 part H_2SO_4, and 1 part $HClO_4$ and heating on a hot plate at 130°-150°C. Keep on adding small amounts of redistilled HNO_3 until a colorless (liquid) ash is obtained. If the ashing is still incomplete, additional $HClO_4$ can be added dropwise.

8.3.4 Continue heating to fumes of SO_3. After cooling the colorless or nearly colorless liquid, add 10 mℓ of distilled water and 5 mℓ of a saturated solution of ammonium oxalate. The mixture is again taken to fumes of SO_3 to free the ashed solution of all traces of nitric acid.

8.3.5 Allow the mixture to cool, transfer to a 25 mℓ volumetric flask, and make up to volume with distilled water.

8.3.6 Pipet a 5 mℓ aliquot of the 25 mℓ sample into an arsine generation flask with balloon attached.

8.3.7 Be sure the stopcocks of the arsine generation equipment are turned such that the argon flow bypasses the arsine generation system. At this point, the arsine can be generated by either of the two methods described.

1. **Reduction with Zinc.** Add *in order* 15 mℓ of distilled water, 10 mℓ concentrated HCl, 2 mℓ of KI solution, and 2 mℓ $SnCl_2$ solution. (Swirl solution after the addition of each reagent for a homogeneous mixing.) Mix well and allow to stand for 15 minutes to insure the conversion of arsenic to the trivalent form. Add 1.5 g of zinc to the sample solution and connect the flask *immediately* to the generating system (seal ground glass joints with silicone grease).

2. **Reduction with Sodium Borohydride.** Add 35 mℓ of distilled water, 3 mℓ concentrated HCl and mix well. Connect the sample flask to the generating system. Add to the sample solution, via the addition stopcock, a single sodium borohydride pellet (11/32 in. diameter, 200 mg).

8.3.8 The reaction is vigorous and the balloon fills with the evolved gases thus acting as a reservoir for the generating system.

8.3.9 After one minute, turn the lower stopcock allowing the pressure in the balloon to flush the gases into the flame of the atomic absorption instrument. Before the balloon is deflated, turn the upper stopcock allowing the argon to flush through the generator flask and into the flame. The absorption signal is recorded on a rapid response strip chart recorder. Larger (or smaller) aliquots of the sample solution may be taken if the signal is not in the proper range.

9. Calibration and Standards

9.1 Prepare working standards of 1.0, 3.0, 5.0, 7.5, and 10.0 μg of arsenic in 25 milliliters of solution by dilution of the standard stock solution. These standards should be prepared fresh each time.

9.2 Construct a calibration curve by pipetting 5 mℓ of each of the working standards into arsine generators and proceeding with the analysis from Section 8.3.7. A calibration curve of absorption versus micrograms of arsenic is then drawn and used for the determination of arsenic content of the samples.

10. Calculations

10.1 The concentration of arsenic in the urine sample can be expressed as mg As per liter of urine.

$$\text{mg As}/\ell = \frac{\mu\text{g As}}{\text{m}\ell \text{ of urine}} \text{ (from calibration curve, Section 9.2)}$$

10.1.1 The use of a specific gravity correction factor to normalize values to 1.024, the average specific gravity of urine, has been proposed. There are two ways of using this correction.

10.1.2 One way is to use a straightforward gravity correction, in which case the magnitude of the factor is small.

$$\text{corrected mg As}/\ell = \text{mg As}/\ell \times \frac{1.024}{\text{specific gravity}}$$

10.1.3 The other method corrects for differences in total solids or salt content of various urine specimens, whereby the specific gravity of water is initially subtracted from the urine specific gravities. Because of the wide range of reported urine specific gravities, 1.002 to 1.040, the use of such a correction factor can lead to unusually or erroneously high results.

$$\text{corrected mg As/}\ell = \text{mg As/}\ell \times \frac{(1.024 - 1.000)}{(\text{specific gravity} - 1.000)}$$

10.2 The concentration of arsenic in air can be expressed as mg As per cubic meter of air, which is numerically equal to micrograms As per liter of air.

$$\text{mg As/m}^3 = \mu\text{g As/V}_s$$

where:

μg As = micrograms As from calibration curve (Section 9.2)

V_s = volume of air sampled in ℓ at 25°C and 760 mm Hg.

11. References

11.1 Atomic Absorption Analytical Method No. As-3, Jarrell-Ash Co.

11.2 Atomic Absorption Application Study No. 468, The Perkin-Elmer Corp., June 1971.

11.3 Fernandez, Frank, J., "Atomic Absorption Determination of Gaseous Hydrides Utilizing Sodium Borohydride Reduction," Atomic Absorption Newsletter, 12, 93-97 (1973).

ARSENIC IN URINE AND AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Arsenic	**Method No.:**	P&CAM 140
Matrix:	Urine and Air	**Range:**	1.0 to 25 μg/sample
Procedure:	Arsine Generation – Colorimetric	**Precision:**	4-9% Average deviation
Date Issued:	3/24/72		
Date Revised:	1/10/74	**Classification:**	A (Recommended)

1. **Principle of the Method**

   1.1 Samples are ashed with a mixture of nitric, perchloric, and sulfuric acids to destroy the organic matrix.

   1.2 The sample ash is treated with ammonium oxalate and taken to fumes of SO_3 to remove all traces of nitric acid.

   1.3 The sample is transferred to an arsine generator where the arsenic is converted to the trivalent form by the addition of KI, HCl, and $SnCl_2$.

   1.4 Arsine is generated by the addition of metallic zinc and is absorbed by a solution of pyridine – silver diethyldithiocarbamate. The absorbance of this solution is measured spectrophotometrically at 560 mμ.

2. **Range and Sensitivity**

   2.1 For a 25 mℓ urine sample, the range extends from 0.01 mg/ℓ to 1.0 mg/ℓ.

   2.2 For a 30 liter air sample, the range extends from 0.01 mg/m^3 to 0.8 mg/m^3.

   2.3 The range can be extended by taking smaller (or larger) aliquots for analysis.

3. **Interferences**

   Antimony will interfere when present in relatively high concentrations, but such concentrations are not likely to be found.

4. **Precision and Accuracy**

This method deviates only slightly from the A.C.G.I.H. recommended method for the determination of arsenic in air. For that method eight cooperating laboratories analyzed four arsenic samples (0.5-1.5 $\mu g/m\ell$) with a percent average deviation from the known of 4.0 to 9.1.

5. **Advantages and Disadvantages of the Method**

5.1 This method has the advantage of being a well established, reliable method for the analysis of arsenic. In addition, very little specialized equipment is required.

5.2 The disadvantages are that the method is tedious and that the use of pyridine as a solvent renders it somewhat objectionable. The sampling method will not collect arsine gas.

6. **Apparatus**

6.1 **Sampling Equipment**. The sampling unit for the collection of personal air samples has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate cassette filter holder, either a 2- or 3-piece filter cassette. (Millipore Filter Corporation, Bedford, Massachusetts.)

6.1.2 Battery operated diaphragm pump with belt clip – this should operate for 4-5 hours continuously at 1.7 ℓpm and 20 cm water resistance. (Monitaire Sample – Mine Safety Appliances Co., Pittsburgh, Pennsylvania.)

6.1.3 Thermometer.

6.1.4 Manometer.

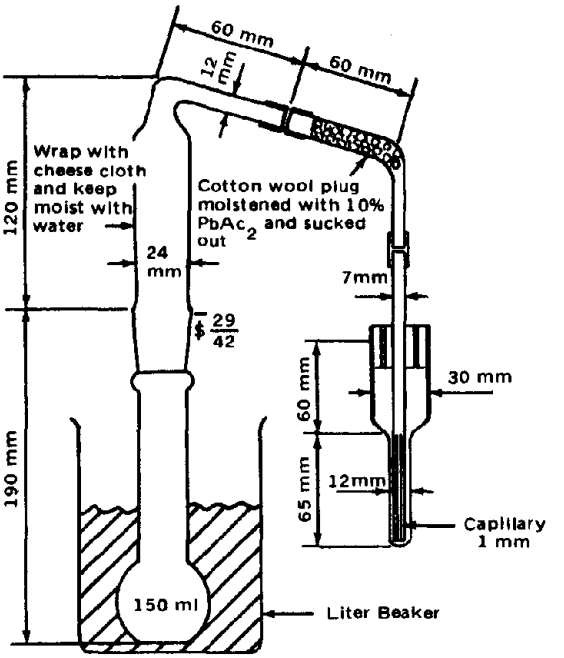
6.1.5 Stopwatch.

6.1.6 Various clips, tubing, spring connectors, and belt for connecting sampling apparatus to worker being sampled.

6.2 Type HA millipore filter (or equivalent), 37 mm.

6.3 125 mℓ borosilicate Phillips beakers.

6.4 Arsine generation equipment (Reference 11.3, and attached illustration).



APPARATUS FOR ARSINE GENERATION

6.5 Hood facilities capable of handling perchloric acid fumes.

6.6 Spectrophotometer capable of measurements at 560 mμ.

6.7 1 cm spectrophotometer cells.

6.8 Specific gravity meter or hydrometer capable of measuring in the range 1.000 to 1.040 ± 0.001 units.

6.9 150 mℓ polyethylene bottles for collection of urine samples.

7. Reagents

All reagents must be ACS reagent grade or better.

7.1 Silver Diethyldithiocarbamate.

7.2 Pyridine.

7.3 **Arsine Absorbing Solution.** Dissolve 1.0 g of silver diethyldithiocarbamate in 200 mℓ of pyridine, shake well and filter.

7.4 Hydrochloric acid, 36%.

7.5 Nitric Acid, 68%, distilled reagent grade.

7.6 Perchloric Acid, 72%.

7.7 Sulfuric Acid, 98%.

7.8 **Ammonium Oxalate.** Prepare a saturated solution in double distilled water.

7.9 **Potassium Iodide Solution.** Dissolve 15 g of potassium iodide in 100 mℓ double distilled water.

7.10 **Stannous Chloride Solution.** Dissolve 40 g of stannous chloride dihydrate in 100 mℓ hydrochloric acid.

7.11 **Zinc**, 20 mesh granular, low arsenic.

7.12 **Lead Acetate.** Dissolve 10 g of lead acetate in 100 mℓ double distilled water. The glass wool in the scrubber is soaked in this solution, drained and dried.

7.13 **Arsenic Standard Stock Solution.** Dissolve 1.320 g of arsenic trioxide in 10 mℓ of 40% sodium hydroxide and dilute to 1 liter with distilled water. Working standards are made by diluting this solution.

7.14 The water used is double distilled in pyrex.

8. **Procedure**

8.1 **Cleaning of Equipment.** All glassware must be cleaned with a detergent solution followed by both tap water and distilled water rinses. Then the glassware is treated with hot concentrated nitric acid and thoroughly rinsed with tap water followed by distilled water. (Arsine generators are rinsed with concentrated HCl following the nitric acid wash.)

8.2 **Collection and Shipping of Samples**

8.2.1 **Urine Samples** are collected in polyethylene bottles which are precleaned in nitric acid. About 0.1 g EDTA is added as a preservative. At least 75 mℓ should be collected. Care should be taken to prevent leaking of bottles in transit.

8.2.2 **Air Samples** are collected on 37 mm HA millipore filter (or equivalent) as follows:

1. Assemble the filter unit by mounting the filter disc in the filter cassette.

2. Connect the exit end of the filter unit to the pump with a short piece of flexible tubing.

3. Turn on pump to begin sample collection. The flow rate, times, and/or volume must be measured as accurately as possible. Record atmospheric pressure and temperature. The sample should be taken at a flow rate of 1.7 liters per minute. A minimum sample of 30 liters should be collected. Larger sample volumes are encouraged, provided the filters do not become loaded with dust to the point that loose material might fall off or the filter become plugged.

4. The sample cassettes should be shipped in a suitable container designed by NIOSH to minimize contamination and to prevent damage in transit. Care must be taken during storage and shipping that no part of the sample is dislodged from the filter, nor that the sample surface may be disturbed in any way. Loss of sample from heavy deposits on the filter may be prevented by mounting a clean filter in the cassette on top of the sample filter.

5. With each batch of samples, one filter, labeled as a blank, must be submitted. No air should be drawn through this filter.

8.3 **Analysis of Samples**

8.3.1 Determine the specific gravity of the urine sample at room temperature. This may be done with the use of a specific gravity meter or a reliable hydrometer.

8.3.2 Transfer 25 mℓ of the urine sample or the filter paper sample into a 125 mℓ Phillips beaker.

8.3.3 Ash the sample by treating with 5 mℓ of a mixture of 3 parts HNO_3, 1 part H_2SO_4, and 1 part $HClO_4$ and heating on a hot plate at 130°-150°C. Keep on adding small amounts of redistilled HNO_3 until a colorless (liquid) ash is obtained. If the ashing is still incomplete, additional $HClO_4$ can be added dropwise.

8.3.4 Continue heating to fumes of SO_3. After cooling the colorless or nearly colorless liquid, add 10 mℓ of distilled water and 5 mℓ of a saturated

solution of ammonium oxalate. The mixture is again taken to fumes of SO_3 to free the ashed solution of all traces of nitric acid.

8.3.5 Allow the mixture to cool and then transfer to the flask of an arsine generator with 20 mℓ of distilled water. Rinse the Phillips beaker with 5 mℓ of concentrated HCl and add these washings to the arsine generator. (If high As concentrations are expected, the solution may be made to a known volume, and only an aliquot is added to the arsine generator.)

8.3.6 Add to the arsine receiver 3 mℓ of the pyridine – silver diethyldithiocarbamate absorbing solution.

8.3.7 To the sample solution in the arsine generator flask, add *in order* 2 mℓ of 15% KI solution and 0.5 mℓ of 40% $SnCl_2$. Swirl the flask and allow to stand 15 minutes to insure conversion of all the pentavalent arsenic to the trivalent form.

8.3.8 Add to the sample flask 7.0 g of zinc (granular 20 mesh), and close the flask *immediately* (sealing ground glass joints by wetting with distilled water).

8.3.9 Heat the flask in a beaker of hot water and allow thirty minutes for the evolution of arsine.

8.3.10 Transfer the arsine absorbing solution to a 1 cm cell and read the absorbance of this solution on a spectrophotometer at 560 mμ.

9. Calibration and Standards

9.1 Prepare working standards of 1.0, 5.0, 10.0, 15.0, and 20.0 μg of arsenic per milliliter of solution by dilution of the standard stock solution. These standards should be prepared fresh weekly.

9.2 Construct a calibration curve by pipetting 1 mℓ of each of the working standards into arsine generators, adding 20 mℓ double distilled water, 5 mℓ concentrated hydrochloric acid, and proceeding from Step 8.3.6 of the procedure. A calibration curve of absorbance versus micrograms of arsenic is then drawn and used for determination of arsenic content of the samples.

10. Calculations

10.1 The concentration of arsenic in the urine sample can be expressed as mg As per liter of urine:

$$\text{mg As}/\ell = \frac{\mu\text{g As}}{\text{m}\ell \text{ of urine}} \text{ (from calibration curve, Section 9.2)}$$

10.1.1 The use of a specific gravity correction factor to normalize values to 1.024, the average specific gravity of urine, has been proposed. There are two ways of using this correction.

10.1.2 One way is to use a straightforward gravity correction, in which case the magnitude of the factor is small.

$$\text{corrected mg As/}\ell = \text{mg As/}\ell \times \frac{1.024}{\text{specific gravity}}$$

10.1.3 The other method corrects for differences in total solids or salt content of various urine specimens, whereby the specific gravity of water is initially subtracted from the urine specific gravities. Because of the wide range of reported urine specific gravities, 1.002 to 1.040, the use of such a correction factor can lead to unusually or erroneously high results.

$$\text{corrected mg As/}\ell = \text{mg As/}\ell \times \frac{(1.024 - 1.000)}{(\text{specific gravity} - 1.000)}$$

10.2 The concentration of arsenic in air can be expressed as mg As per cubic meter of air, which is numerically equal to micrograms As per liter of air.

$$\text{mg As/m}^3 = \mu\text{g As/V}_s$$

where:

μg As = micrograms As from calibration curve (Section 9.2)

V_s = volume of air sampled in ℓ at 25°C and 760 mm Hg.

11. References

11.1 "Determination of Arsenic in Air," *Manual of Analytical Methods,* A.C.G.I.H. (1958).

11.2 Thomas and Collier, "The Concentration of Arsenic in Tobacco Smoke Determined by a Rapid Titrimetric Method," Journal of Industrial Hygiene and Toxicology, 27, 201 (1945).

11.3 *Methods of Analysis,* Association of official Agricultural Chemists, p. 632, 10th Edition, 1965.

11.4 Fernandez, Frank, J., "Atomic Absorption Determination of Gaseous Hydrides Utilizing Sodium Borohydride Reduction," Atomic Absorption Newsletter, 12, pp. 93-97 (1973).

2,4 TOLUENEDIISOCYANATE (TDI) IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	TDI	**Method No.:**	P&CAM 141
Matrix:	Air	**Range:**	0.007 ppm – 0.140 ppm
Procedure:	Colorimetric		
Date Issued:	11/17/72	**Precision:**	Unknown
Date Revised:	1/10/74	**Classification:**	D (Operational)

1. **Principle of the Method**

   1.1 TDI is hydrolyzed by the absorbing solution to the corresponding toluenediamine derivative.

   1.2 The diamine is diazotized by the sodium nitrite – sodium bromide solution.

   1.3 The diazo compound is coupled with N-(1-Naphthyl)-ethylenediamine to form a colored complex.

   1.4 The amount of colored complex formed is in direct proportion to the amount of TDI present. The amount of colored complex is determined by reading the absorbance of the solution at 550 nm.

   1.5 Toluenediamine is formed via hydrolysis of TDI on a mole to mole basis. This amine is used in place of the TDI for standards. This accomplishes two things. First, the amine is not as toxic as the TDI. Second, TDI liquifies to a semi-solid at room temperature. Weighing the semi-solid is more difficult than weighing the dry amine. Both compounds have been tested by this method and the results compare favorably.

   1.6 TDI kits based on the Marcali method are commercially available but have not been thoroughly tested to date.

2. **Range and Sensitivity**

   2.1 The range of the standards used is equivalent to 1.0 – 20.0 μg TDI. In a 20 liter air sample, this range converts to 0.007 ppm – 0.140 ppm.

2.2 For samples of high concentration whereby absorbance is greater than the limits of the standard curve (1.0 – 20.0 μg TDI) sample dilution with absorbing solution and rereading the absorbance extends the upper limit of the range.

2.3 It is not known how much TDI would saturate 15 mℓ of the absorbing solution. It may be possible that, in extremely high concentrations, some of the TDI would not be absorbed by the absorbing solution. Therefore, if a sample is diluted and reread, it could give an erroneously low value.

2.4 A single bubbler absorbs 95% of the diisocyanate if the air concentration is below 2 ppm. Above 2 ppm, about 90% of the diisocyanate is recovered. At high levels, it is suggested that two impingers in series be used.

3. Interferences

3.1 Any free aromatic amine may give a coupling color and thus may be a positive interference.

3.2 Methylene-di-(4-phenylisocyanate) (MDI) will form a colored complex in this reaction. However, its color development time is about 1 – 2 hours compared with 5 minutes for TDI. Therefore, MDI is not a serious problem.

4. Precision and Accuracy

4.1 This method is a modification of the Marcali method. Its precision and accuracy are unknown.

4.2 There has been no collaborative testing.

5. Advantages and Disadvantages of the Method

5.1 This method is based on the well tested Marcali method.

5.2 Any free organic amine will interfere. The method cannot be considered specific for TDI.

6. Apparatus

6.1 **Sampling Equipment.** The sampling unit for personal samples by the impinger collection method consists of the following components:

6.1.1 An all glass, calibrated midget impinger containing the absorbing solution or reagent.

6.1.2 Battery operated personal sampling pump – MSA Model G or equivalent. The sampling pump is protected from splashover or water condensation by an adsorption tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump.

6.1.3 An integrating volume meter such as a dry gas or wet test meter.

6.1.4 Thermometer.

6.1.5 Manometer.

6.1.6 Stopwatch.

6.1.7 Various clips, tubing, spring connectors, and belt for connecting sampling apparatus to worker being sampled.

6.2 Beckman Model B spectrophotometer or equivalent.

6.3 Cells, 1-cm and 5-cm matched quartz cells.

6.4 Volumetric flasks (several of each), glass stoppered: 50, 100, 1000 mℓ.

6.5 Balance capable of weighing to at least three decimal places, preferably 4 decimal places.

6.6 Pipets: 0.5, 1, 15 mℓ.

6.7 Graduated cylinders: 25, 50 mℓ.

7. Reagents

All reagents must be made using ACS reagent grade or a better grade.

7.1 Double distilled water.

7.2 2,4-toluenediamine.

7.3 Hydrochloric acid, concentrated, 11.7 N.

7.4 Glacial acetic acid, concentrated, 17.6 N.

7.5 Sodium nitrite.

7.6 Sodium bromide.

7.7 **Sodium nitrite solution:** Dissolve 3.0 g sodium nitrite and 5.0 g sodium bromide in about 80 mℓ double distilled water. Adjust volume to 100 mℓ with double distilled water. This solution is stable for one week if refrigerated.

7.8 Sulfamic acid.

7.9 **Sulfamic acid solution,** 10% w./v.: Dissolve 10 g sulfamic acid in 100 mℓ double distilled water.

7.10 N-(1-Naphthyl)-ethylenediamine dihydrochloride.

7.11 **N-(1-Naphthyl)-ethylenediamine solution:** Dissolve 50 mg in about 25 mℓ double distilled water. Add 1 mℓ concentrated hydrochloric acid and dilute to 50 mℓ with double distilled water. Solution should be clear and colorless; coloring is due to contamination by free amines, and solution should not be used. The solution is stable for four days.

7.12 **Absorbing solution:** Add 35 mℓ concentrated hydrochloric acid and 22 mℓ glacial acetic acid to approximately 600 mℓ double distilled water. Dilute the solution to 1-liter with double distilled water. 15 mℓ is used in each impinger.

7.13 **Standard solution A:** Weigh out 140 mg of 2,4 – toluenediamine (equivalent to 200 mg of 2,4 – toluenediisocyanate). Dissolve in 660 mℓ of glacial acetic acid, transfer to a 1-liter glass stoppered volumetric flask, and make up to volume with distilled water.

7.14 **Standard solution B:** Transfer 10 mℓ of standard solution A to a glass-stoppered 1-liter volumetric flask. Add 27.8 mℓ of glacial acetic acid so that when solution B is diluted to 1-liter with distilled water, it will be 0.6N with respect to acetic acid. This solution contains an equivalent of 2 μg TDI/mℓ.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Wash all glassware in a hot detergent solution, such as Alconox to remove any oil.

8.1.2 Rinse well with hot tap water.

8.1.3 Rinse well with double distilled water. Repeat this rinse several times.

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8.2 Collection and Shipping of Samples

8.2.1 Pipet 15 mℓ of the absorbing solution (Section 7) into the midget impinger.

8.2.2 Connect the impinger (via the absorption tube) to the vacuum pump and the prefilter assembly (if needed) with a short piece of flexible tubing. The minimum amount of tubing necessary should be used between the breathing zone and impinger. The air being sampled should not be passed through any other tubing or other equipment before entering the impinger.

8.2.3 Turn on pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible. Record atmospheric pressure and temperature. The sample should be taken at a flow rate of 1 ℓpm. Sample for 20 minutes, making the final air volume 20 liters.

8.2.4 After sampling, the impinger stem can be removed and cleaned. Tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Wash the stem with a small amount (1-2 mℓ) of unused absorbing solution and add the wash to the impinger. Then the impinger is sealed with a hard, non-reactive stopper (preferably Teflon or glass). Do not seal with rubber. The stoppers on the impingers should be tightly sealed to prevent leakage during shipping. If it is preferred to ship the impingers with the stems in, the outlets of the stem should be sealed with Parafilm or other non-rubber covers, and the ground glass joints should be sealed (i.e., taped) to secure the top tightly.

8.2.5 Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within a day.

8.2.6 Whenever possible, hand delivery of the samples is recommended. Otherwise, special impinger shipping cases designed by NIOSH should be used to ship the samples.

8.2.7 A "blank" impinger should be handled as the other samples (fill, seal and transport) except that no air is sampled through this impinger.

8.3 Analysis of Samples

8.3.1 Remove bubbler tube, if it is still attached, taking care not to remove any absorber solution.

8.3.2 Start reagent blank at this point by adding 15 mℓ fresh absorbing solution to a clean bubbler cylinder.

8.3.3 To each bubbler, add 0.5 mℓ of 3% sodium nitrite solution, gently agitate, and allow solution to stand for 2 minutes.

8.3.4 Add 1 mℓ of 10% sulfamic acid solution, agitate for 30 seconds and allow solution to stand 2 minutes to destroy all the excess nitrous acid present.

8.3.5 Add 1 mℓ of 0.1% N-(1-Naphthyl)-ethylenediamine solution. Agitate and allow color to develop. Color will be developed in 5 minutes. A reddish blue color indicates the presence of TDI.

8.3.6 Add double distilled water to adjust the final volume to 20 mℓ in the bubbler cylinder. Mix.

8.3.7 Transfer each solution to a 1-cm or 5-cm quartz cell.

8.3.8 Using the blank, adjust the spectrophotometer to 0 absorbance at 550 nm.

8.3.9 Determine the absorbance of each sample at 550 nm.

9. **Calibration and Standards**

9.1 To each of a series of eight graduated cylinders add 5 mℓ of 1.2N hydrochloric acid.

9.2 To these cylinders add the following amounts of 0.6N acetic acid: 10.0, 9.5, 9.0, 8.0, 7.0, 6.0, 5.0 and 0.0 mℓ, respectively.

9.3 To the cylinder add standard solution B in the same order as the acetic acid was added: 0.0, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0 and 10 mℓ, so that the final volume is 15 mℓ (i.e., 0.0 mℓ of the standard is added to the 10 mℓ acetic acid; 0.5 mℓ of the standard is added to the 9.5 mℓ acid; et cetera). The cylinders now contain the equivalent of 0.0, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0 and 20.0 μg TDI, respectively. The standard containing 0.0 mℓ standard solution is a blank.

9.4 Add 0.5 mℓ of the 3.0% sodium nitrite reagent to each cylinder. Mix. Allow to stand 2 minutes.

9.5 Add 1 mℓ of the 10% sulfamic acid solution. Mix. Allow to stand for 2 minutes.

9.6 Add 1 mℓ of the N-(1-Naphthyl)-ethylenediamine solution. Mix. Let stand for 5 minutes.

9.7 Make up to 20 mℓ with double distilled water.

9.8 Transfer each solution to a 1-cm or 5-cm quartz cell.

9.9 Using the blank, adjust the spectrophotometer to 0 absorbance at 550 nm.

9.10 Determine the absorbance of each standard at 550 nm.

9.11 A standard curve is constructed by plotting the absorbance against micrograms TDI.

10. **Calculations**

10.1 Subtract the blank absorbance, (Section 8.2.7), if any, from the sample absorbance.

10.2 From the calibration curve (Section 9.11), read the micrograms TDI corresponding to the absorbance of the sample.

10.3 Calculate the concentration of TDI in air in ppm, defined as $\mu\ell$ TDI per liter of air.

$$ppm = \frac{\mu g}{V_s} \times \frac{24.45}{MW}$$

where:

ppm = parts per million TDI
μg = micrograms TDI (Section 10.2).
V_s = corrected volume of air in ℓ (Section 10.4).
24.45 = molar volume of an ideal gas at 25°C and 760 mm Hg
MW = molecular weight of TDI, 174.15.

10.4 Convert the volume of air sampled to standard conditions of 25°C and 760 mm Hg:

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

V_s = volume of air in liters at 25°C and 760 mm Hg
V = volume of air in liters as measured
P = Barometric Pressure in mm Hg
T = Temperature of air in degree centigrade.

11. References

11.1 Marcali, K., "Microdetermination of Toluenediisocyanates in Atmosphere," Analytical Chemistry, 4, 552 (1957).

11.2 Larkin, R.L. and R.E. Kupel, "Microdetermination of Toluenediisocyanate Using Toluenediamine as the Primary Standard," American Industrial Hygiene Association Journal, 30, 640 (1969).

p,p- DIPHENYLMETHANE DIISOCYANATE (MDI) IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	MDI	**Method No.:**	P&CAM 142
Matrix:	Air	**Range:**	0.007-0.073 ppm
Procedure:	Colorimetric	**Precision:**	Unknown
Date Issued:	9/13/72		
Date Revised:	1/10/74	**Classification:**	D (Operational)

1. Principle of the Method

1.1 MDI is hydrolyzed by the absorbing solution to methylene dianiline.

1.2 The methylene dianiline is diazotized by sodium nitrite – sodium bromide.

1.3 The diazo compound is coupled with N-(1-Naphthyl)-ethylenediamine to form the colored complex.

1.4 The amount of colored complex formed is in direct proportion to the amount of MDI present. The amount of colored complex is determined by reading the absorbance of the solution at 555 nm.

2. Range and Sensitivity

2.1 The range of the standards used is 1.5-15 μg MDI. In a 20 liter air sample, this range converts to 0.007 ppm-0.073 ppm.

2.2 For samples of high concentration whereby absorbance is greater than the limits of the standard curve, sample dilution with absorber solution and rereading absorbance can extend the upper limit of the range.

2.3 It is not known how much MDI would saturate 15 mℓ of the absorber solution. Therefore, if a sample is diluted and reread, it could give an erroneously low value. It may be possible that, in extremely high concentrations, some of the MDI would not be absorbed by the absorber solution. In such cases two impingers should be used in series, and the appropriate corrections are made for efficiency.

3. **Interferences**

3.1 Any free aromatic amine may be diazotized and coupled forming a positive interference.

3.2 Toluenediisocyanate (TDI) also interferes.

4. **Precision and Accuracy**

4.1 The precision and accuracy are unknown.

4.2 There has been no collaborative testing.

5. **Advantages and Disadvantages of the Method**

5.1 This method is a modification of the Marcali method. This method has altered the concentration of acidity during the coupling reaction, reducing the final reaction time to fifteen minutes compared to two hours for the Marcali method.

5.2 Since any free aromatic amine may interfere and TDI definitely interferes the method is not specific for MDI.

6. **Apparatus**

6.1 **Sampling Equipment.** The sampling unit for personal samples by the impinger collection method consists of the following components:

6.1.1 A midget impinger containing the absorbing solution or reagent.

6.1.2 Battery operated personal sampling pump – MSA Model G or equivalent. The sampling pump is protected from splashover or water condensation by an adsorption tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump.

6.1.3 An integrating volume meter such as a dry gas or wet test meter.

6.1.4 Thermometer.

6.1.5 Manometer.

6.1.6 Stopwatch.

6.1.7 Various clips, tubing, spring connectors, and belt for connecting sampling apparatus to worker being sampled.

6.2 Beckman Model B spectrophotometer or equivalent.

6.3 Cells, 5-cm matched quartz cells.

6.4 Volumetric flasks (several of each): 100 mℓ and 1-liter.

6.5 Balance capable of weighing to at least three places, preferably four places.

6.6 Pipets, delivery: 0.5, 1, 2, 5, 10, 15 mℓ.
graduated: 2 mℓ

6.7 Graduated cylinders: 50, 100 mℓ.

7. **Reagents**

All reagents must be made using ACS reagent grade or a better grade.

7.1 Double distilled water.

7.2 Sodium nitrite.

7.3 Sodium bromide.

7.4 Sulfamic acid.

7.5 Concentrated hydrochloric acid, 11.7N.

7.6 Glacial acetic acid, 17.6N.

7.7 N-(1-Naphthyl)-ethylenediamine dihydrochloride.

7.8 Sodium carbonate.

7.9 Methylene Dianiline.

7.10 **Sodium Nitrite – Sodium Bromide Solution:** Dissolve 3.0 g sodium nitrite and 5.0 g sodium bromide in double distilled water and dilute to 100 mℓ. The solution maybe stored in the refrigerator for one week.

7.11 **Sulfamic Acid Solution.** Dissolve 10.0 g sulfamic acid in 90 mℓ double distilled water.

7.12 **Absorbing Solution.** Add 35 mℓ concentrated hydrochloric acid and 22 mℓ glacial acetic acid to about 600 mℓ double distilled water and dilute to 1-liter with double distilled water.

7.13 **Coupling Solution.** Dissolve 1.0g N-(1-Naphthyl)-ethylenediamine dihydrochloride in 50 mℓ water, add 2 mℓ concentrated hydrochloric acid and dilute to 100 mℓ with double distilled water. This solution is stable for about ten days.

7.14 **Sodium Carbonate.** Dissolve 16.0 g sodium carbonate in double distilled water and dilute to 100 mℓ.

7.15 **Solution A.** Dissolve 0.3000 g MDI in 700 mℓ glacial acetic acid. Dilute to 1-liter with double distilled water.

7.16 **Solution B.** Immediately after making solution A, pipet 10 mℓ solution A into a 1-liter volumetric flask. Add 35 mℓ concentrated hydrochloric acid, 15 mℓ glacial acetic acid, dilute to volume with double distilled water. This solution contains 3 μg MDI/mℓ.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Wash all glassware in hot detergent solution, such as alconox, to remove any oil.

8.1.2 Rinse well with hot tap water.

8.1.3 Rinse well with double distilled water. Repeat this rinse several times.

8.2 Collection and Shipping of Samples

8.2.1 Pipet 15 mℓ of the absorbing solution (Section 7) into the midget impinger.

8.2.2 Connect the impinger (via the absorption tube) to the personal sampling pump with a short piece of flexible tubing. The minimum amount of tubing should be used between the sampling zone and impinger. The air being sampled should not be passed through any other tubing or other equipment before entering the impinger.

8.2.3 Turn on pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible. Record atmospheric pressure and temperature. The sample should be taken at a flow rate of 1 ℓpm. Sample for 20 minutes making the final volume 20 liters.

8.2.4 After sampling, the impinger stem can be removed and cleaned. Tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Wash the stem with a small amount (1-2 mℓ) of unused absorbing solution and add the wash to the impinger. Then the impinger is sealed with a hard, non-reactive stopper (preferably Teflon or glass). Do not seal with rubber. The stoppers on the impingers should be tightly sealed to prevent leakage during shipping. If it is preferred to ship the impingers with the stems in, the outlets of the stem should be sealed with Parafilm or other non-rubber covers, and the ground glass joints should be sealed (i.e., taped) to secure the top tightly.

8.2.5 Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within a day.

8.2.6 Whenever possible, hand delivery of the samples is recommended. Otherwise, special impinger shipping cases designed by NIOSH should be used to ship the samples.

8.2.7 A "blank" impinger should be handled as the other samples (fill, seal and transport) except that no air is sampled through this impinger.

8.3 **Analysis of Samples**

8.3.1 Remove the bubbler tube, if it is still attached, taking care not to remove any absorbing solution.

8.3.2 Start reagent blank at this point by adding 15 mℓ fresh absorbing solution to a clean bubbler cylinder.

8.3.3 To each cylinder, add 0.5 mℓ sodium nitrite solution, stir well, and allow to stand for 2 minutes.

8.3.4 Add 1 mℓ 10% sulfamic acid solution, stir for 30 seconds, and allow to stand for 2 minutes.

8.3.5 Add 1.5 mℓ sodium carbonate solution and stir.

8.3.6 Add 1 mℓ coupling solution and stir. Allow color to develop for 15 to 30 minutes.

8.3.7 Transfer each solution to a 5-cm quartz cell.

8.3.8 Using the blank, adjust the spectrophotometer to 0 absorbance at 555 nm.

8.3.9 Determine the absorbance of each sample at 555 nm.

9. Calibration and Standards

9.1 To a series of five impinger cylinders, add the following amounts of absorbing solution: 15.0, 14.5, 14.0, 13.0, 10.0 mℓ respectively.

9.2 To the cylinder add standard solution B in the same order as the absorbing solution was added: 0.0, 0.5, 1.0, 2.0, 5.0 mℓ, so that the final volume is 15 mℓ (i.e., 0.0 mℓ of standard is added to the 15 mℓ absorbing solution; 0.5 mℓ of standard is added to the 14.5 absorber solution, etc.). The cylinders now contain 0.0, 1.5, 3.0, 6.0, 15 μg MDI, respectively. The standard containing 0.0 mℓ standard solution is a blank.

9.3 To each cylinder, add 0.5 mℓ sodium nitrite solution, stir well and allow to stand for 2 minutes.

9.4 Add 1 mℓ of 10% sulfamic acid solution, stir for 30 seconds, and allow to stand for 2 minutes.

9.5 Add 1.5 mℓ sodium carbonate solution and stir.

9.6 Add 1 mℓ coupling solution and stir. Allow color to develop for 15 to 30 minutes.

9.7 Transfer each solution to a 5-cm quartz cell.

9.8 Using the blank, adjust the spectrophotometer to 0 absorbance at 555 nm.

9.9 Determine the absorbance of each standard at 555 nm.

9.10 A standard curve is constructed by plotting the absorbance against micrograms MDI.

10. Calculations

10.1 Blank values (Section 8.2.7), if any, should first be subtracted from each sample.

10.2 From the calibration curve (Section 9.10), read the micrograms MDI corresponding to the absorbance of the sample.

10.3 Calculate the concentration of MDI in the air sampled in ppm, defined as μℓ MDI per liter of air.

$$ppm = \frac{\mu g}{V_s} \times \frac{24.45}{MW}$$

where:

ppm = parts per million MDI

μg = micrograms MDI (Section 10.2)

V_s = corrected volume of air (Section 10.4)

24.45 = molar volume of an ideal gas at 25°C and 760 mm Hg

MW = molecular weight of MDI, 250.27.

10.4 Connect the volume of air sampled to standard conditions of 25°C and 760 mm Hg:

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

V_s = volume of air in liters at 25°C and 760 mm Hg

V = volume of air in liters as measured

P = Barometric Pressure in mm Hg

T = Temperature of air in degree centigrade.

11. References

11.1 Grim, K.E., and A.L. Linch, "Recent Isocyanate-in-Air Analysis Studies," American Industrial Hygiene Association Journal, 25, 285 (1964).

SULFUR DIOXIDE IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Sulfur Dioxide	**Method No:**	P&CAM 146
Matrix:	Air	**Range**	0.01-10 ppm
Procedure:	Collection via Impinger Peroxide Absorption/Titration	**Precision:**	± 10% below the 0.1 ppm level
Date Issued:	9/14/72		
Date Revised:	1/15/74	**Classification:**	C (Tentative)

1. **Principle of the Method**

   1.1 Sulfur dioxide in air is absorbed via midget impingers, in 0.3N hydrogen peroxide (H_2O_2) reagent, adjusted to about pH 5.

   1.2 The stable and nonvolatile sulfuric acid formed in this process is then titrated with standardized sodium hydroxide.

2. **Range and Sensitivity**

   The method is applicable to the determination of SO_2 in air in the concentration range from about 0.01 to 10.0 ppm. For SO_2 concentrations greater than 0.8 ppm a second impinger connected in series can be used to maintain a 98% recovery efficiency.

3. **Interferences**

   3.1 Strong acidic gases trapped in the sample solution give erroneously high results, whereas the presence of alkaline gases or reactive solids such as NH_3 and CaO gives erroneously low results.

   3.2 Sulfuric acid does not interfere since it is not appreciably separated from the air stream owing to its small particle size. One possible exception when the relative humidity is greater than 85%, which could result in particle sizes greater than 1 micron (Reference 11.3).

   3.3 Sulfur trioxide gas, if present, would be a positive interference.

3.4 Sulfates do not interfere. Carbon dioxide does not interfere since it is not absorbed in the acid-absorbing reagent.

3.5 If large amounts of solid materials are present, a filter may be employed upstream advantageously. However, SO_2 may be lost, the extent of loss depending upon the composition of the particulate matter and the nature and retentive capacity of the filter used.

4. **Precision and Accuracy**

The error for the combined sampling and analytical technique is ± 10% at concentrations below 0.1 ppm with increasing accuracy at concentrations of 0.1 to 1 ppm. Measurements should be reported to the nearest 0.01 ppm.

5. **Advantages and Disadvantages**

5.1 Aside from the advantages and disadvantages indicated by the discussion of interferences, this method has other distinct advantages. It requires only simple equipment and can be performed by analysts having lesser skills.

5.2 It is preferable to the West-Gaeke method if SO_2 is the principal gaseous pollutant and if the samples must be stored for long periods prior to analysis.

6. **Apparatus**

6.1 **Sampling Equipment.** The sampling unit for the impinger collection method consists of the following components:

6.1.1 A prefilter unit (if needed) which consists of the filter media and cassette filter holder.

6.1.2 A midget impinger containing the absorbing solution or reagent.

6.1.3 A pump suitable for delivering desired flow rates. The sampling pump is protected from splashover or water condensation by an adsorption tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump.

6.1.4 An integrating volume meter such as a dry gas or wet test meter.

6.1.5 Thermometer.

6.1.6 Manometer.

6.1.7 Stopwatch.

6.2 **Burette.** A 25 or 50 mℓ burette graduated in 0.1 mℓ subdivisions, preferably with Teflon plug, should be capable of measuring volume with an accuracy of 0.05 mℓ.

6.3 Assorted Glassware

7. Reagents

7.1 **Absorbing Solution.** Hydrogen Peroxide, 0.3N, pH 5. Dilute 17 mℓ of 30% H_2O_2 solution to 1.0 liter with distilled water. Determine the alkalinity of the solution by taking a measured aliquot, adding 3 drops of mixed indicator, and titrating with 0.002N HCl or HNO_3 until a pink color persists (pH 5). Calculate the amount of acid necessary to adjust the acidity of the bulk absorbing solution and add the required amount. The zero blank obtained by titrating an aliquot of this adjusted reagent with 0.002N NaOH to the equivalence point (green) should be no more than a few drops. The reagent is stable for at least one month at room temperature.

7.2 **Mixed Indicator, 0.1%.** Dissolve 0.06 bromocresol green and 0.04 methyl red in 100 mℓ of methanol. When stored in an amber bottle at room temperature the reagent is stable for at least six months.

7.3 **Sulfuric Acid Solution, 1N.** Prepare by slowly adding 28 mℓ of concentrated sulfuric acid (36N) to about 700 mℓ of distilled water in a 1-liter volumetric flask. Cool mixture and dilute to volume.

7.4 **Standard Sulfuric Acid Solution, 0.002N.** Prepare by diluting 4.0 mℓ of the 1N sulfuric acid solution to volume with distilled water in a 2-liter volumetric flask. Determine the normality of this solution either by a gravimetric barium sulfate method or with a primary standard such as $Na_2B_4O_7 \cdot 10H_2O$ or sodium carbonate. This standard sulfuric acid solution may be stored indefinitely without change in strength.

7.5 **Sodium Hydroxide Solution, 1N.** Dissolve 40 g of sodium hydroxide in 1 liter of water.

7.6 **Standard Sodium Hydroxide Solution, 0.002N.** Prepare 2 liters of this solution by diluting 4.0 mℓ of the 1N solution with freshly boiled CO_2 free distilled water. This solution is standardized as described in Section 9. Store the reagent in a polyethylene or other alkali-resistant bottle and restandardize bimonthly.

8. Procedure

8.1 **Cleaning of Equipment.** All glassware used in this method must be free of acidity and alkalinity. The following procedure is recommended:

8.1.1 Wash in detergent – tap water and follow with tap water and distilled water rinses.

8.1.2 Soak in chromic acid for at least 30 minutes and follow with tap and distilled water rinses.

8.1.3 Soak in concentrated nitric acid for at least 30 minutes and follow with several tap, distilled, and double distilled water rinses.

This entire procedure need only be used when initially preparing glassware. For each following successive use of equipment previously subjected to the entire cleaning procedure, it is necessary only to wash the glassware in detergent and water, making sure to rinse it thoroughly with distilled and double distilled water.

8.2 **Collection and Shipping of Samples**

8.2.1 Pour 15 mℓ of the absorbing solution (Section 7) into the midget impinger, using a graduated cylinder to measure the volume.

8.2.2 Connect the impinger (via the adsorption tube) to the vacuum pump and the prefilter assembly (f needed) with a short piece of flexible tubing. The minimum amount of tubing necessary to make the joint between the prefilter and impinger should be used. The air being sampled should not be passed through any other tubing or other equipment before entering the impinger.

8.2.3 Turn on pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible. The sample should be taken at a flow rate of 1-2 ℓpm. A sample size of not more than 100 liters and no less than 10 liters should be collected. The minimum volume of air sampled will allow the measurement at least 1/10 times the TLV, 1.3 mg/m^3 (760 mm Hg, 25°C).

8.2.4 After sampling, the impinger stem can be removed and cleaned. Tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Wash the stem with a small amount (1-2 mℓ) of unused absorbing solution and add the wash to the impinger. Then the impinger is sealed with a hard, nonreactive stopper (preferably Teflon). Do not seal with rubber. The stoppers on the impingers should be tightly sealed to prevent leakage during shipping. If it is preferred to ship the impingers with the stems in, the outlets of the stem should be sealed with Parafilm or other nonrubber covers, and the ground glass joints should be sealed (i.e., taped) to secure the top tightly.

8.2.5 Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within a day.

8.2.6 Whenever possible, hand delivery of the samples is recommended. Otherwise, special impinger shipping cases designed by NIOSH should be used to ship the samples.

8.2.7 A "blank" impinger should be handled as the other samples (fill, seal and transport) except that no air is sampled through this impinger.

8.2.8 Where a prefilter has been used, the filter cassettes are capped and placed in an appropriate cassette shipping container. One filter disc should be handled like the other samples (seal and transport) except that no air is sampled through, and this is labeled as a blank.

8.3 **Analysis of Samples**

8.3.1 Transfer the collected sample from the impingers to a convenient titration-vessel. Rinse each impinger with two to three 1-mℓ portions of distilled water. Add the rinsings to the titration vessel.

8.3.2 Add three drops of mixed indicator solution and titrate the solution with standard 0.002N sodium hydroxide until the color changes from red to green.

8.3.3 A reagent blank should be titrated at the same time and in the same manner. The result, which should be less than 0.1 mℓ, should be subtracted from the sample titer.

9. **Calibration and Standards**

The measured concentration of absorbed SO_2 in the samples is based on the proper standardization of the sodium hydroxide solution. The solution is standardized by pipetting 25 mℓ of the standard sulfuric acid solution into an Erlenmeyer flask, adding 3 drops of mixed indicator and titrating with the NaOH solution to the green equivalence point. This determination must be done at least in duplicate and the solution must be restandardized periodically.

10. **Calculations**

10.1 Determine the normality of the standard sulfuric acid solution.

10.2 Determine the normality of the standard sodium hydroxide solution:

$$m\ell_{NaOH} \times N_{NaOH} = m\ell_{H_2SO_4} \times N_{H_2SO_4}$$

10.3 The analytical results are computed on the basis of the following reactions:

$$SO_2 + H_2O_2 \longrightarrow H_2SO_4$$

$$H_2SO_4 + 2\,NaOH \longrightarrow Na_2SO_4 + 2\,H_2O$$

Therefore,

$$\mu g\ SO_2 = m\ell_{NaOH} \times N_{NaOH} \times \frac{64}{2000} \times 10^6$$

Where:

$m\ell_{NaOH}$ = volume of NaOH standard needed to titrate the sample minus the blank value

N_{NaOH} = normality of NaOH standard

$\frac{64}{2000}$ = gram-milliequivalent weight of SO_2

10^6 = equivalent μg per gram

10.4 Convert the volume of air sampled to standard conditions of 25°C and 760 mm Hg.

$$V_s = V \times \frac{P}{760} \times \frac{298}{(T + 273)}$$

where:

V_s = volume of air in liters at 25°C and 760 mm Hg
V = volume of air in liters as measured
P = Barometric pressure in mm Hg
T = Temperature of air in degrees centigrade

10.5 The concentration of the SO_2 in the sample can be expressed in $\mu g/\ell$ which is numerically equal to mg/m^3.

$$mg/m^3 = \mu g/\ell = \frac{\mu g\ SO_2}{V_s}$$ (as calculated in 10.3) (as calculated in 10.4)

10.6 The SO_2 concentration in the sample can also be expressed in ppm, defined as $\mu\ell$ of SO_2 per liter of air.

$$\text{ppm} = \frac{\mu\ell SO_2}{V_s}$$

$$= \frac{24.45}{MW} \times \frac{\mu g\ SO_2}{V_s}$$

$$= \frac{0.382 \times \mu g\ SO_2}{V_s}$$

where:

24.45 = molar volume at 25°C and 760 mm Hg

MW = 64, molecular weight of SO_2

11. References

11.1 Jacobs, M.B., Greenburg, L., "Sulfur Dioxide in New York City Atmosphere," *Ind.*, 48:1517, 1956.

11.2 Jacobs, M.B., "The Chemical Analysis of Air Pollutants," *Interscience,* New York, 1960.

11.3 Hochheiser, Seymour, "Methods of Measuring and Monitoring Atmospheric Sulfur Dioxide," PHS Publication No. 999-AP-6.

11.4 Croxford, S.R., Slimming, D.W., Wilkins, E.T., "The Measurement of Atmospheric Pollution: The Accuracy of the Instruments and the Significance of the Results," Proceeding of the Harrogate Conference, London, England, 1960.

CADMIUM IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Cadmium	**Method No.:**	P&CAM 151
Matrix:	Air	**Range:**	0.01 to 0.2 mg Cd/m^3
Procedure:	Atomic Absorption	**Precision:**	4% RSD
Date Issued:	5/17/72		
Date Revised:	1/10/74	**Classification:**	D (Operational)

1. **Principle of the Method**

   1.1 Cadmium dust or fume is collected on a cellulose membrane filter.

   1.2 The resulting filter is ashed with nitric acid then hydrolyzed with hydrochloric acid and diluted to volume.

   1.3 Cadmium in the sample is determined by atomic absorption spectroscopy, using the 228.8 nm Cd wavelength to measure absorbance.

2. **Range and Sensitivity**

   2.1 By AA, the detection limit for cadmium in aqueous solution is 0.001 μg/mℓ. If the ashed sample is diluted to 10 mℓ, this would correspond to a detection limit of 0.010 μg/filter. For a 100 liter air sample this would represent a cadmium concentration of 0.100 μg/m^3. The sensitivity varies depending on the instrument used.

   2.2 The working range for Cd is linear up to concentrations of approximately 2 μg/mℓ in aqueous solution. If necessary, dilutions can be made to get the sample into the proper range.

3. **Interferences**

   There are no known interferences for this method.

4. **Precision and Accuracy**

In the range given, the precision was 4% RSD for spiked samples and sample recovery was from 98 to 107% (36 samples). No collaborative tests have been performed on this method.

5. **Advantages and Disadvantages of the Method**

The method is fast and does not require a high degree of technical skill. Once the samples are ashed, they can be run by atomic absorption in a matter of seconds.

6. **Apparatus**

6.1 **Sampling Equipment.** The sampling unit for the filter-collection method has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate cassette filter holder, either a 2- or 3-piece filter cassette.

6.1.2 A vacuum pump such as a personal sampling pump. This pump must be properly calibrated so the volume of air sampled can be measured as accurately as possible. The pump must be calibrated with a representative filter unit in the line. Flow rate, times, and/or volume must be known.

6.1.3 Thermometer.

6.1.4 Manometer.

6.1.5 Stopwatch.

6.2 0.45-μ cellulose membrane filters, or type HA millipore filters.

6.3 125-mℓ Phillips borosilicate glass beakers.

6.4 15-mℓ pyrex graduated centrifuge tubes.

6.5 Atomic absorption spectrophotometer equipped with a Cd lamp, air-acetylene flame system, and recorder or concentration readout system. Top of the line instruments from most companies are probably adequate.

7. **Reagents**

7.1 Redistilled concentrated nitric acid (16 N).

7.2 Redistilled hydrochloric acid (6 N).

7.3 Double distilled water or equivalent.

7.4 **Cadmium stock solution,** 1000 μg/mℓ. Dissolve 1.000 g of cadmium metal in a minimum volume of 1:1 HCl. Dilute to 1 liter with 1% (V/V) HCl.

8. **Procedure**

8.1 **Cleaning of Equipment.** All glassware should be cleaned using the following procedure:

8.1.1 Wash in detergent – tap water and follow with tap water and distilled water rinses.

8.1.2 Soak in chromic acid for at least 30 minutes and follow with tap and distilled water rinses.

8.1.3 Soak in concentrated nitric acid for at least 30 minutes and follow with tap, distilled, and double distilled water rinses.

8.2 **Collection and Shipping of Samples.**

8.2.1 Cadmium dust or fume is collected on 0.45μ cellulose membrane filters (or equivalent) mounted into either 2 or 3 piece filter cassettes.

8.2.2 Air is drawn through the filter by means of a personal sampling pump at the rate of 2 liters per minute. The volume of air sampled is normally between 100 and 1000 liters. Some *minimum* sampling volumes are as follows:

Concentration to be Measured (mg/m^3)	Minimum Required Sample Size (liters)
0.05	200
0.1	100
0.2	50
0.3	34
0.6	17

8.2.3 Larger sample volumes are encouraged provided the filters do not become loaded with dust to the point where portions of the sample might fall off or the filter becomes plugged.

8.2.4 With each batch of samples, one filter, labelled as a blank, should be submitted. This filter is subjected to exactly the same handling as for the samples except that no air is drawn through it.

8.2.5 The cassettes in which samples are collected should be shipped in a suitable container, designed to prevent damage in transit. Loss of samples from heavy deposits on the filter may be prevented by mounting a clean filter in the cassette on top of the sample filter.

8.3 **Analysis of Samples**

8.3.1 Transfer sample and blank filters into a 125 mℓ Phillips beaker to which 3 mℓ of concentrated nitric acid has been added.

8.3.2 Heat each beaker on a hotplate in a fume hood until a moist residue, pale yellow to white in color, remains. More than one addition of nitric acid may be needed to reach this point. When all of the organic matter has been destroyed, as evidenced by the color of the residue, add 1 mℓ of HCl and 5 mℓ of distilled water to the beaker and heat slowly. When the residue has dissolved, transfer the solution quantitatively to a clean 15 mℓ centrifuge tube and make up to 10 mℓ with distilled water. Prepare suitable dilutions of aliquots of this solution when later analysis indicates that the cadmium concentration is beyond the working range of the calibration curve.

8.3.3 Aspirate the solution into an air-acetylene AA Flame and measure its absorbance at the Cd 228.8 nm wavelength using a recorder or digital read-out.

9. **Calibration and Standards**

9.1 Using the 1000 μg/mℓ stock solution, prepare working standards in the range of 0.05 ppm to 2.0 ppm Cd by appropriate dilutions with 1% HCl. The stock standard is stable for six months. Low working standards should be made up fresh weekly.

9.2 A calibration curve is constructed by aspirating the working standards into the flame and measuring absorbance. A calibration curve is then drawn up plotting absorbance vs. concentration in μg Cd/mℓ.

10. **Calculations**

10.1 Blank values, if any, should first be subtracted from each sample.

10.2 The calculations for determining the sample concentration in μg Cd per cubic meter of air sampled is as follows:

$$\mu g\ Cd/m^3 = \frac{\mu g\ Cd/m\ell}{V_s} \times m\ell\ \text{sample}$$

where:

μg Cd/mℓ = concentration of Cd derived from the calibration curve (Section 9.2).

mℓ sample = final sample volume including any dilution factor.

V_s = volume of air sampled in m^3 at 25°C and 760 mm Hg (1000 ℓ = 1 m^3).

11. References

11.1 Y.C. Athanassiadis, "Air Pollution Aspects of Cadmium and Its Compounds," Environmental Systems Technical Report. "Guidelines for Air Sampling," NIOSH.

11.2 NIOSH Sampling Data Sheet #7.01, "NIOSH Manual of Sampling Data Sheets," Engineering Branch, DLCD, 1974.

TOTAL PARTICULATE CHROMIUM IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Total Particulate Chromium	**Method No:**	P&CAM 152
Matrix:	Air	**Range:**	0.01 to < 0.4 mg/m^3 Air
Procedure:	Atomic Absorption		
Date Issued:	11/20/72	**Precision:**	Less than 5% relative standard deviation
Date Revised:	12/1/73	**Classification:**	D (Operational)

1. **Principle of the Method**

   1.1 Atmospheric samples are obtained by drawing a measured volume of air through a 0.8-μ filter.

   1.2 The filter is wet ashed and analyzed for chromium by atomic absorption spectroscopy using a nitrous oxide-acetylene flame.

2. **Range and Sensitivity**

   2.1 The sensitivity for chromium in solution by atomic absorption using a nitrous oxide-acetylene flame is about 0.1 $\mu g/m\ell$ and the linear range extends to about $4\mu g/m\ell$.

   2.2 The range in air, therefore, is from 0.01 mg/m^3 to greater than 0.4 mg/m^3 using the recommended volumes of 100 liters of air and 10 $m\ell$ of solution.

3. **Interferences**

   3.1 A number of metallic elements may interfere with the atomic absorption analysis of chromium, but the interferences that are possible are only serious at high levels of interfering ion concentration. These levels are not likely in the present analysis. Most notable among the interfering metals are iron and nickel. The interference is usually a suppression effect.

   3.2 These spectral interferences in the chromium determination are minimized by the proper choice of flame conditions. A nitrous oxide-acetylene flame is recommended in this method. If greater sensitivity is needed, an air-acetylene flame can

be used and sensitivity is aided by making the flame luminous (fuel rich), while interferences are minimized in a blue (lean, oxidizing) flame.

4. **Precision and Accuracy**

The relative standard deviation for determination of 10 spiked filters near the threshold limit value was found to be less than 5%. The overall accuracy is not known but good recoveries are indicated.

5. **Advantages and Disadvantages**

5.1 The method has the advantage of using filter paper for convenience in sampling and shipping. The method is straightforward and requires few chemicals.

5.2 This method does not differentiate between hexavalent chromium and other forms. Moreover, the ashing procedure is long and somewhat tedious.

5.3 The possible degradation of the filters when H_2SO_4 mist is present has not been evaluated.

6. **Apparatus**

6.1 **Sampling Equipment.** The sampling unit for the filter-collection method has the following components:

6.1.1 The filter unit, consisting of the filter media and appropriate cassette filter holder, either a 2- or 3-piece filter cassette.

6.1.2 A vacuum pump such as a personal sampling pump. This pump must be properly calibrated so the volume of air sampled can be measured as accurately as possible. The pump must be calibrated with a representative filter unit in the line. Flow rate, times, and/or volume must be known.

6.1.3 Thermometer.

6.1.4 Manometer.

6.1.5 Stopwatch.

6.2 Millipore 37 mm HA type filter.

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6.3 Atomic absorption spectrophotometer with a nitrous oxide-acetylene burner head, and requisite gas equipment.

6.4 Laboratory glassware for standards and sample handling.

7. Reagents

7.1 Double distilled water.

7.2 Redistilled HNO_3.

7.3 Chromium standard stock solution: Weigh 3.735 g of dry K_2CrO_4 into a clean 1000-mℓ volumetric flask, dissolve in double distilled water, add 50 mℓ of redistilled HNO_3, and dilute to mark with double distilled water. This solution contains 1000 μg Cr per mℓ.

8. Procedure

8.1 Cleaning of Glassware

8.1.1 All glassware should be detergent washed and tapwater rinsed.

8.2 Collection and Shipping of Samples

8.2.1 Weigh the filter disc, if needed. Assemble the filter unit by mounting the filter disc in the filter cassette.

8.2.2 Connect the exit end of the filter unit to the pump with a short piece of flexible tubing.

8.2.3 Turn on pump to begin sample collection. The flow rate, time, and/or volume must be measured as accurately as possible. The sample should be taken at a flow rate of 2 liters per minute. A minimum sample of 100 liters should be collected. Larger sample volumes are encouraged, provided the filters do not become loaded with dust to the point that loose material might fall off or the filter become plugged.

8.2.4 The sample cassettes should be shipped in a suitable container designed by NIOSH to minimize contamination and to prevent damage in transit. Care must be taken during storage and shipping that no part of the sample is dislodged from the filter nor that the sample surface be disturbed in any way. Loss of sample from heavy deposits on the filter may be prevented by mounting a clean filter in the cassette on top of the sample filter.

8.2.5 With each batch of samples, one filter, labelled as a blank, must be submitted. No air should be drawn through this filter.

8.3 **Analysis**

8.3.1 To prepare the sample, place the filter carefully in a 125 mℓ Phillips beaker and add 3 mℓ of redistilled HNO_3. Cover the beaker with a watch glass and place on a hotplate. Heat the beaker to dryness. Continue adding HNO_3 one mℓ at a time and taking to dryness until no organic matter remains. Then add 0.5 mℓ of HNO_3 and several mℓ of water, swirl and place on the hotplate but do not take to dryness. Transfer the solution to a clean graduated centrifuge tube with several washings until the volume is 10 mℓ. Mix the contents well.

8.3.2 Analyze the samples for chromium by atomic absorption spectrophotometry using aspiration into a nitrous oxide-acetylene flame, a 357.9 nanometer wavelength setting and a 0.3-nanometer spectral band width unless sensitivity and signal-to-noise ratio are favorable to a narrower slit width. Record the concentration of chromium in the sample.

8.3.3 If necessary the samples can be diluted to bring the concentration down to the working range.

8.3.4 The blanks are treated and analyzed in the same manner as the sample.

9. **Calibration**

Working standards covering the analytical range of 0.1 μg/mℓ to 4 μg/mℓ should be made by diluting the standard stock solution with double distilled water and redistilled HNO_3 in sufficient quantity to maintain the 5% acid level. These should be used to make a calibration curve of μg Cr/mℓ solution versus absorbance.

10. **Calculations**

10.1 The concentration of Cr for the samples is read from the calibration curve and multiplied by the solution volume of 10 mℓ to give total Cr content.

10.2 The total chromium content can be expressed as CrO_3 by the following equation.

$$\frac{\mu g\ Cr}{0.52} = \mu g\ CrO_3$$

10.3 Convert the volume of air sampled to standard conditions of 25°C and 760 mm Hg.

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

V_s = volume of air in liters at 25°C and 760 mm Hg

V = volume of air in liters as measured

P = barometric pressure in mm Hg

T = temperature of air in degree centigrade.

10.4 The concentration of CrO_3 in the air sample can be expressed in mg CrO_3 per cubic meter or μg CrO_3 per liter of air.

$$\text{mg } CrO_3/m^3 = \mu\text{g } CrO_3/V_s$$

11. References

11.1 *Industrial Toxicology,* Lawrence T. Fairhall, 2nd Edition, The Williams and Wilkins Company, pp. 37-38, 1957.

11.2 "Atomic Absorption Newsletter," F.L. Vogliotti, Vol. 9, No. 6, pp. 125-126, 1970.

11.3 "Analytical Methods for Atomic Absorption Spectrophotometry," Perkin-Elmer Corp., Cr. Standard Conditions, p. 2, 1971.

11.4 *Atomic Absorption Spectroscopy,* Christian, G.D., and Feldman, F.J., Wiley Interscience, pp. 285-292, 1970.

OZONE IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Ozone	**Method No.:**	P&CAM 153
Matrix:	Air	**Range:**	0.01 to 10 ppm
Procedure:	KI Absorption -- Colorimetric	**Precision:**	± 5% Deviation from the mean (Ref. 11.1)
Date Issued:	9/8/72	**Classification:**	B (Accepted)
Date Revised:	1/15/74		

1. **Principle of the Method**

   1.1 Air containing ozone is drawn through a midget impinger containing 10 mℓ of 1% potassium iodide in a neutral (pH 6.8) buffer composed of 0.1M disodium hydrogen phosphate and 0.1M potassium dihydrogen phosphate.

   1.2 The iodine liberated in the absorbing reagent is determined spectrophotometrically by measuring the absorption of the tri-iodide ion at 352 nm.

   1.3 The stoichiometry (Reference 11.1) is approximated by the following reaction:

$$O_3 + 3\,KI + H_2O \rightarrow KI_3 + 2KOH + O_2$$

   1.4 The analysis must be completed within 30 minutes to 1 hour after sampling.

2. **Range and Sensitivity**

   2.1 The range extends from 0.01 ppm to about 10 ppm.

   2.2 The sensitivity of the method is dependent on the volume of air sampled.

3. Interferences

3.1 The negative interference of reducing gases such as sulfur dioxide and hydrogen sulfide are very serious (probably on a mole-to-mole equivalency).

3.2 Interference from high concentrations of sulfur dioxide can be eliminated by using a prefilter consisting of a U-tube filled with strips of glass fiber paper impregnated with chromium trioxide.

3.3 The procedure is very sensitive to reducing dusts which may be present in the air or on the glassware. Losses of iodine occur even on clear glass surfaces, and thus the manipulations should minimize the exposure.

3.4 Halogens, hydrogen peroxide, organic peroxides, organic nitrites and various other oxidants will liberate iodine as well as ozone by this method.

3.5 Peroxyacetyl nitrate gives a response approximately equivalent to 50% of that of an equimolar concentration of ozone (Reference 11.1). Concentrations in the atmosphere may range up to 0.1 ppm.

4. Precision and Accuracy

The accuracy and precision of this method have not been completely determined at this time. No collaborative tests have been performed on this method.

5. Advantages and Disadvantages

5.1 The method is simple.

5.2 The analysis must be completed during the period of 30 to 60 minutes after sampling due to the instability of the colors.

6. Apparatus

6.1 **Sampling Equipment.** The sampling unit for the impinger collection method consists of the following components:

6.1.1 A graduated midget impinger containing the absorbing solution or reagent.

6.1.2 A pump suitable for delivering desired flow rates. The sampling pump is protected from splashover or water condensation by an absorption tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump.

6.1.3 An integrating volume meter such as a dry gas or wet test meter.

6.1.4 Thermometer.

6.1.5 Manometer.

6.1.6 Stopwatch.

6.2 Spectrophotometer capable of measuring the yellow color at 352 nm.

6.3 Matched cells or cuvettes of 2 cm path length.

6.4 Associated laboratory glassware.

7. **Reagents**

The reagents described must be made up using ACS reagent grade or better grade of chemical.

7.1 **Double distilled water.** Double distilled water should be used for all reagents. The double distilled water can be prepared in an all-glass still by adding potassium permanganate to produce a faint pink color and barium hydroxide to alkalize the distilled water before the second distillation.

7.2 **Absorbing reagent.** (1% KI in 0.1 M phosphate buffer). Dissolve 13.61g of potassium dihydrogen phosphate, 14.20g of anhydrous disodium hydrogen phosphate (or 35.82g of dodecahydrate salt) and 10.00g of potassium iodide successively and dilute the mixture to exactly 1 liter with double distilled water. Age at room temperature for at least 1 day before using. This solution may be stored for several weeks in a glass stoppered brown bottle in the refrigerator or for shorter periods of time at room temperature. Do *not* expose to sunlight.

7.3 **Standard iodine solution,** 0.025 M I_2 (0.05N). Dissolve successively 16.0g of potassium iodide and 3.1730g of iodine with double distilled water and make up to a volume of exactly 500 mℓ. Age for at least 1 day before using. Standardize shortly before use against 0.025 M $Na_2S_2O_3$. The sodium thiosulfate is standardized against primary standard bi-iodate, $KH(IO_3)_2$, or potassium dichromate, $K_2Cr_2O_7$.

8. Procedure

8.1 **Cleaning of equipment.** All glassware should be cleaned with *dichromate* cleaning solution followed by thorough rinsing with tap water and distilled water.

8.2 **Collection and Shipping of Samples**

8.2.1 Pipet 10 mℓ of the absorbing solution (Section 7) into the midget impinger.

8.2.2 Connect the impinger (via the absorption tube) to the vacuum pump and the prefilter assembly (if needed) with a short piece of flexible tubing (not rubber). The minimum amount of tubing necessary to make the joint between the prefilter and impinger should be used. The air being sampled should not be passed through any other tubing or other equipment before entering the impinger.

8.2.3 Turn on pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible. The sample should be taken at a flow rate of 0.2-1 ℓpm. If the sample air temperature and pressure deviate greatly from 25°C and 760mmHg, measure and record these values.

8.2.4 Sufficient air should be sampled so that the equivalent of 0.5 to 10 μ1 of ozone is absorbed. Sampling periods of longer than 30 minutes should be avoided. For a flow rate of 2 liters per minute, a 30 minute sample should yield a sensitivity of 0.01 ppm. Do *not* expose the absorbing reagent to direct sunlight.

8.2.5 After sampling, the impinger stem can be removed and cleaned. Tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Wash the stem with a small amount (<1 mℓ) of unused absorbing solution and add the wash to the impinger. Then the impinger is sealed with a hard, non-reactive stopper (preferably Teflon). Do not seal with rubber.

8.2.6 The sample solutions must be analyzed within 60 minutes after sampling.

8.2.7 A "blank" impinger should be handled as the other samples (fill and seal) except that no air is sampled through this impinger.

8.3 **Analysis**

8.3.1 Record the total volume of sample solution present in the graduated impinger. This is usually 10 mℓ.

8.3.2 Transfer the exposed absorbing reagent (avoiding dilution with rinse water) to a clean cell or cuvette.

8.3.3 Determine the absorbance at 352 nm using a matched cell or cuvette freshly filled with distilled water as the reference. This measurement must be done within 30 to 60 minutes after sampling.

8.3.4 Determine daily the blank correction (to be deducted from sample absorbance) by reading the absorbance of the "blank" sample using distilled water as the reference.

8.3.5 Samples having a color too dark to read may be quantitatively diluted with additional absorbing reagent and the absorbance of the diluted solution read. The dilution factor must then be introduced into the calculations.

9. **Calibration and Standards**

9.1 Freshly prepare 0.00125 M (0.0025 N) iodine standard by pipetting exactly 5 mℓ of the 0.025 M (0.05 N) standard stock solution into a 100 mℓ volumetric flask and diluting to the mark with the absorbing reagent.

9.2 Pipet 0.2, 0.4, 0.6, and 0.9 mℓ portions of the diluted standard iodine in separate 25 mℓ volumetric flasks and dilute to the mark with absorbing reagent. Mix thoroughly. The concentrations of these solutions (must be based on exact molar concentration as determined from the molarity of the standard iodine solution) are respectively – 0.25, 0.50, 0.75, and 1.125 μmoles I_2 per 25 mℓ; or more conveniently expressed as 0.10, 0.20, 0.30, and 0.45 μmoles of I_2 per 10 mℓ of absorbing reagent.

9.3 Immediately after the preparation of this known series, read the absorbance of each at 352 nm in the usual manner.

9.4 Plot the corrected absorbances (absorbance minus absorbance of reagent blank) of the known standards against the exact calculated molar concentrations (in μmoles per 10 mℓ). Draw the straight line that gives the best fit. Beer's Law is followed.

10. Calculations

10.1 The absorbance of the "blank" sample (Section 8.3.7) must first be subtracted from the sample absorbances.

10.2 As indicated by the stoichiometric equation in Section 1.3, it has been empirically determined that 1 mole of ozone (O_3) liberates 1 mole of iodine (I_2) by this procedure. Thus, one can read directly from the calibration curve (Section 9.4) the equivalent μmoles of O_3 per 10 mℓ of absorbing reagent. If the total volume of the sample solution is not 10 mℓ, or if the sample solution has been diluted prior to analysis, the dilution factor must be included in the calculation.

10.3 The concentration of ozone in the air sampled can be expressed as ppm of ozone, defined as $\mu\ell$ ozone per liter of air.

$$\text{ppm, } O_3 = \frac{\mu\text{moles } O_3 \times 24.45}{V_s}$$

where:

μmoles O_3 = micromoles ozone determined from calibration curve (Section 9.4) including the dilution factor, if any.

24.45 = molar volume of ozone ($\mu\ell/\mu$mole) at 25°C and 760 mm Hg.

V_s = volume of air sampled in ℓ at 25°C and 760 mm Hg.

11. References

11.1 "Tentative Method for the Manual Analysis of Oxidizing Substances in the Atmosphere," 44101-02-70T, American Public Health Association, Washington, D.C., 1972.

11.2 "Selected Methods for the Measurement of Air Pollutants," USDHEW Public Health Service Publication Number 999-AP-11, 1965.

LEAD IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Lead	**Method No:**	P&CAM 155
Matrix:	Atmospheric Dust and Fume	**Range:**	1.0 μg to 400 μg
Procedure:	Atomic Absorption	**Precision:**	Unknown
Date Issued:	6/6/72	**Classification:**	D (Operational)
Date Revised:	12/1/73		

1. **Principle of the Method**

   1.1 Airborne dust and fume samples are collected on cellulose membrane filters.

   1.2 The filter samples are ashed using nitric acid to destroy the organic matrix and solubilize the lead.

   1.3 The lead content of the ashed material is determined by conventional aqueous atomic absorption spectroscopy.

2. **Range and Sensitivity**

   2.1 By atomic absorption the detection limit for lead in aqueous solution is about 0.1 μg/mℓ. Assuming the ashed sample is diluted to 10 mℓ this would correspond to 1 μg of lead per filter. For a 100 liter air sample this would represent a lead concentration of 0.01 mg/m^3.

   2.2 The optimum working range for Pb extends up to about 40 μg/mℓ. If necessary the sample solution can be diluted to extend the upper limit of the analysis.

3. **Interferences**

   There are no known interferences for this method.

4. **Precision and Accuracy**

   The precision and accuracy of this method have not been completely determined; however, limited tests show good agreement with the dithizone method of analysis.

5. **Advantages and Disadvantages of the Method**

5.1 The method is simple and fast and does not require a high degree of technical skill. Ashing of samples requires very little time and the analysis using the AA requires only a few seconds per sample.

5.2 The equipment used is not extremely expensive but may not be available to some small laboratories.

6. **Apparatus**

6.1 **Sampling Equipment.** The sampling unit for the filter-collection method has the following components:

6.1.1 The filter unit, consisting of the filter media and appropriate cassette filter holder, either a 2- or 3-piece filter cassette.

6.1.2 A vacuum pump such as a personal sampling pump. This pump must be properly calibrated so the volume of air sampled can be measured as accurately as possible. The pump must be calibrated with a representative filter unit in the line. Flow rate, times, and/or volume must be known.

6.1.3 Thermometer.

6.1.4 Manometer.

6.1.5 Stopwatch.

6.2 0.8- or 0.45-μ cellulose membrane filters.

6.3 125-mℓ Phillips borosilicate glass beakers.

6.4 10-mℓ volumetric flasks.

6.5 Atomic absorption spectrophotometer equipped with Pb lamp, air-acetylene flame system, and recorder or concentration readout system. Top of the line instruments from most companies are probably adequate.

7. **Reagents**

7.1 Redistilled concentrated nitric acid.

7.2 Double distilled water or equivalent.

7.3 Lead stock solution 1000 μg/mℓ. Dissolve 1.598 g lead nitrate, Pb $(NO_3)_2$, in 1 liter of 1% HNO_3.

8. Procedure

8.1 Cleaning of Glassware

8.1.1 Wash in detergent solution and follow with tap water and distilled water rinses.

8.1.2 Soak volumetric flasks in 1:1 HNO_3 for several minutes and rinse thoroughly with distilled and double distilled water.

8.1.3 Place beakers for ashing samples on hot plate. Add about 3 mℓ concentrated HNO_3 and heat until acid is condensing and running down the sides. Remove and rinse thoroughly with tap, distilled and double distilled water.

8.2 Collection and Shipping of Samples

8.2.1 Assemble the filter unit by mounting the filter disc in the filter cassette.

8.2.2 Connect the exit end of the filter unit to the pump with a short piece of flexible tubing.

8.2.3 Turn on pump to begin sample collection. The flow rate, times, and/or volume must be measured as accurately as possible. The sample should be taken at a flow rate of 2 liters per minute. A minimum sample of 100 liters should be collected. Larger sample volumes are encouraged, provided the filters do not become loaded with dust to the point that loose material might fall off or the filter become plugged.

8.2.4 The sample cassettes should be shipped in a suitable container designed by NIOSH to minimize contamination and to prevent damage in transit. Care must be taken during storage and shipping that no part of the sample is dislodged from the filter, nor that the sample surface be disturbed in any way. Loss of sample from heavy deposits on the filter may be prevented by mounting a clean filter in the cassette on top of the sample filter.

8.2.5 With each batch of samples, one filter, labelled as a blank, must be submitted. No air should be drawn through this filter.

8.3 **Analysis of Samples**

8.3.1 Sample and blank filters are placed in clean 125-mℓ Phillips beakers; then 2 to 3 mℓ concentrated HNO_3 is added to each.

8.3.2 Each beaker is heated on a hot plate in a fume hood until a clear or slightly yellow solution remains and the volume has been reduced to less than 1 mℓ. (Some HNO_3 should be left in the flask to maintain low pH in resulting solution.) More than one addition of HNO_3 may have to be made to achieve the clear solution. At this point all organic matter has been adequately destroyed and the solution is allowed to cool. It is then quantitatively transferred (by rinsing with double distilled water) to a 10-mℓ volumetric flask and brought to the mark. Aliquots of this solution may be diluted should analysis indicate that the lead concentration is above the working range.

8.3.3 The solution is aspirated into an air-acetylene AA flame and its absorbance is measured at the 2833Å line using a recorder or digital readout. For lower concentrations it is generally desirable to expand the readout by 10X. Instrument settings and flame conditions should be those recommended by the manufacturer.

9. **Calibration and Standards**

9.1 Using the 1000 μg/mℓ stock solution, prepare working standards in the 0.5 ppm to 40 ppm range by appropriate dilution in 1% HNO_3. The stock solution is stable for at least six months but low standards may deteriorate rather quickly.

9.2 A calibration curve is constructed by aspirating the working standards into the flame and measuring absorbance. A calibration curve is then drawn by plotting absorbance vs. concentration in μg/mℓ. Best results are obtained if the calibration standards are run with the samples.

10. **Calculations**

10.1 Calculate the total amount of lead in the sample.

$$\mu g\ Pb = \mu g/m\ell \times \text{solution volume}$$

where:

$\mu g\ Pb$ = total micrograms of lead in air sampled.
$\mu g/m\ell$ = measured concentration of lead in the sample solution derived from the calibration curve.

solution volume = total volume of the solution analyzed; if the original solution has been diluted, this dilution factor must be included.

10.2 Blank value, if any, is subtracted from each sample.

$$\mu g_c Pb = \mu g\ Pb - \mu g_b\ Pb$$

where:

μg_c Pb = μg of lead corrected for blank contribution
μg Pb = section 10.1
μg_b Pb = μg of lead present in blank filter

10.3 Convert the volume of air sampled to standard conditions of 25°C and 760 mm/Hg.

$$V_s = V \times \frac{P}{760} \times \frac{298}{T + 273}$$

where:

V_s = volume of air in liters at 25°C and 760 mm Hg
V = volume of air in liters as measured
P = Barometric pressure in mm Hg
T = Temperature of air in degree centigrade.

10.4 The concentration of lead in the sample is expressed in mg Pb per cubic meter or μg Pb per liter.

$$mg\ Pb/m^3 = \mu g_c Pb/V_s$$

11. References

11.1 *Analytical Methods for Atomic Absorption Spectrophotometry,* The Perkin-Elmer Corp., March 1971.

11.2 *Atomic Absorption Spectroscopy,* Walter Slavin, Interscience, 1968.

PARATHION IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Parathion	**Method No:**	P&CAM 158
Matrix:	Air	**Range:**	5-250 $\mu g/M^3$
Procedure:	Collection via impinger/ ethylene glycol, extraction into hexane, glc analysis		
Date Issued:	11/3/72	**Precision:**	Unknown
Date Revised:	5/21/73	**Classification:**	C (Tentative)

1. **Principle of Method**

Parathion from the air is trapped in ethylene glycol contained in an impinger. The ethylene glycol solution is diluted with water and extracted with hexane. The resulting hexane solution of the parathion is concentrated and subjected to gas chromatographic analysis using a phosphorus flame photometric detector.

2. **Range and Sensitivity**

The linear range of the flame photometric detector is 0.5 ng to 25 ng of parathion. For a 50 liter air sample, carried through the following procedure to solution in 1 mℓ of hexane, 2 $\mu\ell$ of which is injected into the gas chromatograph, this is 5 to 250 $\mu g/m^3$. These limits can be lowered or raised by changing: (1) the volume of air sampled, (2) the volume of the final hexane solution, or (3) the size of the aliquot injected into the gas chromatograph.

3. **Interferences**

Phosphorus compounds having retention times close to that of parathion will interfere with the analysis. The equipment used must be scrupulously cleaned to remove any traces of phosphate detergents.

4. **Precision and Accuracy**

Unknown

5. **Advantages and Disadvantages**

5.1 The method is very sensitive, and the detector exhibits high specificity for phosphorus compounds. The analysis is performed directly on the compound of interest. Separation and quantitation are accomplished in a reasonable amount of time.

5.2 The cost of the equipment and supplies may tax the budget of some laboratories. The sensitivity of the equipment depends on careful adjustment of the operating parameters. Contamination can occur easily through equipment and/or reagents. This method presumes the presence of parathion. If interfering compounds are anticipated a lengthy clean-up procedure is required (Reference 11.3).

6. **Apparatus**

6.1 **Sampling Equipment.** The sampling unit for the impinger collection method consists of the following components:

6.1.1 A prefilter unit (if needed) which consists of the filter media and cassette filter holder.

6.1.2 A midget impinger containing the absorbing solution or reagent.

6.1.3 A pump suitable for delivering desired flow rates. The sampling pump is protected from splashover or water condensation by an adsorption tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump.

6.1.4 An integrating volume meter such as a dry gas or wet test meter.

6.1.5 Thermometer.

6.1.6 Manometer.

6.1.7 Stopwatch.

6.2 Filter cassette with glass-fiber filter, 8-μ, 37-mm

6.3 Forceps.

6.4 Glass stirring rods.

6.5 Separatory funnels, 60 mℓ and 125 mℓ with Teflon stopcocks.

6.6 Beakers, 100 mℓ.

6.7 Funnels, 65 or 75 mm (diameter at top).

6.8 Glass wool.

6.9 Hot water bath.

6.10 Kuderna-Danish evaporator-concentrator, consisting of a 125 mℓ Erlenmeyer-type flask, 3-ball Snyder column, and 10 mℓ receiver graduated in milliliters.

6.11 Glass beads, 3 mm.

6.12 Volumetric flasks for standards.

6.13 Tracor MT 220 gas chromatograph, or equivalent, with attendant equipment, including a phosphorus flame photometric detector. Alternatively, a gas chromatograph fitted with a KCl thermoionic detector may be used. (Reference 11.5).

6.14 Gas-chromatography column constructed from 6-ft x 4-mm I.D. borosilicate glass packed with one of the following:

A. 10% DC-200 (12,500 cst) on 80 to 100-mesh Gas Chrom Q (References 11.4 and 11.5).

B. 7.5% QF-1 (10,000 cst) /5% DC-200 (12,500 cst) on 80-100 Gas Chrom Q (References 11.4 and 11.5).

C. 2% diethylene glycol succinate (DEGS) (C6 stabilized) on 80-100 mesh Gas Chrom Q (References 11.4 and 11.5).

D. 4% SE-30/6% OV-210 on 80-100 mesh Chromosorb W, H.P. (Reference 11.3).

Columns A and B are conditioned by heating 2-4 days at 240-250°C under nitrogen flowing at 60 mℓ/min, then primed by repeated injections of standard parathion solution under the conditions of analysis given below. Column C is conditioned by heating 12 hrs at 225-230°C under nitrogen flowing at 60 mℓ/min. Column D is conditioned for at least 3 days at 245°C under nitrogen flowing at 60 mℓ/min. A column of 10% Carbowax 20M on 80-100 mesh silanized support (2-in. x 4-mm I.D. glass tubing) is then inserted before Column D and the assembly is heated at 230-235°C for 17 hrs under nitrogen flowing at 20 mℓ/min. The 10% Carbowax 20M column is subsequently removed.

6.15 Syringes, 5 or 10 $\mu\ell$ and 100 $\mu\ell$.

7. **Reagents**

7.1 Ethylene glycol, chromatoquality; this is the absorbing solution.

7.2 Hexane, pesticide quality.

7.3 Distilled water, interference free.

7.4 Saturated aqueous NaCl, interference free.

7.5 Anhydrous Na_2SO_4.

7.6 Parathion of known purity.

8. **Procedure**

8.1 **Cleaning of Equipment.** All glassware used must be scrupulously cleaned and given a final hexane rinse immediately before use.

8.2 **Collection and Shipping of Samples**

8.2.1 Pour 15 mℓ of the absorbing solution (Section 7) into the midget impinger, using a graduated cylinder to measure the volume.

8.2.2 Connect the impinger (via the adsorption tube) to the vacuum pump and the prefilter assembly (if needed) with a short piece of flexible tubing. The minimum amount of tubing necessary to make the joint between the prefilter and impinger should be used. The air being sampled should not be passed through any other tubing or other equipment before entering the impinger.

8.2.3 Turn on pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible. The sample should be taken at a flow rate of 1-2 ℓpm. A sample size of not more than 30 liters and no less than 25 liters should be collected. The minimum volume of air sampled will allow the measurement at least 1/10 times the TLV, 0.01 mg/m^3 (760 mm Hg, 25°C).

8.2.4 After sampling, the impinger stem can be removed and cleaned. Tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Wash the stem with a small amount (1-2 mℓ) of unused absorbing solution and add the wash to the

impinger. Then the impinger is sealed with a hard, non-reactive stopper (preferably Teflon). Do not seal with rubber. The stoppers on the impingers should be tightly sealed to prevent leakage during shipping. If it is preferred to ship the impingers with the stems in, the outlets of the stem should be sealed with Parafilm or other non-rubber covers, and the ground glass joints should be sealed (i.e., taped) to secure the top tightly.

8.2.5 Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within a day.

8.2.6 Whenever possible, hand delivery of the samples is recommended. Otherwise, special impinger shipping cases designed by NIOSH should be used to ship the samples.

8.2.7 A "blank" impinger should be handled as the other samples (fill, seal and transport) except that no air is sampled through this impinger.

8.2.8 Where a prefilter has been used, the filter cassettes are capped and placed in an appropriate cassette shipping container.

One filter disc should be handled like the other samples (seal and transport) except that no air is sampled through, and this is labeled as a blank.

8.3 **Analysis** (References 11.3 – 11.5)

8.3.1 The sample in 17-20 mℓ of ethylene glycol is transferred to a 125-mℓ separatory funnel (#1). Wash the sample container with a measured amount of water and add the washings to the separatory funnel. Dilute the ethylene glycol with a total of 70 mℓ of water.

Note: All procedural instructions from here on assume the extraction of 20 mℓ of ethylene glycol. Should a different volume be extracted, the glassware sizes and reagent amounts should be scaled proportionately.

8.3.2 Transfer the glass-fiber filter to a 100-mℓ beaker with a clean pair of forceps. Add 12 mℓ of hexane and agitate with a glass rod. Quantitatively transfer the hexane to separatory funnel #1 and extract by shaking vigorously for 2 minutes. If an emulsion is formed, add 0.5 mℓ of saturated NaCl to the separatory funnel. After the layers have separated, transfer the aqueous layer to a second 125-mℓ separatory funnel (#2) and the hexane layer to a 60-mℓ separatory funnel (#3).

8.3.3 Extract the filter with a second 12-mℓ portion of hexane. Transfer the solution to separatory funnel #2 and extract for 2 minutes. After the

layers have separated, transfer the aqueous layer to separatory funnel #1 and the hexane layer to separatory funnel #3.

8.3.4 Extract the filter with a third 12-mℓ portion of hexane, transfer the solution to separatory funnel #1, and extract for 2 minutes. After the layers have separated, discard the aqueous layer and transfer the hexane layer to separatory funnel #3.

8.3.5 Add 10 mℓ of water to separatory funnel #3 and extract for 1 minute. Discard the aqueous layer and extract with a second 10-mℓ portion of water, again discarding the aqueous layer.

8.3.6 Dry the hexane solution by passing it through 2.6 g of anhydrous Na_2SO_4 contained in a funnel with a glass wool retaining plug at the top of the stem. Collect the eluate in a 125-mℓ Kuderna-Danish flask which has been fitted with a 10-mℓ receiving tube containing one 3-mm glass bead. When the extract has eluted, rinse the separatory funnel with three consecutive 2-mℓ portions of hexane, washing down the walls of the funnel. Allow each rinse to elute before adding the next. Finally, rinse the funnel and the Na_2SO_4 with two more 2-mℓ portions of hexane.

8.3.7 Place the Kuderna-Danish assembly in a boiling water bath and concentrate the extract to ca. 5 mℓ. Remove the assembly from the bath and, after it is cool, disconnect the receiving tube from the flask, rinsing the joint with a little hexane. Place the tube under a nitrogen stream at room temperature and further concentrate the extract to ca. 0.5 mℓ. Rinse down the wall of the tube with hexane, delivered from a 100-μℓ syringe, diluting the extract to exactly 1.0 mℓ, and stir.

8.3.8 Inject an aliquot of the hexane solution into the gas chromatograph and obtain a chromatogram. The chromatographic conditions are:

Column temperature	220°C for columnns A and B 210°C for column C 200°C for column D
Injection port temperature	225°C
Detector temperature	200°C
Transfer line and switching valve	235°C
Carrier gas (N_2) flow	60 mℓ/min

The retention times (relative to parathion) at these conditions for parathion, related analytes, and interfering organophosphorus pesticides are tabulated below.

Column	A	B	C	D
Parathion	1.00 (4.4 min)	1.00 (8 min)	1.00 (3.4 min)	1.00
Paraoxon	0.77	1.13	1.23	1.10
Amino parathion	1.04	0.78		
Methyl parathion	0.73	0.78	1.18	0.75
Methyl paraoxon	0.56	0.88	1.41	0.83
Dursban	1.00			
Fenthion	0.97			
Ruelene		1.01		
Phosphamidon				1.02

The solvent-flush sample injection technique is recommended. Duplicate injections should be made. The hexane, which precedes the parathion, should be vented so the detector flame will not be extinguished. The conditions of the run should be such that no parathion is lost during the venting process.

8.3.9 By comparison to a standard curve for parathion, the average of the areas under the parathion peaks is converted to the amount (ng) of parathion seen by the detector. Paraoxon, or another analyte, can be quantitated by comparison of its peak area with a standard curve for the appropriate compound.

9. Calibration and Standards

9.1 Prepare at least three standard solutions in the concentration range 100 ng/mℓ to 10,000 ng/mℓ from a stock solution of parathion in hexane.

Note: Extreme care should be taken to avoid skin contact with parathion and parathion solutions.

9.2 Make duplicate injections of aliquots of each standard solution onto the gas chromatograph and determine the peak areas.

9.3 Plot the amount (ng) of parathion seen by the detector vs the peak area. Straight lines passing through the origin should result. If these conditions are not observed, either the linear range of the detector has been exceeded or a system malfunction has occurred.

9.4 Injections of standards should be interspersed among sample injections so a watch can be maintained on detector sensitivity.

10. Calculations

10.1 Determine the total amount in ng of parathion present in the sample.

$$\text{Total ng} = ng_o \times \frac{\text{Soln vol}}{\text{Inj vol}}$$

where:

ng_o = Nanograms of parathion determined from calibration curve based on peak area responses

Soln vol = volume in $\mu\ell$ of the final hexane solution (usually 1000 $\mu\ell$)

Inj vol = volume in $\mu\ell$ of the aliquot of the final hexane solution injected into the gas chromatograph

10.2 Convert the volume of air sampled to standard conditions of 25°C and 760 mm Hg.

$$V_s = V \times \frac{P}{760} \times \frac{298}{(T + 273)}$$

where:

V_s = volume of air in liters at 25°C and 760 mm Hg

V = volume of air in liters as measured

P = Barometric Pressure in mm Hg

T = Temperature of air in degrees centigrade.

10.3 The concentration of parathion can be expressed in ng per liter or μg per m^3.

$$\mu g/m^3 = ng/\text{liter}$$

$$\mu g/m^3 = \frac{\text{total ng}}{V_s} \quad \begin{matrix}\text{(Section 10.1)} \\ \text{(Section 10.2)}\end{matrix}$$

11. References

11.1 H.F. Enos, J.F. Thompson, J.B. Mann, and R.F. Moseman, "Determination of Pesticide Residues in Air," presented at the 163rd American Chemical Society National Meeting, Boston, Massachusetts, April 1972.

11.2 J.W. Miles, L.E. Fetzer, and G.W. Pearce, *Environmental Science and Technology,* 4, 420 (1970).

11.3 "Analysis of Pesticide Residues in Human and Environmental Samples," ed. F. Thompson, Perrine Primate Research Laboratories, EPA, Perrine, Florida, 1972, Section 4B and 8.

11.4 R.R. Watts and R.W. Storkerr, *Journal of the Association of Official Analytical Chemists,* 52, 513 (1969).

11.5 "Pesticide Analytical Manual, Volume I," P.E. Cornelliussen, ed., Food & Drug Administration, USDHEW, Rockville, Md., 1972, Section 313.

OIL MIST IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Oil Mist	**Method No.:**	P&CAM 159
Matrix:	Air	**Range:**	5 – 500 μg of oil
Procedure:	Fluorescence	**Precision:**	Unknown
Date Issued:	8/8/72		
Date Revised:	1/10/74	**Classification:**	D (Operational)

1. **Principle of Method**

   1.1 Air samples are collected using 37 mm membrane filters.

   1.2 Oil mist is extracted from the filters with chloroform.

   1.3 The chloroform solution is analyzed for oil content using fluorescence spectrophotometry.

2. **Range and Sensitivity**

   2.1 The sensitivity varies between oil types but is about 0.05 mg/m^3 for a 100 liter air sample.

   2.2 For a 100 liter air sample the working range is linear to at least 5 mg/m^3 and can easily be extended by dilution.

3. **Interferences**

   Highly fluorescent compounds may interfere in this analysis; however this type of compound is not generally found where oil mists are being used.

4. **Precision and Accuracy**

   The precision and accuracy of this method have not been completely determined at this time.

5. Advantages and Disadvantages of the Method

5.1 The method is simple and fast. It is specific for the oil used in the calibration and is relatively free from interference.

5.2 A disadvantage is that in all cases a bulk sample of the oil in question must be provided for use in the preparation of standards for the analysis. Some very light oils do not fluoresce readily and cannot be analyzed using this method.

6. Apparatus

6.1 **Sampling Equipment.** The sampling unit for the filter-collection method has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate cassette filter holder, either a 2- or 3-piece filter cassette.

6.1.2 A vacuum pump such as a personal sampling pump. This pump must be properly calibrated so the volume of air sampled can be measured as accurately as possible. The pump must be calibrated with a representative filter unit in the line. Flow rate, times, and/or volume must be known.

6.1.3 Thermometer.

6.1.4 Manometer.

6.1.5 Stopwatch.

6.2 0.8-μ cellulose membrane filters, or 5.0 μ PVC filters, 37 mm.

6.3 Fluorescence spectrophotometer with both excitation and analyzer scanning capabilities in the range of 250-550 mμ.

6.4 1 cm cells for fluorescence spectrophotometer.

6.5 Small glass stoppered bottles or vials for desorption of samples.

7. Reagents

7.1 **Chloroform** – Distilled reagent grade.

7.2 **Stock Solution, 100 mg/mℓ** – Weigh 10.00 g of oil into a 100 mℓ volumetric flask and dissolve with chloroform to volume.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Wash in detergent solution and follow with tap water and distilled water rinses.

8.1.2 Rinse thoroughly with acetone, then with portions of the distilled chloroform, and allow to dry.

8.2 Collection and Shipping of Samples

8.2.1 Assemble the filter unit by mounting the filter disc in the filter cassette.

8.2.2 Connect the exit end of the filter unit to the pump with a short piece of flexible tubing.

8.2.3 Turn on pump to begin sample collection. The flow rate, times, and/or volume must be measured as accurately as possible. The sample should be taken at a flow rate of 2 liters per minute. A minimum sample of 100 liters should be collected. Larger sample volumes are encouraged, provided the filters do not become loaded with dust to the point that loose material might fall off or the filter become plugged.

8.2.4 The sample cassettes should be shipped in a suitable container designed by NIOSH to minimize contamination and to prevent damage in transit. Care must be taken during storage and shipping that no part of the sample is dislodged from the filter, nor that the sample surface be disturbed in any way. Loss of sample from heavy deposits on the filter may be prevented by mounting a clean filter in the cassette on top of the sample filter.

8.2.5 With each batch of samples, one filter, labeled as a blank, must be submitted. No air should be drawn through this filter.

8.2.6 A bulk sample of the oil being used must be collected and sent to the laboratory for use as a standard material in the analysis. To prevent contamination, the bulk should not be shipped in the same container as the samples.

8.3 Analysis of Samples

8.3.1 Transfer sample and blank filters into separate small glass stoppered bottle or vial containing 5 mℓ of chloroform. The chloroform must completely cover the filter.

8.3.2 Seal each bottle and allow to stand for at least 30 minutes with occasional agitation. At this point the oil is in solution and the samples are ready for analysis.

8.3.3 Determine the proper excitation wavelength for the analysis using an oil solution containing 100 μg/mℓ. This solution is prepared by proper dilution of the stock solution with chloroform.

8.3.4 Transfer the sample and blank solutions to 1 cm cells and record a fluorescence spectrum for each solution using the previously determined excitation wavelength.

8.3.5 The peak-height of the largest fluorescent peak is used to measure the oil concentration from the calibration curve prepared from the bulk samples (Section 8.2.6).

9. Calibration and Standards

9.1 Appropriate dilutions of the stock solution with chloroform are made to obtain working standards in the range of 1.0 μg/mℓ to 100 μg/mℓ.

9.2 The working standards are transferred to 1 cm cells and a fluorescence spectrum is obtained for each standard. A calibration curve is constructed by measuring the peak height of the largest fluorescent peak and plotting this value vs. concentration in μg/mℓ.

10. Calculations

10.1 Blank values, if any, should first be subtracted from each sample.

10.2 The concentration of oil in the air sampled can be calculated as mg of oil per cubic meter or μg oil per liter.

$$\text{mg oil/m}^3 = \mu\text{g oil/}\ell$$

$$\text{mg oil/m}^3 = \frac{\mu\text{g oil/m}\ell}{V_s} \times \text{m}\ell \text{ solution}$$

where:

μg oil/mℓ = concentration of oil derived from the proper calibration curve (Section 9.2)
mℓ solution = final volume of sample analyzed including any dilution factor
V_s = volume of air sampled in ℓ at 25°C and 760 mm Hg.

11. References

11.1 Roy, E.M., American Industrial Hygiene Journal, 31, 472 (1970).

11.2 Lippmann, M., et al, Arch. Environ. Health, 21, 591 (1970).

SULFUR DIOXIDE IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Sulfur Dioxide	**Method No:**	P&CAM 160
Matrix:	Air	**Range:**	0.003-5.0 ppm SO_2
Procedure:	Collection via Impinger/ Colorimetric	**Precision:**	$\pm$5%
Date Issued:	11/22/72		
Date Revised:	1/15/74	**Classification:**	C (Tentative)

1. **Principle of the Method**

1.1 Sulfur dioxide is absorbed by aspirating a measured air sample through a solution of potassium or sodium tetrachloromercurate (TCM). This procedure results in the formation of a dichlorosulfitomercurate complex, which resists oxidation by the oxygen in the air.

1.2 Ethylenediaminetetraacetic acid disodium salt (EDTA) is added to this solution to complex heavy metals that can interfere by oxidation of the sulfur dioxide before formation of the dichlorosulfitomercurate. After the absorption is completed, any ozone in the solution is allowed to decay.

1.3 The sample is first treated with 0.6% sulfamic acid to destroy any nitrite anions formed from the absorption of oxides of nitrogen in the air.

1.4 Next the sample is treated with formaldehyde and specially purified acid – bleached pararosaniline containing phosphoric acid to control pH. This forms the intensely colored pararosaniline methyl sulfonic acid which behaves as a pH indicator.

1.5 The pH of the final solution is adjusted to 1.6 ± 0.1 by the addition of 3M phosphoric acid.

1.6 Maximum absorbance is read spectrophotometrically at the 548 nm wavelength.

2. Range and Sensitivity

2.1 The lower limit of detection of sulfur dioxide in 10 mℓ of potassium or sodium tetrachloromercurate is 0.3 μℓ (based on twice the standard deviation), representing a concentration of 0.01 ppm (26 $\mu g/m^3$) of SO_2 in an air sample of 30 liters.

2.2 Beer's Law is followed through the working range from 0.005 to 1.0 absorbance units (0.2 to 35.0 μg in 25 mℓ of final solution). One cannot extrapolate beyond these ranges by changing volumes of atmosphere sampled unless the absorption efficiency of the particular system is known or determined at the volumes and concentrations under study.

2.3 Atmospheric sulfur dioxide concentrations of interest usually range from a few pphm to a few ppm. Higher concentrations (5 to 500 ppm) employed in special studies must be analyzed by using smaller gas samples, by analyzing an aliquot of the sample, or by diluting the sample with absorbing solution.

2.4 Collection efficiency falls off rapidly below 0.01 ppm and varies with the geometry of the absorber, the size of the gas bubbles, and the contact time with the solution.

3. Interferences

3.1 Interferences by oxides of nitrogen are minimized by the addition of sulfamic acid.

3.2 Interference from ozone is eliminated by a 20 minute delay prior to analysis, permitting any ozone present to decay.

3.3 Heavy metal concentrations in the atmosphere should not produce significant interference. However, addition of EDTA is recommended when low levels of sulfur dioxide are to be measured or when contamination by heavy metals is unusually high. A minimum EDTA concentration of 7 times the anticipated amount of metal interference should be added. At least 60 μg of Fe (III), 10 μg of Mn (II), and 10 μg of Cr (III) in 10 mℓ of absorbing reagent can be tolerated in the procedure. No significant interference was found with 10 μg of Cu (II) and 22 μg of V (V).

4. Precision and Accuracy

Standard deviation at the 95% confidence level is 5%.

5. Advantages and Disadvantages of the Method

5.1 The method is selective, sensitive, reproducible, and suitable for field use. However, many critical variables such as pH, temperature, impurities in reagents and in water must be carefully controlled for reliable results.

5.2 Solutions of bisulfite or sulfite are unstable as calibration standards. Careful standardization and immediate dilution with potassium tetrachloromercurate (TCM) are required for accurate results. Care must be taken with this reagent because it is very poisonous.

6. Apparatus

6.1 **Sampling Equipment.** The sampling unit for the impinger collection method consists of the following components:

6.1.1 A prefilter unit (if needed) which consists of the filter media and cassette filter holder.

6.1.2 A midget impinger containing the absorbing solution or reagent.

6.1.3 A pump suitable for delivering desired flow rates. The sampling pump is protected from splashover or water condensation by an adsorption tube loosely packed with a plug of glass wool and inserted between the exist arm of the impinger and the pump.

6.1.4 An integrating volume meter such as a dry gas or wet test meter.

6.1.5 Thermometer.

6.1.6 Manometer.

6.1.7 Stopwatch.

6.2 Volumetric flasks – 25, 100, 250, and 1000 mℓ capacity.

6.3 Pipets and Graduates.

6.4 Spectrophotometer suitable for measurement of color at 548 nm, preferably with a spectral band width less than 16 nm.

6.5 Glass cuvettes with 1 cm path length.

7. Reagents

All chemicals except for the dye are analytical reagent grade. The pararosaniline dye should meet the specifications as outlined below:

7.1 Double distilled water, free from oxidants.

7.2 **Absorbing Reagent, 0.04M Potassium Tetrachloromercurate (TCM).** Dissolve 10.86 g of mercuric chloride and 5.96 of potassium chloride in water and bring to volume in a 1-liter volumetric flask.

Caution: highly poisonous. If spilled on skin, flush with water immediately.

If excessive heavy metal interferences are expected add 0.07 g of ethylenediaminetetraacetic acid disodium salt (EDTA). The absorbing solution is normally stable for six months but if a precipitate forms, discard the solution. To prevent deterioration, the absorbing reagent must be shielded from sunlight during storage, and during and after sampling by covering the containers with a suitable wrapping, such as aluminum foil.

7.3 **Sulfamic Acid** (0.6%). Dissolve 0.6 g of sulfamic acid in 100 mℓ of water. This reagent can be kept for a few days if protected from air.

7.4 **1-Butanol.** Certain batches of 1-butanol contain oxidants that create an SO_2 demand. Check by shaking 20 mℓ of 1-butanol with 5 mℓ of 15% potassium iodide (KI solution). If a yellow color appears in the alcohol phase redistill the 1-butanol from silver oxide.

7.5 **Buffer Stock Solution (pH 4.69).** In a 100-mℓ volumetric flask, dissolve 13.61 g of sodium acetate trihydrate in water. Add 5.7 mℓ of glacial acetic acid and dilute to volume with water.

7.6 **Hydrochloric Acid (1M).** Dilute 86 mℓ of concentrated hydrochloric acid (HCl, sp gr 1.19) to 1 liter.

7.7 **Phosphoric Acid (3M).** Dilute 205 mℓ of concentrated phosphoric acid (H_3PO_4, sp gr 1.69) to 1 liter.

7.8 **Purified Pararosaniline** (99% or better), 0.2% (nominal) stock solution. Specifically purified pararosaniline dye 99.0 percent is used. Weigh 0.200 g and completely dissolve the dye by shaking with 100 mℓ of 1M HCl in a 100-mℓ graduated cylinder that is glass-stoppered.

7.9 **Pararosaniline Reagent.** To a 250-mℓ volumetric flask add 20 mℓ of stock pararosaniline reagent. Add an additional 0.2 mℓ of stock for each percent the stock assays below 100 percent. Then add 25 mℓ of 3M H_3PO_4 and dilute to volume with water. These reagents are stable for at least 9 months.

7.10 **Formaldehyde (0.2%).** Dilute 5 mℓ of 36 to 38% formaldehyde to 1 liter with water. Prepare this solution daily.

7.11 **Reagents for Standardization**

7.11.1 **Stock Iodine Solution (0.1N).** Place 12.7 g of iodine in a 250-mℓ beaker, add 40 g of KI and 25 mℓ of water. Stir until all is dissolved, then dilute to 1 liter with water.

7.11.2 **Working Iodine Solution (0.01N).** Prepare approximately 0.01N iodine solution by diluting 50 mℓ of the stock solution to 500 mℓ with distilled water.

7.11.3 **Starch Indicator Solution.** Triturate 0.4 g of soluble starch and 0.002 g of mercuric iodide (preservative) with a little water, and add the paste slowly to 200 mℓ of boiling water. Continue boiling the solution until it is clear; cool and transfer it to a glass stoppered bottle.

7.11.4 **Sodium Thiosulfate, Standard Solution (0.1N).** Dissolve 25 g of sodium thiosulfate ($Na_2S_2O_3-5H_2O$) in 1 liter of freshly boiled, cooled distilled water and add 0.1 g of sodium carbonate to the solution. Allow the solution to stand for one day before standardizing. To standardize, weigh 1.5 g of potassium iodate, primary standard grade, that was dried at 180°C and dilute to volume in a 500-mℓ volumetric flask. To a 500-mℓ iodine flask, pipet 50 mℓ of the iodate solution. Add 2 g of potassium iodide and 10 mℓ of a 1 + 10 dilution of concentrated hydrochloric acid. Stopper the flask. After 5 minutes titrate with thiosulfate to a pale yellow color. Add 5 mℓ of starch indicator and complete the titration. Calculate the normality of sodium thiosulfate, N, as follows:

$$N = [\text{weight (g } KIO_3) \times 10^3 \times 0.1]/(\text{mℓ of titer} \times 35.67)$$

7.11.5 **Standard 0.01N Sodium Thiosulfate.** Dilute 50.0 mℓ of standard 0.1N sodium thiosulfate to 500 mℓ with distilled water and mix. This 0.01N solution is not stable, and must be prepared fresh on the day it is used by diluting the standard 0.1N sodium thiosulfate.

7.11.6 **Standard Sulfite Solution.** Dissolve 0.4 g of sodium sulfite (Na_2SO_3) or 0.3 g of sodium metabisulfite ($Na_2S_2O_5$) in 500 mℓ of recently boiled and cooled distilled water. (Double distilled water that has been deaerated is preferred.) This solution contains from 320 to 400 μg/mℓ as SO_2. The actual concentration in the standard solution is determined by adding excess iodine and back titrating with sodium thiosulfate that has been standardized against potassium iodate or dichromate (primary standard). Sulfite solution is unstable.

Back titration is performed in the following manner: Add 25 mℓ of distilled water to a 500-mℓ iodine flask and pipet 50 mℓ of the 0.01N iodine solution into the flask designated flask A (blank). Pipet in order 25 mℓ of the standard sulfite solution to a second 500-mℓ iodine flask and pipet 50 mℓ of the 0.01N iodine into this flask designated B (sample). Stopper the flasks and allow to react for 5 minutes. By means of a buret containing standard 0.01N thiosulfate solution, titrate each flask in turn to a pale yellow color. Then add 5 mℓ of starch solution and continue the titration to the disappearance of the blue color. Calculate the concentration of SO_2 in the standard solution as follows:

$$SO_2, \mu g/m\ell = (A - B)\, NK\, /V$$

where:

A = milliliters of thiosulfate solution required for titration of the blank

B = milliliters of thiosulfate solution required for titration of the sample

N = normality of the thiosulfate solution

K = micro-equivalent weight for SO_2 = 32,030

V = milliliters of sample taken

8. **Procedure**

8.1 **Cleaning of Equipment.** All glassware should be cleaned initially using the following procedure:

8.1.1 Wash in detergent – tap water and follow with tap and distilled water rinses.

8.1.2 Soak in chromic acid cleaning solution for at least 30 minutes and follow with tap and distilled water rinses.

8.1.3 Soak in concentrated nitric acid for at least 30 minutes and follow with thorough tap, distilled, and double distilled water rinses, making sure no trace of acid remains.

8.2 **Collection and Shipping of Samples**

8.2.1 Pour 10 mℓ of the absorbing solution (Section 7) into the midget impinger, using a graduated cylinder to measure the volume.

8.2.2 Connect the impinger (via the absorption tube) to the vacuum pump and the prefilter assembly (if needed) with a short piece of flexible tubing. The minimum amount of tubing necessary to make the joint between the prefilter and impinger should be used. The air being sampled should not be passed through any other tubing or other equipment before entering the impinger.

8.2.3 Turn on pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible. The sample should be taken at a flow rate of 0.2-1 ℓpm. A sample size of not more than 5 liters and no less than 4 liters should be collected. The minimum volume of air sampled will allow the measurement at least 1/10 times the TLV, 1.3 mg/m^3 (760 mm Hg, 25°C).

8.2.4 After sampling, the impinger stem can be removed and cleaned. Tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Wash the stem with a small amount (1-2 mℓ) of unused absorbing solution and add the wash to the impinger. Then the impinger is sealed with a hard, non-reactive stopper (preferably Teflon). Do not seal with rubber. The stoppers on the impingers should be tightly sealed to prevent leakage during shipping. If it is preferred to ship the impingers with the stems in, the outlets of the stem should be sealed with Parafilm or other non-rubber covers, and the ground glass joints should be sealed (i.e., taped) to secure the top tightly.

8.2.5 Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within a day.

8.2.6 Whenever possible, hand delivery of the samples is recommended. Otherwise, special impinger shipping cases designed by NIOSH should be used to ship the samples.

8.2.7 A "blank" impinger should be handled as the other samples (fill, seal and transport) except that no air is sampled through this impinger.

8.2.8 Where a prefilter has been used, the filter cassettes are capped and placed in an appropriate cassette shipping container. One filter disc should be handled like the other samples (seal and transport) except that no air is sampled through, and this is labeled as a blank.

8.3 **Analysis of Samples**

8.3.1 Transfer the collected sample quantitatively to a 25-mℓ volumetric flask, using about 5 mℓ of water for rinsing. Aliquots may be taken at this point if the concentration or volume of reagent is large.

8.3.2 If the presence of ozone is suspected, delay analysis for 20 minutes after sampling to allow the ozone to decompose.

8.3.3 For each set of determinations, prepare a reagent blank by adding 10 mℓ of the unexposed absorbing reagent to a 25-mℓ volumetric flask.

8.3.4 To each flask add 1 mℓ of 0.6% sulfamic acid and allow to react for 10 minutes to destroy the nitrite from oxides of nitrogen.

8.3.5 Accurately pipet in 2 mℓ of the 0.2% formaldehyde, then 5 mℓ of pararosaniline reagent.

8.3.6 Start a laboratory timer that has been set for 30 minutes. Bring all flasks to volume with freshly boiled distilled water.

8.3.7 After 30 minutes, determine the absorbances of the sample and of the blank at the wavelength of maximum absorbance, 548 nm. Use water (not the reagent blank) in the reference cell. Do not allow the colored solution to stand in the absorbance cell or a film of dye will be deposited.

8.3.8 If the absorbance of the sample solution ranges between 1.0 and 2.0, the sample can be diluted 1 to 1 with a portion of the reagent blank and read within a few minutes. Solutions with high absorbance can be diluted up to sixfold with the reagent blank in order to obtain on-scale readings within 10% of the true absorbance value.

9. **Calibration and Standards**

9.1 Immediately after standardization of the sulfite solution, pipet 2 mℓ of the freshly standardized solution into a 100-mℓ volumetric flask and bring to mark with 0.04M TCM. This solution is stable for 30 days if stored at 5°C.

9.2 Pipet graduated amounts of the diluted sulfite solution (such as 0, 1, 2, 3, 4, and 5 mℓ) into a series of 25-mℓ volumetric flasks.

9.3 Add sufficient 0.04M TCM to each flask to bring the volume of its contents to approximately 10 mℓ.

9.4 Add the remaining reagents as described in the procedure. For greater precision, a constant-temperature bath is preferred. The temperature of calibration should not differ from the temperature of analysis by more than a few degrees.

9.5 Plot total absorbance of these solutions (as ordinates) against the total micrograms of SO_2. A linear relationship is obtained.

9.6 The absorbance should be read on the samples and standards in the same cell; if more than one cell is used, the cells should be matched spectrophotometrically.

9.7 The intercept with the vertical axis of the line best fitting the points is usually within 0.2 absorbance unit of the blank (zero standard) reading. Under these conditions the plot need be determined only once to evaluate the calibration factor (reciprocal of the slope of the line). This calibration factor can be used for calculating results provided there are no radical changes in temperature or pH. At least one control sample is recommended per series of determinations to ensure the reliability of this factor.

10. Calculations

10.1 Calculate the concentration of SO_2 in the sample as follows:

$$SO_2, \text{ ppm} = (A - Ao)\ 0.382B/V$$

where:

A = sample absorbance

Ao = reagent blank absorbance

0.382 = volume ($\mu\ell$) of 1 μg of SO_2 at 25°C, 760 mm Hg

B = calibration factor, μg/absorbance unit

V = sample volume in liters corrected to 25°C, 760 mm Hg by PV = nRT

10.2 The SO_2 concentration can also be expressed in mg/m^3 of air which is numerically equal to $\mu g/\ell$ of air.

$$mg/m^3 = \mu g\ SO_2/\ell$$

$$= (A - Ao)\ B/V$$

11. References

11.1 Scaringelli, F.P., Saltzman, B.E., and Prey, S.A., "Spectrophotometric Determination of Atmospheric Sulfur Dioxide," *Analytical Chemistry, Vol.*, 39, No. 14, 1967, p. 1709.

11.2 "Sulfur Dioxide Content of the Atmosphere," ASTM Standard D2914, 1971.

SULFUR DIOXIDE IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Sulfur Dioxide	**Method No:**	P&CAM 163
Matrix:	Air	**Range:**	0.01-5 mg
Procedure:	Collection via Impinger by Peroxide Absorption/Titration with Barium Perchlorate	**Precision:**	4% RSD at 2.5 ppm
Date Issued:	1/26/73		
Date Revised:	5/1/73	**Classification:**	D (Operational)

1. **Principle of the Method**

1.1 Sulfur dioxide in the air is absorbed and oxidized in 0.3N hydrogen peroxide (H_2O_2) reagent.

1.2 The pH of the sample solution is adjusted with dilute perchloric acid. After isopropyl alcohol is added, bringing the alcohol concentration to approximately 80% by volume, the resulting solution is titrated with 0.005M barium perchlorate using Thorin as the indicator. There is a sharp change from yellow to pink at the end point.

2. **Range and Sensitivity**

This method is sensitive to 0.1 mg SO_2 per cubic meter assuming a 100-liter air sample. This level corresponds to approximately 0.25 ppm SO_2 in air. The upper limit is the amount of SO_2 absorbed in the hydrogen peroxide reagent and is at least 5 mg.

3. **Interferences**

3.1 Trapped particulate sulfates, and sulfuric acid in the air sample would give erroneously high sulfur dioxide values. However, these can be eliminated by placing a 0.8μ cellulose filter upstream of the impinger in the sampling train.

3.2 Metal ion interferences can be eliminated either by the use of a prefilter or by passing the solution through an ion exchange column.

3.3 Concentrations of phosphate ions greater than the sulfate ion concentration cause appreciable interference. Phosphate can be removed by precipitation with magnesium carbonate. The use of a prefilter should also remove phosphates.

4. **Precision and Accuracy**

At 2.5 ppm, the accuracy is 5% with a relative standard deviation of 4%. At 25 ppm, accuracy and relative standard deviation can be improved to about 1%.

5. **Advantages and Disadvantages**

5.1 The samples are easily collected and conveniently shipped to the laboratory for analysis in glass vials.

5.2 The sulfuric acid formed is stable and nonvolatile, making this manner of collection of SO_2 desirable.

5.3 The analysis is relatively rapid and simple.

6. **Apparatus**

6.1 **Sampling Equipment.** The sampling unit for the impinger collection method consists of the following components:

6.1.1 A prefilter unit (if needed) which consists of the filter media and cassette filter holder.

6.1.2 A midget impinger containing the absorbing solution or reagent.

6.1.3 A pump suitable for delivering desired flow rates. The sampling pump is protected from splashover or water condensation by an adsorption tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump.

6.1.4 An integrating volume meter such as a dry gas or wet test meter.

6.1.5 Thermometer.

6.1.6 Manometer.

6.1.7 Stopwatch.

6.2 Millipore 0.8μ cellulose AA filters and cassettes.

6.3 Necessary glassware.

6.4 **Burette.** A burette of 10 milliliter capacity graduated in 0.05 milliliter subdivisions.

6.5 Daylight fluorescent lamp aids in identifying the end point.

6.6 **Ion Exchange Resin.** Dowex 50 x 8, 20-50 mesh, hydrogen form ion exchange columns may be constructed using glass burettes or tubing. A column with an inside diameter of 8 mm and 7 inches of resin has a capacity of approximately 25 milliequivalents.

7. **Reagents**

7.1 **Alcohol,** Isopropanol, reagent grade.

7.2 **Barium Perchlorate, 0.005M.** Dissolve 2.0 g of barium perchlorate trihydrate in 200 mℓ of water and add 800 mℓ of isopropanol. Adjust apparent pH to about 3.5 with perchloric acid. Standardize against 0.005M H_2SO_4.

7.3 **Thorin.** Prepare a 0.1% to 0.2% solution in distilled water.

7.4 **Standard Sulfate Solution.** Prepare a 0.005M solution of H_2SO_4 and standardize by titration with 0.02N sodium hydroxide or dissolve 0.7393 g anhydrous Na_2SO_4 in distilled water and dilute to one liter (1 mℓ = 0.5 mg SO_4). The sodium is removed by passage of the standard through the ion exchange column.

7.5 **Hydrochloric Acid, 4N.** Add 300 mℓ concentrated HCl to 600 mℓ of distilled water. Needed only to regenerate the column if the ion exchange procedure is used.

7.6 **Absorbing Solution – Hydrogen Peroxide, 0.3N.** Dilute 17 mℓ of 30% H_2O_2 solution to one liter with distilled water.

7.7 **Perchloric Acid, 1.8%.** Dilute 25 mℓ of reagent grade perchloric acid (70-72%) to one liter with distilled water.

8. **Procedure**

8.1 **Cleaning of Equipment.** The glassware should be chemically clean. Wash in detergent, and rinse thoroughly with tap water and distilled water.

8.2 Collection and Shipping of Samples

8.2.1 Pour 15 mℓ of the absorbing solution (Section 7) into the midget impinger, using a graduated cylinder to measure the volume.

8.2.2 Connect the impinger via the absorption tube to the vacuum pump, and the prefilter assembly (if needed) with a short piece of flexible tubing. The minimum amount of tubing necessary to make the joint between the prefilter and impinger should be used. The air being sampled should not be passed through any other tubing or other equipment before entering the impinger.

8.2.3 Turn on pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible. The sample should be taken at a flow rate of 1-2 ℓpm. A sample size of not more than 100 liters and no less than 10 liters should be collected. The minimum volume of air sampled will allow the measurement at least 1/10 times the TLV, 1.3 mg/m^3 (760 mm Hg, 25°C).

8.2.4 After sampling, the impinger stem can be removed and cleaned. Tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Wash the stem with a small amount (1-2 mℓ) of unused absorbing solution and add the wash to the impinger. Then the impinger is sealed with a hard, non-reactive stopper (preferably Teflon). Do not seal with rubber. The stoppers on the impingers should be tightly sealed to prevent leakage during shipping. If it is preferred to ship the impingers with the stems in, the outlets of the stem should be sealed with Parafilm or other non-rubber covers, and the ground glass joints should be sealed (i.e., taped) to secure the top tightly.

8.2.5 Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within a day.

8.2.6 Whenever possible, hand delivery of the samples is recommended. Otherwise, special impinger shipping cases designed by NIOSH should be used to ship the samples.

8.2.7 A "blank" impinger should be handled as the other samples (fill, seal and transport) except that no air is sampled through this impinger.

8.2.8 Where a prefilter has been used, the filter cassettes are capped and placed in an appropriate cassette shipping container. One filter disc should be handled like the other samples (seal and transport) except that no air is sampled through, and this is labeled as a blank.

8.3 **Ion Exchange Procedure.** (Used to purify Standard Sulfate Solution and for samples only when filters were not used in front of the impinger.)

8.3.1 When about two-thirds of the resin's capacity has been exhausted (deterioration in sharpness of the end point), regenerate the resin by passing 30 mℓ of 4N hydrochloric acid through the column.

After thorough washing with distilled water, the column is ready for use.

8.3.2 Since small volumes of sample solution are passed through the ion exchange column, care must be taken not to dilute the sample with distilled water that remains on the resin. One way this can be accomplished is by blowing some air through the resin with a squeeze bulb to remove most of the distilled water from the ion exchange resin. One or two milliliters of sample are passed through the column and discarded after air is again blown through the resin. The remainder of the sample is then passed through the ion exchange column, and an aliquot is titrated according to the general procedure (Section 8.4.3).

8.3.3 The column is flushed with distilled water between samples to prevent contamination from the previous sample.

8.4 **Analysis of Samples**

8.4.1 Measure the volume of the sample solution or dilute it to a given volume.

8.4.2 Although all samples may be passed through the ion exchange column, it is necessary to do so only when the metal concentration exceeds that of the sulfate. The ion exchange procedure is detailed in Section 8.3. Use of a prefilter upstream from the impinger should remove most metal ions, however, and thus eliminate this entire step.

8.4.3 To a 10-mℓ aliquot, add 40 mℓ isopropanol. If necessary, adjust the pH, to between 2.5 and 4.0 with perchloric acid. Add 1-3 drops Thorin indicator and titrate with barium perchlorate, taking the change from yellow or yellow-orange to pink as the end point.

8.4.4 Analyze the standard and absorbing solution blank in the same manner.

9. **Calibration and Standards**

9.1 The barium perchlorate solution is standardized by titrating a 5-mℓ aliquot of the standardized H_2SO_4 (0.005M) to the end point with Thorin as indicator. The molarity of the solution is calculated as follows:

$$M_{Ba\,(ClO_4)_2} = \frac{m\ell_{H_2SO_4} \times M_{H_2SO_4}}{m\ell_{Ba(ClO_4)_2}}$$

The molarity of the $Ba(ClO_4)_2$ solution should be checked periodically following this same procedure.

9.2 If anhydrous sodium sulfate is used to standardize the barium perchlorate, it must first be ion exchanged since sodium obscures the end point. A 5-mℓ aliquot of the 0.5 mg/mℓ sulfate solution is ample for standardization.

10. Calculations

10.1 The analytical results are computed on the basis of the following reactions:

$$SO_2 + H_2O_2 \longrightarrow H_2SO_4$$

$$H_2SO_4 + Ba(ClO_4)_2 \longrightarrow BaSO_4 \downarrow + 2\,HClO_4$$

10.2 The concentration can be expressed as mg SO_2/m^3,

$$\frac{\text{mg } SO_2}{m^3} = \frac{m\ell_s \times M_{Ba(ClO_4)_2} \times MW_{SO_2}}{Vm^3} \times \frac{V}{V_{aliq}}$$

where:

$m\ell_s$ = mℓ of $Ba(ClO_4)_2$ solution needed to titrate the sample aliquot minus the blank value.

$M_{Ba(ClO_4)_2}$ = molarity of the $Ba(ClO_4)_2$ solution

MW_{SO_2} = molecular weight of SO_2 = 64

Vm^3 = Volume of air sampled, in cubic meters at 760 mm Hg, 25°C (1 m^3 = 1000 ℓ)

V_{aliq} = Volume of sample aliquot used for the titration, in mℓ

V = Original volume of sample in impinger, in mℓ

10.3 The SO_2 concentration of the sample can also be expressed in ppm,

$$\text{ppm } SO_2 \text{ by volume} = \frac{m\ell_s \times M_{Ba(ClO_4)_2} \times 24{,}450}{V_1} \times \frac{V}{V_{aliq}}$$

where:

V_1 = Volume of air sampled in liters at 25°C and 760 mm Hg.

24,450 = mℓ occupied by one mole of ideal gas at 25°C and 760 mm Hg.

11. References

11.1 Fritz, J.S., and Yamamura, S.S., *Anal. Chem.*, 27, 1461 (1955).

11.2 Leithe, W., "The Analysis of Air Pollutants," Ann Arbor Science Press, 1970.

11.3 Kundig, Chem. Rundechau 18, 123 (1965).

11.4 Fielder & Morgan, *Anal. Chem. Acta*, 23, 538 (1960).

11.5 Fielder & Morgan, *Z. Anal. Chem.*, 183, 455 (1961).

MERCURY IN URINE

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Mercury	**Method No.:**	P&CAM 165
Matrix:	Urine	**Range, Urine:**	0.003 – > 0.3 mg/ℓ
Procedure:	Flameless Atomic Absorption	**Precision:**	± 3%
		Classification:	B (Accepted)
Date Issued:	2/13/73		
Date Revised:	1/15/74		

1. **Principle of the Method**

   1.1 After initial decomposition of the urine sample with nitric acid, the mercury is reduced to its elemental state with stannous chloride.

   1.2 Mercury vapor is bubbled through an absorption cell attached to a model MAS-50 (Mercury Analyzer System) or equivalent and the absorption is measured at the 253.7 nanometer line.

   1.3 The absorption signal is recorded and used to determine the concentration of mercury present.

2. **Range and Sensitivity**

   2.1 For a 1.0 mℓ urine sample the sensitivity is 0.003 mg/ℓ or below. This corresponds to an absolute sensitivity of 3 nanograms of mercury.

   2.2 The range extends up to 0.3 mg/ℓ for a 1.0 mℓ aliquot. The range can be extended beyond 0.3 mg/ℓ by taking an aliquot of urine that is less than 1.0 mℓ.

3. **Interferences**

   3.1 Metals such as gold, platinum and copper will interfere since they form an alloy with the reduced Hg.

3.2 Certain organic solvents, such as benzene, that absorb 253.7 nanometer radiation would interfere if present in significant amounts as would any substance with broad absorption such as dust, water droplets, etc.

4. Precision and Accuracy

4.1 Comparisons of bubbler recoveries from water standards and urine samples spiked with identical amounts of radio or stable mercury indicate that the urine samples give a 10% lower signal (Figure 1). Although the use of water standards may reduce the accuracy of the method, results may be acceptable for routine analyses. Where more accurate values are needed a multiple addition technique using the same urine spiked with Hg standard is recommended.

4.2 Absolute deviations from the means between sets of identical samples varied from 0.000 to 0.005 mg/ℓ. The average relative standard deviation (1 σ) was ± 3%.

4.3 The temperature of the water used to dilute the sample should be controlled to within ±1°C.

4.4 At least 5 mℓ of nitric acid per 1 mℓ sample should be used to insure the release of metabolized mercury.

4.5 Only aliquots of urine less than one mℓ should be used if water standards are used. *Larger* aliquots of urine would increase the difference in transfer efficiency between water standards and urine (Figure 1).

5. Advantages of the Method

A trained technician can do 20-40 samples a day.

6. Apparatus

6.1 Mercury Evolution Train

6.1.1 **Bubbler Flask** – 300 mℓ BOD sample bottle as supplied with Coleman Model MAS-50 or equivalent.

6.1.2 **Connecting Tubing** – minimum lengths of either glass or Tygon.

6.1.3 **Drying Tube** – approximately 8 cm length (optional)

6.2 Analytical Equipment

6.2.1 Coleman Mercury Analyzer Model MAS-50 or equivalent.

6.2.2. Pipets

7. Reagents

All reagents used must be analytical reagent grade.

7.1 Double distilled water.

7.2 **Nitric Acid**, concentrated

7.3 **Stannous Chloride Solution**, 20% (w/v) in 6 N HCl – freshly prepared.

7.4 **Standard Stock Mercury Solution**. Add 0.1000 g metallic mercury or 0.1708g mercuric nitrate, $Hg(NO_3)_2 \cdot H_2O$, into a clean, dry 100 mℓ volumetric flask. Add 10 mℓ concentrated HNO_3, dissolve the mercury, and then dilute to the mark with double distilled water. Pipet exactly 10.0 mg of Hg into a one-liter volumetric flask. Add 50 mℓ concentrated HNO_3 and dilute to the mark with water. The final concentration is 10 μg/mℓ. This solution is stable for 6 months.

7.5 **Working Standard Mercury Solution**. Transfer 10.0 mℓ of the standard stock solution to a one-liter volumetric flask. Add 50 mℓ concentrated HNO_3 and dilute to the mark with double distilled water. The final concentration is 0.1 μg/mℓ. This solution should be prepared fresh daily.

7.6 **Potassium Persulfate**, low nitrogen.

7.7 **Magnesium Perchlorate** – anhydrous.

8. Procedure

8.1 **Cleaning of Equipment**. Acid-clean all glassware before use. This can be done by using the following procedure:

8.1.1 Wash in detergent-tap water solution and follow with tap water.

8.1.2 Soak in concentrated HNO_3 for 30 minutes and follow with tap, distilled, and double-distilled water rinses.

8.2 **Collection and Shipping of Samples**

8.2.1 Urine samples must be collected in acid cleaned borosilicate bottles. At least 25 mℓ should be collected.

8.2.2 The samples must be preserved by the addition of 0.1 g potassium persulfate per 100 mℓ of urine. Urine treated with potassium persulfate is stable at room temperature for 2 weeks.

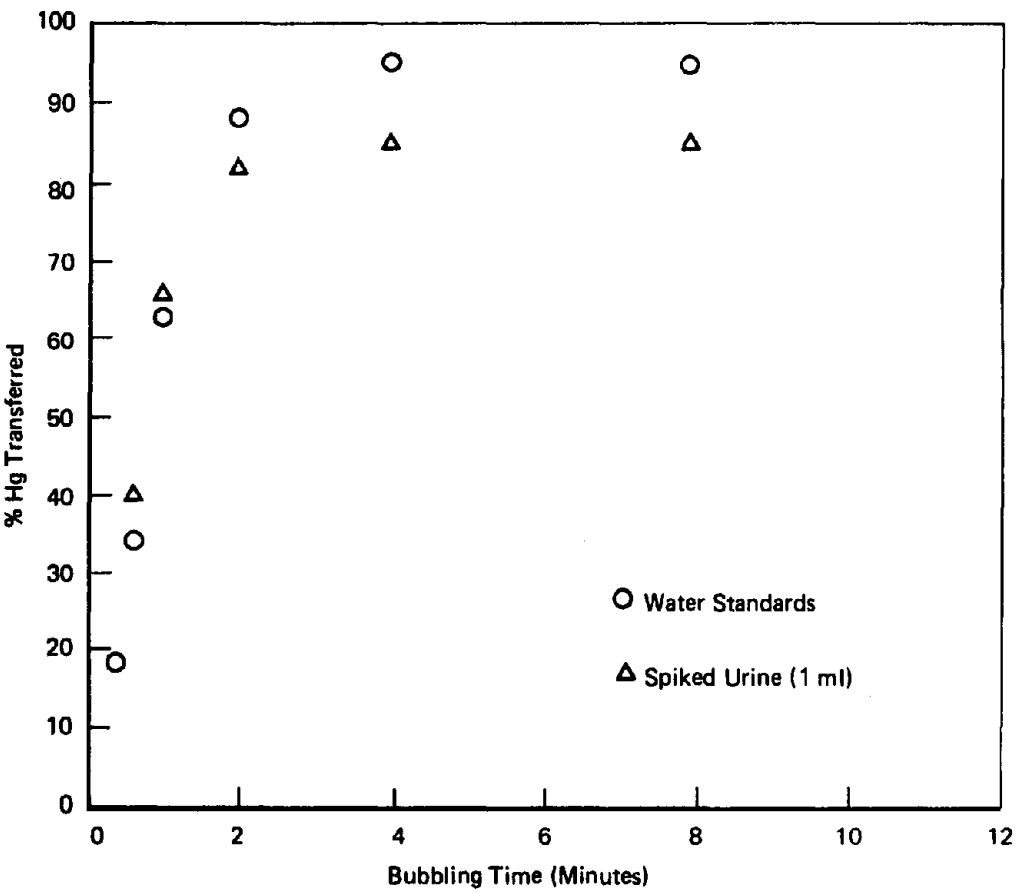


FIGURE 1 TRANSFER EFFICIENCY IN THE BUBBLER SYSTEM

8.3 **Analysis of Samples**

8.3.1 Transfer a 1.0 mℓ urine sample to the BOD bottle. If a sediment is present in the collection bottle, shake well immediately before removing the aliquot. Add 5 mℓ of concentrated HNO_3 to the BOD bottle and allow the sample to stand at room temperature for 3 minutes.

8.3.2 Dilute to 100 mℓ with distilled water at room temperature and gently blow out any mist that may form above the liquid. Add 1.0 mℓ of freshly prepared $SnCl_2$ solution and immediately connect the flask to the generating train shown in Figure 2.

8.3.3 The system is run until maximum signal is attained as shown on a recorder. Peak heights are used in the calculations.

8.3.4 The drying tube in the mercury transfer train results in the loss of some mercury. However, the drying tube will give lower background signals. If a drying tube is used it must be repacked with fresh magnesium perchlorate after 20 analyses.

8.3.5 Remove the BOD bottle and allow the signal to return to zero.

9. **Calibration and Standards**

9.1 Standards for instrument calibration are analyzed exactly as samples except that known amounts of mercury are added to the sample.

9.2 The calibration curve for the multiple addition method is constructed by subtracting the reading of the unspiked urine from that of the spiked aliquots.

9.3 For routine analysis a calibration curve may be constructed using water standards instead of spiked urine; however, this will result in loss of accuracy.

9.4 The calibration is repeated with appropriate quantities of mercury to cover a working range.

10. **Calculations**

10.1 Subtract the background signal, if any, from the sample signal.

10.2 Micrograms of mercury are determined directly from the calibration curve using the corrected signal peak height obtained for each sample.

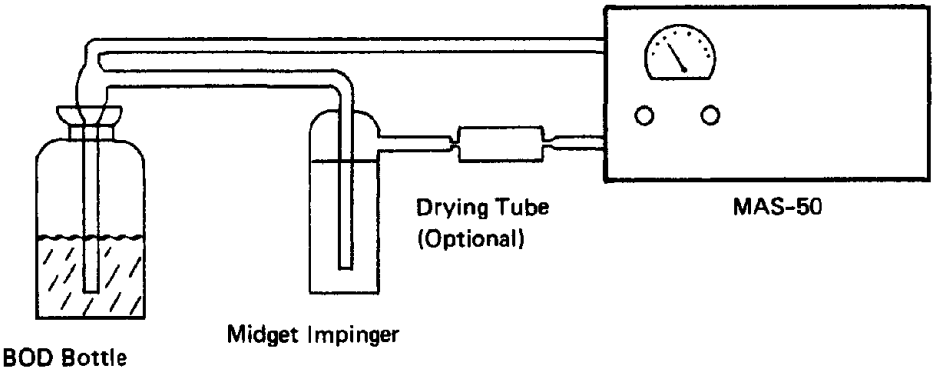


FIGURE 2 ANALYTICAL APPARATUS

10.3 The mercury concentration is calculated by dividing the micrograms of mercury by the sample volume analyzed to give μg Hg/liter.

11. References

11.1 Rathje, Arnold O., "A Rapid Ultraviolet Absorption Method for the Determination of Mercury in Urine," Am. Ind. Hyg. Assoc. J. 30, 126-132 (1969).

MERCURY IN BLOOD

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Mercury	**Method No:**	P&CAM 167
Matrix:	Blood	**Range:**	0.0025 – 4.5 μg/mℓ Not verified
Procedure:	Flameless Atomic Absorption	**Precision:**	Unknown
Date Issued:	2/13/73	**Classification:**	D (Operational)
Date Revised:	1/15/74		

1. **Principle of the Method**

   1.1 Whole blood samples are digested by treating with H_2SO_4 at 54 (±1)°C followed by potassium permanganate solution.

   1.2 After reduction of excess oxidant, elemental mercury is liberated by reduction with $SnCl_2$ solution, and measured by flameless atomic absorption at 2537 Å.

   1.3 In an alternative measurement scheme, the liberated elemental mercury is first trapped on a silver absorbent and subsequently thermally desorbed into the measuring system.

2. **Range and Sensitivity**

   2.1 No actual range or sensitivity has been established. However, the absolute sensitivity is 0.0005 of the adsorbed Hg for Procedure II and 0.005 μg using Procedure I. A recorder, equipped with various MV increments (1-50) per full scale is required to obtain these levels.

   2.2 The range may be extended by increasing sample size, and varying dilution and aliquot size.

3. **Interferences**

   3.1 Since Hg forms very stable organic compounds, adequate digestion of the blood is needed to decompose organic mercurials.

3.2 Acetone and other organic vapors absorb highly at the Hg line and must be absent when using Alternate Procedure I.

4. **Precision and Accuracy**

The accuracy and precision of the method have not been reported up to this time. No collaborative tests have been performed.

5. **Advantages and Disadvantages of the Method**

5.1 Flameless Atomic Absorption is a more sensitive method than either flame spectrometry or colorimetric methods.

5.2 Use of an adsorbtion technique to collect more of the Hg from the bubbler further increases the sensitivity. The peaks obtained on desorbing Hg from the silvered substrate are more clearly defined, less variable, and the peak height is more directly related to concentration than those obtained by the usual flameless methods.

5.3 Total Hg is measured. There is no distinction made between organic and inorganic Hg.

6. **Apparatus**

6.1 5 mℓ mercury-free heparinized vacutainers.

6.2 Rocking constant temperature water bath.

6.3 Coleman MAS-50 Mercury Analyzer System or similar Flameless Atomic Absorption System.

6.4 Mercury Evolution Train.

6.4.1 Bubbler Flask – 300 mℓ BOD bottle or equivalent.

6.4.2 All components are connected with minimum lengths of Tygon tubing.

6.5 Eppendorf pipets or equivalent.

6.6 Absorption cell, 155 mm length made of Pyrex glass (12 mm I.D.) with quartz glass windows.

6.7 Thermal desorption apparatus as shown in Figure 4. The heated sections are made from 16 gauge nichrome wire coiled around quartz glass tubing. The outer cooling jacket is made of Pyrex glass and may be removed for access to the electrical components. The unit should be capable of heating a sampling tube to at least 700°C in 30 seconds. The details of fabrication are pending.

6.8 Equipment for Generating Train and Absorption Sampling Tube.

6.8.1 Vacuum pump

6.8.2 Needle valve

6.8.3 Flowmeter 0-5 ℓpm

6.8.4 150 mℓ glass bubbler flask with glass joints

6.8.5 25 mℓ burette

6.8.6 All-glass midget impinger

6.8.7 Silver coated substrate sampling tubes Figure 2.

7. Reagents

All reagents used must be ACS Reagent Grade or better. Allow all reagents and solutions to reach room temperature before using.

7.1 Double distilled water.

7.2 Concentrated sulfuric acid.

7.3 **Potassium permanganate solution** – Saturated (ca. 6%).

7.4 **Hydroxylamine-Hydrochloride solution** – 20% (w/v) in 6 N HCl or in 5% H_2SO_4 (v/v).

7.5 **Stannous Chloride solution** – 20% (w/v) in 6 N HCl or in 5% H_2SO_4 (v/v), freshly prepared.

7.6 **Standard Stock Mercury Solution**: Dissolve 100 mg of metallic Hg or 0.1708 g mercuric nitrate, $Hg(NO_3)_2 \cdot H_2O$, in 50 mℓ of concentrated nitric acid in a clean acid-washed 1 liter volumetric flask. Dilute to 1 liter with double-distilled water. This solution may be stored as long as six months.

7.7 **Hg working standard** (1 μg/mℓ) – Prepare *daily*, by diluting 1 mℓ of the standard stock solution to 100 mℓ with 2 mℓ concentrated HNO_3 and double-distilled water.

7.8 **Silver coated substrate** – The silvered substrate is prepared by coating a celite material, 30/60 mesh, with silver using Brashear's procedure.

8. **Procedure**

8.1 **Cleaning of Equipment.** Acid clean all glassware before use. This can be accomplished by using the following procedure:

8.1.1 Wash in a detergent-tap water solution and follow with tap water rinses.

8.1.2 Soak in 1:1 or concentrated nitric acid for 30 minutes and follow with tap, distilled, and double-distilled water rinses.

8.2 **Collection and Shipping of Samples**

8.2.1 **Collect** *blood* in Hg-free heparinized vacutainers equipped with sterilized stainless steel needles. The vacutainers should be heparinized before the collection of the blood. Heparinized vacutainers are available commercially from most laboratory supply houses. Adding a preservative after collecting blood can result in error due to volume changes. Exercise caution during handling to prevent any external contamination.

8.2.2 Keep samples as cool as possible (do not freeze) during storage and shipment and ship to the laboratory as quickly as possible. Heparinized, refrigerated blood samples are stable for two weeks.

8.2.3 Two milliliters (2 mℓ) of whole blood are adequate for this determination.

8.3 **Sample Preparation**

8.3.1 Pipet 2 mℓ of blood into a 300-mℓ BOD bottle or 125 mℓ Erlenmeyer flask with stopper. Dilute blood with 5 mℓ double distilled water.

Caution: BOD bottles are not made of "Pyrex" and should not be subjected to rapid temperature changes.

8.3.2 Add 5 mℓ conc. H_2SO_4, Swirl, and Cap.

8.3.3 Heat in a rocking-constant water bath to 54°C until tissue is dissolved (3-4 hours). Add 1 mℓ water or more to provide enough liquid to mix. Digested tissue is a clear, dark reddish solution.

8.3.4 Remove digest from water bath. Cool in ice bath while slowly adding 17 mℓ 6% $KMnO_4$.

8.3.5 Cap and let stand overnight.

8.3.6 Add 2 mℓ 20% Hydroxylamine-Hydrochloride. The solution should turn clear.

8.3.7 Dilute to 50 mℓ volume with water

8.4 **Analysis of Sample**

8.4.1 **Procedure** 1 – Useful range = 0.1 to 2 μg Hg

1. Pipet 25 mℓ of the digest (Section 8.3.7) into the bubbler flask.

2. Add 1 mℓ 20% $SnCl_2$.

3. Immediately connect the flask to the generating train of the apparatus shown in Figure 1.

4. Recycle the evolved Hg until the signal on the recorder reaches a maximum. Use peak height as a measure of the concentration.

5. Repeat Steps 1 to 4 and average the result of the two determinations.

8.4.2 **Procedure** 2 – Useful range = 0.002 to 0.3 μg Hg

1. Prepare absorption tubes from 5 cm lengths of Pyrex glass tubing (4 mm I.D.) by flame sealing one end. Pack the tube with a plug of glass wool, 75 mg of 30/60 mesh silver coated substrate, and another plug of glass wool (Figure 1). The tip of the sampling tube is broken and the tube is inserted into the test apparatus at point 4, Figure 3.

2. Pipet 5 mℓ of the digest (Section 8.3.7) into the bubbler flask and Connect the flask to the test apparatus as shown in Figure 3.

3. Add 1 mℓ 20% $SnCl_2$ from the burette.

4. Pump filtered air thru the system at 1 ℓpm for six minutes.

5. Remove the sampling adsorption tube.

6. Place the tube inside the thermal desorption unit. The mercury in the tube is transferred into the second section of the thermal desorption apparatus by heating to 700°C and passing filtered air through the silvered material at 1 liter/minute. Complete transfer of the mercury from the tube is usually accomplished in 45 seconds although this may vary with the heating rate.

7. After transferring the mercury from the sample tube to the second section of the desorption unit, the mercury is desorbed (by heating to 700°C again) into the cell of the flameless AA unit. The amount of mercury is calculated from the absorption peak and from a standard curve run at the same time as the samples.

9. Calibration and Standards

9.1 Standards for a calibration curve are analyzed exactly as samples except that known amounts of mercury are added to the sample aliquot.

9.2 The calibration curve is constructed by subtracting the reading from the unspiked aliquot from that of the spiked aliquots.

9.3 The calibration is repeated with appropriate quantities of mercury to cover a convenient working range.

10. Calculations

10.1 The micrograms of Hg in the sample aliquot analyzed are determined from the calibration curve using peak heights after subtracting the peak height obtained from the reagent blank from the peak height of the sample aliquot.

10.2 Divide by the volume of the sample aliquot (μg/mℓ).

10.3 Multiply by 50 (or the volume of the sample digest) to obtain μg Hg/sample.

10.4 Divide by 2 (or volume of sample used) to obtain μg Hg/mℓ blood.

11. References

11.1 Applications Data Sheet, Coleman Instruments Division, January 22, 1971.

11.2 Coleman MAS-50 Manual, December 1970.

11.3 Uthe, J.F., Armstrong, F.A.J. and Stainton, M.P., "Mercury Determination in Fish Samples by Wet Digestion and Flameless Atomic Absorption Spectrophotometry." Journal Fisheries Research Board of Canada, 27, 805-11 (1970).

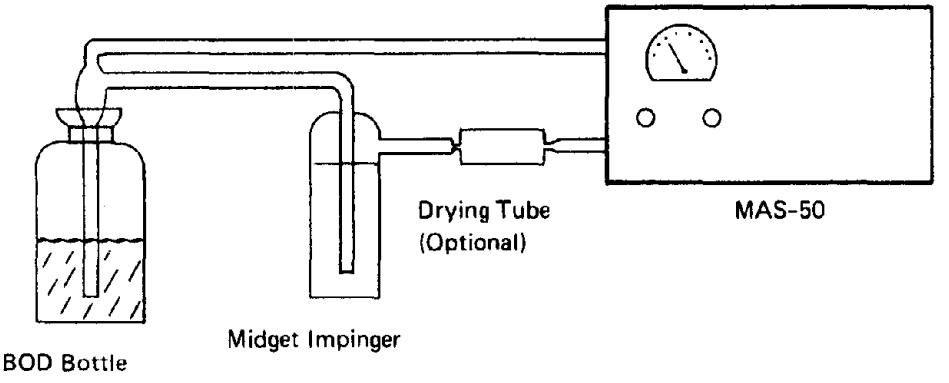


FIGURE 1 APPARATUS FOR ALTERNATE PROCEDURE I

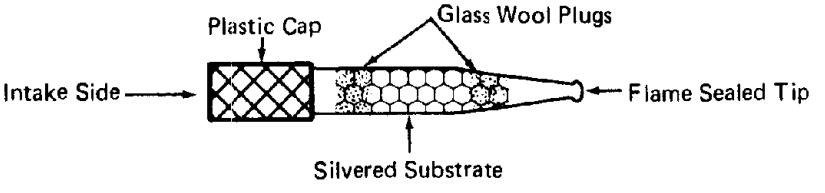


FIGURE 2 SAMPLING TUBE FOR ALTERNATE PROCEDURE II

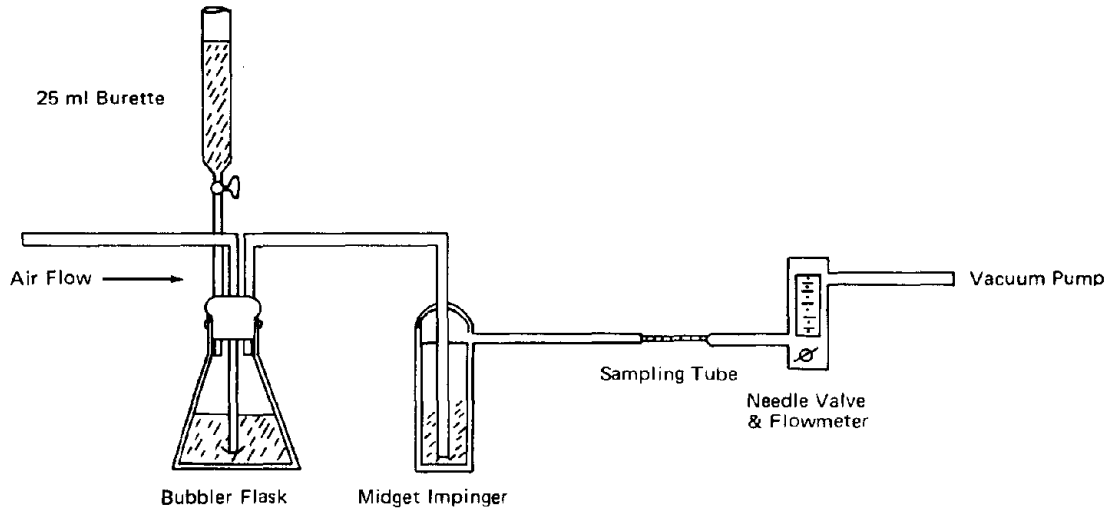


FIGURE 3 APPARATUS FOR ALTERNATE PROCEDURE II

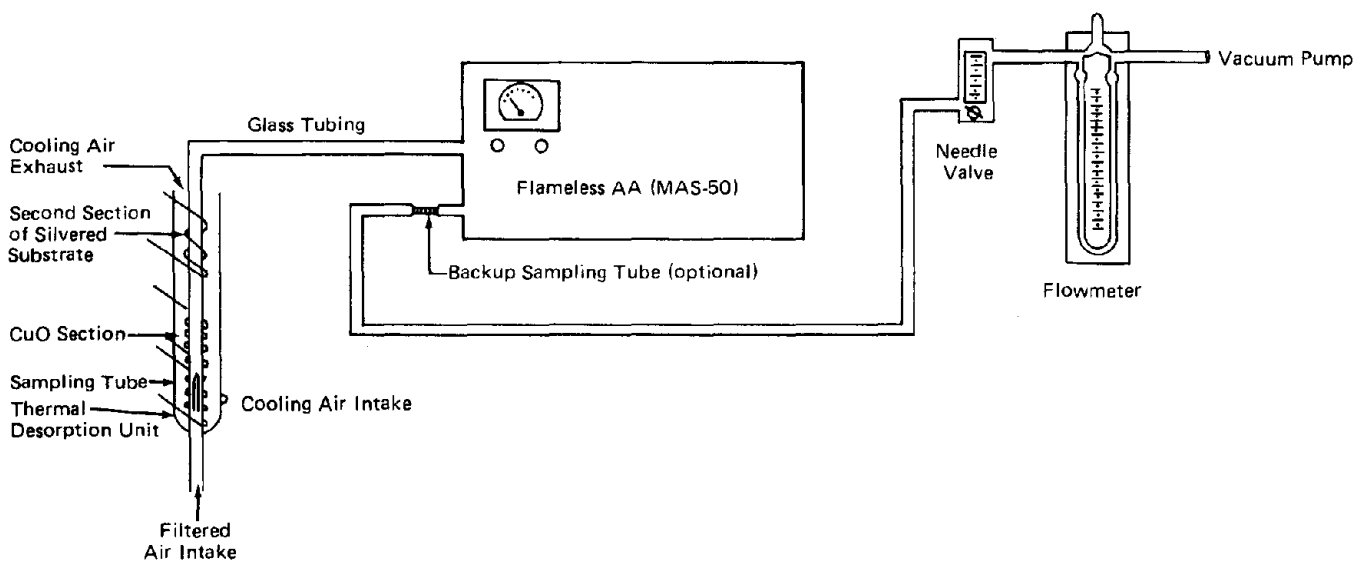


FIGURE 4 ANALYTICAL APPARATUS FOR ALTERNATE PROCEDURE II

AROMATIC AMINES[1] IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Aromatic Amines[1]	Method No:	P&CAM 168
Matrix:	Air	Range:	0.01-14 mg/ sample
Procedure:	Adsorption on silica gel; elution by ethanol; GC analysis		
Date Issued:	11/1/73	Precision:	$2\sigma = \pm 9\%$
Date Revised:	7/15/74	Classification:	D (Operational)

1. Principle of the Method

   1.1 A known volume of air is drawn through a tube containing silica gel to trap the aromatic amines present.

   1.2 The silica gel in the tube is transferred to a glass-stoppered tube and treated with ethanol.

   1.3 An aliquot of the desorbed aromatic amines in ethanol is injected into a gas chromatograph.

   1.4 Peak areas are determined and compared with calibration curves obtained from the injection of standards.

2. Range and Sensitivity

   2.1 The lower limit of this method using a flame ionization detector is 0.01 mg/sample of any one compound when the analyte is desorbed with 5 ml ethanol and a 10-μℓ aliquot is injected into the gas chromatograph. Sensitivity for p-nitroaniline is 5 times less.

   2.2 The upper limit is at least 14 mg/sample. This is a minimum amount of aniline which the large section (700 mg) and the center section (150 mg silica gel) of the sampling tube will retain before 2% of the sample is found on the third (150 mg) section after 8 hours of sampling. (200 ml/min high humidity air containing 150 mg/m^3 aniline) The corresponding upper limit for sampling in the

[1] The list of aromatic amines for which this method has been specifically developed is given in Table I.

reverse direction through the tube is 3.5 mg/sample. The less volatile substituted anilines have higher upper limits than aniline.

3. Interferences

3.1 The most common possible sampling interference is water vapor. The sampling tube has been designed so that 96 liters of high humidity air can be sampled over an 8-hour period at 200 ml/min without displacement of the collected aromatic amines by water vapor.

3.2 Any compound which has nearly the same retention time as one of these aromatic amines at the gas chromatograph analytical conditions described in this method is an interference. This type of interference often can be overcome by changing the operating conditions of the gas chromatograph or selecting another column. Retention time data on a single column, or even on a number of columns, cannot be considered as conclusive proof of chemical identity in all cases. For this reason it is important that whenever practical a sample of the bulk compound or mixture be submitted at the same time as the sample tube (but shipped separately) so that chemical identification can be made by other means.

4. Precision and Accuracy

4.1 The accuracy of the method depends upon collection efficiencies and desorption efficiencies. If a negligible amount of aromatic amine is detected on the backup section, the collection efficiency of the tube must be essentially 100%. Desorption efficiencies for the range of 1-8 mg have been found to be 100% within experimental error of $\pm$ 5%.

4.2 Precision of the analysis is quite dependent upon the precision and sensitivity of the technique used to quantitate gas chromatographic peaks of samples and standards. Electronic digital integrators with baseline correction capabilities can be used to maximize analytical precision, particularly at lower concentrations.

4.3 Precision of preparing chemical standards can be $\pm$ 1%.

4.4 The precision of the overall method, $2\sigma = \pm 9\%$, has been determined from eight consecutive identical samples taken with a personal sampling pump.

4.5 Analytical precision can be improved by reducing or eliminating the error associated with syringe injection into the gas

chromatograph. This is best accomplished by the addition of an internal standard to the ethanol used to both prepare standards and elute samples from the silica gel. Therefore, it is recommended that about 0.1% solution of n-heptanol in ethanol be used. For isothermal analyses at temperatures above 120°C, n-octanol may be preferable.

5. Advantages and Disadvantages

5.1 The sampling method uses a small, portable device involving no liquids. Taking the effect of humidity into account, a sample of up to 8 hours can be taken for an average work day concentration or a 15 minute sample can be taken to test for excursion concentrations. Desorption of the collected sample is simple and is accomplished with a solvent with low toxicity. The analysis is accomplished by a quick instrumental method. Most analytical interferences which occur can be eliminated by altering gas chromatographic conditions. Several aromatic amines can be collected and analyzed simultaneously; this is useful where the composition of the aromatic amine vapors may not be known.

5.2 A major disadvantage of the method is the limitation on its precision due to the use of personal sampling pumps currently available. After initial adjustment of flow any change in the pumping rate will affect the volume of air actually sampled. Furthermore, if the pump used is calibrated for one tube only, as is often the case, the precision of the volume of air sampled will be limited by the reproducibility of the pressure drop across the tubes.

6. Apparatus

6.1 One or more personal sampling pumps whose flow can be set at and maintained at 1 liter/min for 15 min or 200 ml/min for 8 hours.

6.2 Pyrex glass sampling tubes of the dimensions shown in Figure 1 packed with three sections of 45/60 mesh silica gel. The weights of the section in order are 700 mg, 150 mg and 150 mg. The silica gel should be the equivalent of Silica Gel D-08, Chromatograph Grade, Activated and Fines Free, 45/60 Mesh, from Applied Science Laboratories, Inc., State College, Pa. Plugs of 100 mesh stainless steel screen are used to contain the silica gel sections. These plugs of negligible pressure drop are prepared from 11 mm diameter discs pushed into a 8 mm I.D. tube with a 7 mm O.D. rod. Pieces of Pyrex tubing 7 mm O.D. by 12 mm long and located between the sorbent sections greatly reduce migration of the sample throughout the tube prior to analysis. The ends of each tube should be flame sealed after packing to prevent contamination before sampling. The pressure drop of such tubes should not exceed 13 in of water at 1 liter/min or 2.5 in of water at 200 ml/min air flows.

6.3 Gas chromatograph equipped with a flame ionization detector. Linear temperature programming capability is desirable but not essential.

6.4 Column (4 ft x 1/8 in O.D.) packed with Silicone OV-25 liquid phase, 10% on 80/100 mesh Supelcoport (or equivalent support). A column (2 ft x 1/8 in O.D.) packed with Chromosorb 103 (80/100 mesh) can be used for all the amines except p-nitroaniline.

6.5 Recorder and some method for determining peak height or area.

6.6 Glass-stoppered tubes or flasks, 2 ml and 10 ml.

6.7 Syringes, 10 µl.

6.8 Pipettes and volumetric flasks for preparation of standard solutions.

7. Reagents

7.1 Ethanol, 95%

7.2 n-Heptanol and n-octanol, reagent grade

7.3 Reagent grade aromatic amines standards

7.4 Bureau of Mines Grade A helium

7.5 Prepurified hydrogen

7.6 Filtered compressed air

8. Procedure

8.1 Cleaning of equipment: All glassware used for the laboratory analysis is detergent washed followed by tap and distilled water rinses.

8.2 Calibration of personal pumps: Each pump must be calibrated with a representative tube in the line to minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, the ends of the tube should be broken so as to provide an opening at least one half the internal diameter of the tube.

8.3.2 The desired sampling direction is chosen, the initial section marked with a permanent marker, and tubing from the sampling pump attached to the other end. For low concentrations, low humidity, and short-term samples, the smaller (150 mg) section is used for the initial section. For expected high concentrations, high humidity, and long-term samples, the largest (700 mg) section is used for the initial section. See Table I footnotes. Sampled air should not pass through any hose or tubing before entering the sampling tube.

8.3.3 The atmosphere is sampled at the desired flow rate for the desired period of time. Recommended sampling volumes based on sensitivity and breakthrough studies are given in Table I. The flow rate and sampling time or the volume of sampled air must be measured as accurately as possible.

8.3.4 The temperature, pressure, and humidity of the atmosphere being sampled is measured and recorded.

8.3.5 The sampling tubes are capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8.3.6 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube is labeled as a blank.

8.3.7 Capped tubes should be packed tightly before shipping to minimize tube breakage during shipping.

8.3.8 Samples of the bulk liquids or solids from which the aromatic amine vapors arise should be submitted to the laboratory also, but not in the same container as the air samples or blank tubes.

8.3.9 Storage: Tubes after sampling should be tightly capped and not subjected to extremes of high temperature or low pressure, if avoidable. If the analysis is to be delayed beyond one week after sampling, each tube should be filled with an inert gas (helium, nitrogen, etc.) to prevent loss of sample by oxidation. Refrigeration is also recommended.

8.4 Analysis of Samples

8.4.1 Preparation of samples: By removing and discarding the stainless steel plugs and glass spacers the silica gel

sections are transferred to separate glass-stoppered tubes or flasks (2 ml for the smaller sections and 10 ml for the larger section). Note or mark which tubes contain the initial section, the backup section, and the third section. These are analyzed separately.

8.4.2 Desorption of samples: Prior to analysis, ethanol containing 0.1% n-heptanol internal standard is pipetted into each flask - 5 ml for the large section and 1 ml for all other sections. Tests indicate that desorption is complete in 30 min if the sample is stirred or shaken occasionally.

8.4.3 Gas chromatograph conditions: Typical operating conditions for the gas chromatograph are: carrier flow (25 ml He/min); injection port (150°C); flame ionization detector (250°C, 50 ml/min H_2, 470 ml/min air); oven temperature program (100°C for 4 min, then increase at 8°C/min to 225°C).

8.4.4 An aliquot of the sample is injected into the gas chromatograph. With an internal standard in the eluent, direct injection of up to 10 µl with amicroliter syringe is acceptably precise. At least duplicate injections of the same sample or standard are recommended.

8.4.5 The areas of the sample peak and the internal standard peak are measured by an electronic integrator or some other suitable method of area measurement. The ratio of these areas is calculated and used to determine sample concentration in the eluent by using a standard curve prepared as discussed below.

9. Calibration and Standards

9.1 For accuracy in the preparation of standards, it is recommended that one standard be prepared in a relatively large volume and at a high concentration. Aliquots of this standard can then be diluted to prepare other standards. The solvent and diluent used must be the same ethanol/n-heptanol mixture used for the elution of the samples. For example, to prepare a 100 ml standard corresponding to a 96 liter sample of air containing 95 mg/m^3 of aniline (density = 1.022 g/ml) desorbed with 5 ml,

$$\frac{(95\ mg/m^3)\ (0.096m^3)}{5\ ml} \times \frac{100\ ml}{1.022\ mg/\mu l} = 178\ \mu l$$

of aniline is added to a 100 ml volumetric flask and diluted to the mark. The resulting concentration is

$$\frac{(178\ \mu l)\quad (1.022\ mg/\mu l)}{100\ ml} = 1.82\ mg/ml$$

If 2 ml of this solution is diluted to 10 ml in a volumetric flask with the ethanol/n-heptanol mixture, the resulting concentration is

$$(1.82\ mg/ml)\quad \frac{2\ ml}{10\ ml} = 0.365\ mg/ml$$

When microliter pipettes are used instead of microliter syringes, it is better to prepare standards using a round number of microliters (e.g., 200 µl aniline instead of 178 µl). For solids the amount of compound used for the first standard should be weighed on an anlytical balance. A series of standards is prepared varying in concentration over the range of interest.

9.2 The standards prepared as above should be analyzed under the same GC conditions and during the same time period as the unknown samples. This will minimize the effect of day-to-day variations of the flame ionization detector response.

9.3 A standard curve is prepared for each compound by plotting ratios of peak areas of the compound to the internal standard against the concentration of the compound. From the resulting curve the concentration of an eluted sample is determined. This concentration (in mg/ml) is then converted to total sample weight by multiplying by the amount of ethanol used for that section (1 or 5 ml).

10. Calculations

10.1 Corrections for the blank must be made for each sample.

$$\text{Correct mg} = mg_s - mg_b$$

where:

mg_s = mg found in front section of sample tube
mg_b = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.2 Add the corrected amounts present in the front and backup sections of the same sample tube to determine the total measured amount (w) in the sample.

10.3 Convert the volume of air sampled to standard conditions of 25°C and 760 mm Hg.

$$V_s = V \times \frac{P}{760} \times \frac{298}{T+273}$$

where:

V_s = volume of air in liters at 25°C and 760 mm Hg
V = volume of air in liters as calculated (sampling time x correct flow rate)
P = Barometric pressure in mm Hg
T = Temperature of air in degree centigrade

10.4 The concentration of the organic solvent in the air sampled can be expressed in mg per m^3, which is numerically equal to µg per liter of air

$$mg/m^3 = \mu g/\ell = \frac{w\ (mg) \times 1000\ (\mu g/mg)}{V_s}$$

10.5 Another method of expressing concentration is ppm, defined as µℓ of compound vapor per liter of air

$$ppm = \mu\ell \text{ of vapor}/V_s$$

$$ppm = \frac{w\ (\mu g)}{V_s} \quad \frac{24.45\ \ell/mole}{MW}$$

where:

24.45 ℓ/mole = molar volume at 25°C and 760 mm Hg
MW = molecular weight of the compound (g/mole)

11. References

11.1 E.E. Campbell, G.O. Wood, and R.G. Anderson, Los Alamos Scientific Laboratory Progress Reports LA-5104-PR, LA-5164-PR, LA-5308-PR, LA-5389-PR, LA-5484-PR, and LA-5634-PR, Los Alamos, N.M., Nov. 1972, Jan. 1973, June 1973, Aug. 1973, Dec. 1973, and June 1974.

TABLE I

AROMATIC AMINES FOR WHICH THE METHOD HAS BEEN TESTED

	OSHA Standard[a]		Recommended Sample Volumes (liters)	
	(ppm)	(mg/m^3)	Minimum[b]	Maximum[c]
Aniline	5	19	5	150
N,N-Dimethylaniline	5	25	5	190
o-Toluidine	5	22	5	300
2,4-Xylidine	5	25	5	430
o-Anisidine	0.1	0.5	250	35,800
p-Anisidine	0.1	0.5	250	33,000
p-Nitroaniline	1	6	80	12,100

[a]Taken or calculated from Federal Register, 37, #202, 22139 (18 October 1972).

[b]Based on analytical sensitivity and 0.1 OSHA standard detection when using the large section as the initial section (See 2.1). When the smaller section is used as the initial section divide these minimum volumes by 5.

[c]Based on breakthrough studies at high humidities and a concentration of 5 times the OSHA standard when using the large section as the initial section. When the smaller section is used as the initial section, divide these maximum volumes by 5.

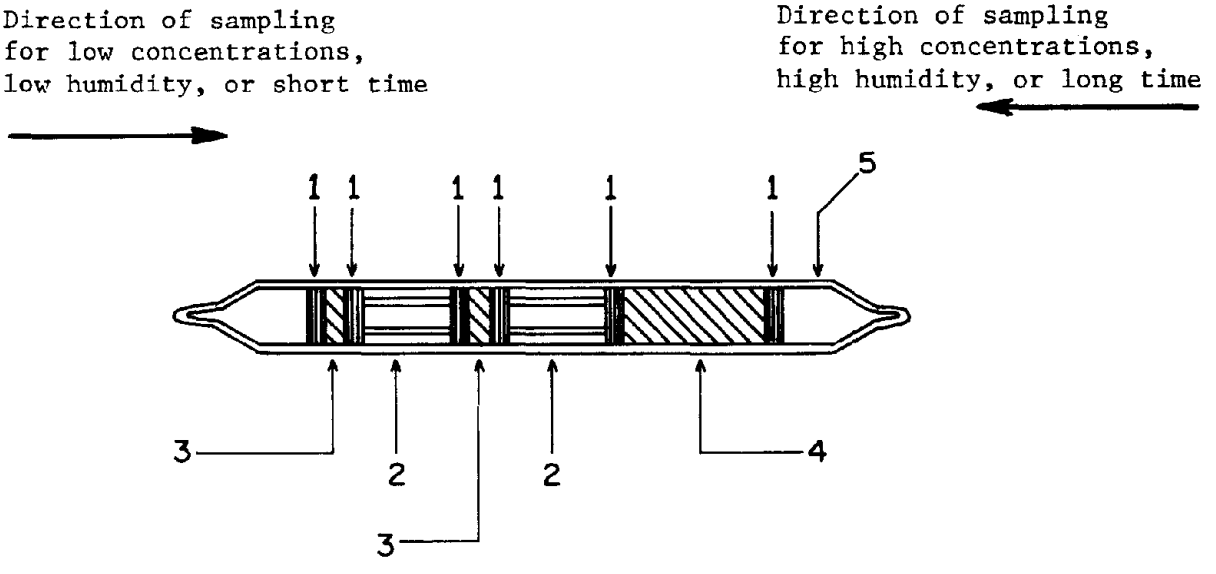


Figure 1. Silica gel sampling tube for aromatic amines. (1) 100 mesh stainless steel screen plugs; (2) 12 mm glass tube separator; (3) 150 mg silica gel section, 45/60 mesh; (4) 700 mg silica gel section, 45/60 mesh; (5) 8 mm I.D. glass tube

CHROMIC ACID MIST IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Chromic Acid Mist	**Method No.:**	P&CAM 169
Matrix:	Air	**Range:**	0.004 to 0.2 mg CrO_3/m^3
Procedure:	PVC Filter-Colorimetric	**Precision:**	~ 4% RSD
Date Issued:	5/1/73		
Date Revised:	1/10/74	**Classification:**	D (Operational)

1. **Principle of the Method**

   1.1 Chromic acid mist is collected on a polyvinyl chloride (PVC) filter.

   1.2 The filter is washed in 0.5N H_2SO_4, diphenylcarbazide is added, and additional acid is added to bring the volume to 15 mℓ.

   1.3 The absorbance of the solution at 540 nm is read and compared to the absorbance of the standards.

2. **Range and Sensitivity**

   2.1 When using 2 cm cells and a 15 mℓ final volume, a 1% absorption occurs with about 0.05 μg of hexavalent chromium. For a 100 liter air sample, this translates to a sensitivity of about 0.001 mg CrO_3/m^3 for the sampled air. It is not recommended to work at this low concentration due to poor precision.

   2.2 The range for the colorimetric method is useful from 0.2 μg Cr(VI) up to about 10 μg Cr(VI) which is from 0.004 to 0.2 mg CrO_3/m^3 for a 100 liter sample of air. Dilutions are easily made.

3. **Interferences**

   Possible interferences for the diphenylcarbazide method include many of the heavy metals. The ones likely to be encountered at appreciable levels are iron, copper, nickel, and vanadium. Tests show that 10 μg of any of these give less than 0.5% absorbance which is equivalent to about 0.04 μg CrO_3.

4. **Precision and Accuracy**

Ten filters spiked with 1.0 μg of hexavalent chromium (a 10 μℓ droplet of 100 ppm Cr(VI) was placed on each filter and allowed to dry) gave recoveries of 93% with a relative standard deviation of 3.2%. Twenty-two filters exposed in a chromic acid mist generator had about 5 μg Cr(VI) per filter and the pooled results showed a precision of 4.3% RSD. No collaborative tests have been performed on this method.

5. **Advantages and Disadvantages**

5.1 The method is simple, specific, and sensitive. The samples collected on PVC filters are stable. There is no significant sample loss when stored for up to two weeks, with sample recoveries still in the order of 96%. Storage for longer periods results in lower recoveries, i.e., after nine weeks the average recovery is about 76%.

5.2 Samples made by spiking PVC filters are not very stable and give poor recoveries. It is, therefore, not recommended to use spiked filters for standards or any other purpose.

6. **Apparatus**

6.1 **Sampling Equipment.** The sampling unit for the filter-collection method has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate cassette filter holder, either a 2- or 3-piece filter cassette.

6.1.2 A vacuum pump such as a personal sampling pump capable of sampling at a rate of 2 ℓpm. This pump must be properly calibrated so the volume of air sampled can be measured as accurately as possible. The pump must be calibrated with a representative filter unit in the line. Flow rate, times, and/or volume must be known.

6.1.3 Thermometer.

6.1.4 Manometer.

6.1.5 Stopwatch.

6.2 VMI (Gelman) – PVC filters or equivalent.

6.3 Spectrophotometer set to operate at 540 nm.

6.4 Matched cuvettes, 2 cm path length.

6.5 All polypropylene or Teflon forceps.

6.6 Assorted laboratory glassware.

7. Reagents

All reagents must be analytical reagent grade or better.

7.1 **Sulfuric Acid**, 0.5N. Add 13.9 mℓ of concentrated H_2SO_4 to some water in a 1ℓ volumetric flask and dilute to mark. For uniformity of results it is suggested that the same solution be used for a complete test -- samples, blanks and standards. After thorough mixing, it is convenient to transfer part of the solution to a small plastic wash bottle.

7.2 **Diphenylcarbazide**. Dissolve 0.50g of *sym*-diphenylcarbazide in a mixture of 100 mℓ of acetone and 100 mℓ of double distilled water. Store in a dark bottle in the refrigerator for up to one month.

7.3 **Chromium-Six Standard.** Dissolve 0.2829g of $K_2Cr_2O_7$ in water in a 1000 mℓ volumetric flask and dilute to mark. This solution is 100 ppm (by weight) in chromium (VI). The chromium (VI) concentration can also be expressed as 0.1 μg per μℓ.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Wash all containers in hot, soapy water and follow with tap and distilled water rinses.

8.1.2 Soak in concentrated nitric acid (10% nitric acid for plastics) for 30 minutes. Rinse thoroughly with tap water, distilled water, and double distilled water.

8.2 Collection and Shipping of Samples

8.2.1 Chromic acid mist is collected on 5 micron PVC filters mounted into a 3-piece filter cassette. It is important that the cassette be assembled properly to assure a tight seal at the face of the filter, otherwise some chromic acid will end up on the backup pad and will be lost from the analysis.

8.2.2 Draw air through the filter by means of a personal sampling pump at the rate of 2 liters per minute. A 100 liter sample is recommended. Some

minimum sampling volumes (for 0.1 absorbance in a 2 cm cell) are as follows:

Concentration to be Measured ($\mu g\ CrO_3/m^3$)	Minimum Required Sample Size (liters)
.01	200
.05	40
.1 (TLV)	20
.2	10

8.2.3 With each batch of samples, one filter, labeled as a blank, should be submitted. This filter is subjected to exactly the same handling as the samples except that no air is drawn through it.

8.2.4 The cassettes in which samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8.3 **Analysis of Samples**

8.3.1 Pipette 15 mℓ of water into each cuvette to be used. Put a piece of tape on the cuvette so that its bottom edge matches the meniscus. Rinse the cuvettes.

8.3.2 Blank filters are folded and placed directly into 2 cm cuvettes. Sample filters are folded and placed in cuvettes or large test tubes.

8.3.3 Add six or seven mℓ of 0.5N H_2SO_4 to each tube and shake the tube to assure that all surfaces of the filter are washed. Remove the filters from the tubes with small forceps carefully washing all surfaces with an additional mℓ or two of 0.5N H_2SO_4. The washed filters are discarded.

8.3.4 To remove suspended dust, solutions from actual samples should be filtered in transferring them from the original tubes to 2 cm cuvettes. A No. 5, 2-hole stopper, if altered by enlarging one hole, can accommodate a small Buchener funnel and vacuum line and will fit a 2 cm cuvette. After the solution has filtered through, wash the funnel and filter with several mℓ of the 0.5N H_2SO_4. Standards should be set up along with each set of samples being analyzed as in Section 9 below.

8.3.5 Add 0.5 mℓ of the diphenylcarbazide solution to each cuvette. Then add additional 0.5N H_2SO_4 until the meniscus matches the bottom edge of the tape. Shake the cuvette to mix and wipe the outside clean with absorbent tissue.

8.3.6 Read the absorbance of the solutions on a spectrophotometer at 540 nm with 0.0 absorbance being set with the 0 μg standard described below.

9. Calibration and Standards

9.1 Transfer 6 or 7 mℓ of 0.5N H_2SO_4 into each of 6 of the 2 cm cuvettes. Pipette 0, 5, 10, 20, 50, and 100 μℓ of the 100 ppm standard into the 6 cuvettes respectively. Add 0.5 mℓ of the diphenylcarbazide solution and sufficient 0.5N H_2SO_4 to bring to the 15 mℓ mark. Shake and wipe clean. These standards are respectively the 0 μg standard, 0.5 μg standard . . . etc. The zero microgram standard is used to set the zero absorbance reading of the spectrophotometer at 540 nm. The absorbance of the other standards is read and recorded along with that of the samples.

9.2 A calibration curve is drawn by plotting the absorbance of the standards against μg of chromium-six.

10. Calculations

10.1 Blank absorbance values, if any, should be subtracted from each sample absorbance value.

10.2 The concentration of CrO_3 in air can be expressed as mg CrO_3 per cubic meter or μg CrO_3 per liter.

$$\text{mg } CrO_3/m^3 = \mu\text{g } CrO_3/\ell$$

$$\text{mg } CrO_3/m^3 = \frac{\mu\text{g Cr (VI)}}{V_s} \times \frac{CrO_3}{Cr}$$

where:

μg Cr (VI)	=	concentration of Cr (VI) derived from calibration curve
V_s	=	volume of air sampled in ℓ at 25°C, 760 mm Hg
CrO_3	=	molecular weight of CrO_3, 100
Cr	=	molecular weight of Cr, 52.

11. References

11.1 Snell and Snell, *Colorimetric Methods of Analysis*, Volume IIA, D. Van Nostrand Co., pp. 212-215, 19

11.2 Jacobs, M.B., *The Analytical Toxicology of Industrial Inorganic Poisons*, Interscience Publishers, pp. 396-402, 19

11.3 Abell, M.T., and J.R. Carlberg, "A Simple Reliable Method for the Determination of Airborne Hexavalent Chromium," Amer. Ind. Hyg. Jour. To be published.

GENERAL PROCEDURE FOR METALS

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Metals (See Table)	**Method No:**	P&CAM 173
Matrix:	Industrial Hygiene Samples	**Range:**	See Table
		Precision:	2% RSD (analytical)
Procedure:	Atomic Absorption		
Date Issued:	9/17/73	**Classification:**	B (Accepted)
Date Revised:	1/15/74		

1. **Principle of the Method**

   1.1 Samples are ashed using nitric acid to destroy the organic matrix and the metals are solubilized in an acidic solution maintaining a pH of 1.

   1.2 Samples and standards are aspirated into the appropriate AA flame. A hollow cathode lamp for each metal of interest provides the characteristic line for that particular metal. The absorption of this line by the ground state atoms in the flame is proportional to the metal concentration in the aspirated sample.

2. **Range and Sensitivity**

   2.1 The optimum working range for each metal is given in the Table. This value can be extended to higher concentrations by dilution of the sample.

   2.2 The sensitivity of this method for each metal in aqueous solution is also given in the Table. This value will vary somewhat depending upon the instrument used.

3. **Interferences**

   3.1 Known interferences may occur when analyzing for metals listed in the table. Therefore, procedures for eliminating or overcoming these interferences are listed. Whenever additions are made to the samples to overcome or eliminate interferences, similar additions must be made to the standards.

   3.2 Chemical interferences in the flame prevent conversion of the metal being determined to the atomic state. Higher flame temperatures (N_2O-C_2H_2) can overcome this problem in some cases.

4. **Precision and Accuracy**

4.1 In general, this method will provide a coefficient of variation for the analysis of approximately 2% depending upon the instrument used and the absorbance of the samples. (If absorbence is less than 0.1, the coefficient of variation is higher.)

4.2 No data on accuracy is available at this time.

5. **Advantages and Disadvantages of the Method**

5.1 The sensitivity is adequate for all metals in air samples but only for certain metals in biological matrices. The sensitivity of this direct aspiration method is not adequate for Be, Cd, Ca, Cr, Mn, Mo, Ni, and Sn in biological samples.

5.2 A disadvantage of the method is that at least 1 to 2 mℓ of solution is necessary for each metal determination. For small samples, the necessary dilution would decrease sensitivity.

6. **Apparatus**

6.1 **Sampling Equipment.** The sampling unit for the collection of personal air samples for the determination of metal content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate cassette filter holder, either a 2- or 3-piece filter cassette (Millipore Filter Corporation, Bedford, Massachusetts).

6.1.2 A vacuum pump such as a personal sampling pump. This pump must be properly calibrated so the volume of air sampled can be measured as accurately as possible. The pump must be calibrated with a representative filter unit in the line. Flow rate, times, and/or volume must be known.

6.1.3 Thermometer.

6.1.4 Manometer.

6.1.5 Stopwatch.

6.1.6 Various clips, tubing, spring connectors, and belt for connecting sampling apparatus to worker being sampled.

6.2 0.8μ cellulose membrane filter (or equivalent), 37 mm.

6.3 Hollow cathode lamps for each metal.

6.4 **Atomic absorption spectrophotometer**, having a monochromotor with a reciprocal linear dispersion of about 6.5 Å/mm in the ultraviolet region. The instrument must have the necessary burner heads for air-acetylene and nitrous oxide-acetylene flames.

6.5 **Oxidant:**

6.5.1 Air, which has been filtered to remove water, oil, and other foreign substances is the usual oxidant.

6.5.2 Nitrous oxide is required as an oxidant when higher temperatures are required in the analysis of refractory-type metals.

6.6 **Fuel**

Acetylene, commercially available for atomic absorption use.

6.7 **Pressure-reducing valves**, a 2-gauge, 2-stage pressure reducing valve and appropriate hose connections are needed for each compressed gas tank used. When using nitrous oxide, heating tape, with the temperature controlled by a rheostat, is wound around the second stage of the regulator and connecting hose to prevent freeze-up of the line.

6.8 **Glassware, borosilicate:**

6.8.1 125 mℓ Phillips beakers with watchglass covers

6.8.2 15 mℓ graduated centrifuge tubes

6.8.3 10 and 100 mℓ volumetric flasks

6.8.4 125 mℓ polyethylene bottles

6.9 Three-switch hot plates capable of reaching 400°C

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Double distilled or deionized water

7.2 Redistilled concentrated nitric acid

7.3 Distilled 1:1 hydrochloric acid

7.4 Commercially prepared *aqueous stock standards* (1000 μg/mℓ) for each metal listed in the Table.

7.5 **Lanthanum stock solution (for Ca determination)** – 5% La in 25% HCl (v/v). Wet 29.33 g La_2O_3 with double distilled water. Add 125 mℓ concentrated HCl. Dilute to 500 mℓ.

7.6 **Aluminum solution (for Mo determination)** – commercially prepared aqueous aluminum stock containing 1000 μg Al/mℓ.

8. **Procedure**

8.1 **Cleaning of Equipment**

8.1.1 Before initial use, glassware is cleaned with a saturated solution of sodium dichromate in concentrated sulfuric acid (Note: Do not use for chromium analysis) and then rinsed thoroughly with warm tap water, concentrated nitric acid, tap water and deionized water, in that order, and then dried.

8.1.2 All glassware is soaked in a mild detergent solution immediately after use to remove any residual grease or chemicals.

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, it is not necessary to use the chromic acid cleaning solution.

8.2 **Collection and Shipping of Samples**

8.2.1 **Dusts** and **fumes** containing metal can be sampled with a 0.8 μ cellulose membrane filter. The filters must not be loaded to the point where portions of the sample might be dislodged from the collecting medium during handling. Personal filter samples should be sealed in individual plastic filter holders during shipment. A two-hour sampling period at 1.5 liters per minute will provide enough sample for air concentrations of 0.2 x TLV. Beryllium requires a full eight-hour sample at 0.2 x TLV.

8.2.2 **Blood** samples – 10 mℓ should be collected in chemically clean, heparinized vacutainers. If the vacutainers have not been pretreated, 1-2 mℓ of a heparin sodium solution should be injected into the vacutainer. Refrigerate for shipment if possible.

8.2.3 **Urine** samples – 50 mℓ should be collected in chemically clean, borosilicate or polyethylene bottles. The urine samples should be preserved by the addition of approximately 2.5 mg of thymol and refrigerated for shipment if possible.

8.2.4 Tissue samples should be collected in chemically clean jars and preserved in dry ice. Tissue samples must be shipped back to the laboratory immediately.

8.3 Analysis of Samples

8.3.1 Samples are transferred to clean 125 mℓ Phillips beakers and several mℓ of concentrated HNO_3 is added to each. Each beaker is covered with a watchglass and heated on a hot plate (140°C) in a fume hood until the sample chars or until a slightly yellow solution remains. Several additions of HNO_3 may be needed to completely ash and destroy the organic material. Completion of the digestion procedure is indicated by a white residue in the beaker.

8.3.2 For samples containing arsenic (a fairly volatile element), the residue is dissolved in 2 mℓ of 6N HCl using the low temperature hot plate (140°C) and quantitatively transferred to a graduated centrifuge tube with deionized water.

8.3.3 For samples not containing arsenic, the residue is heated several minutes on the high temperature hot plate (400°C) and converted to a salt by three successive evaporations with 1:1 HCl or concentrated HNO_3. The ash is then dissolved with 1:1 HCl or concentrated HNO_3 and deionized water and quantitatively transferred to a graduated centrifuge tube. Aliquots of this can be diluted if necessary or the volume can be reduced by evaporation to get the metal concentration within the working range of the method.

8.3.4 The sample solution is then aspirated into the appropriate flame for each metal as indicated in the Table. The analytical wavelength is also listed in the Table. The other operating parameters are set according to the instrument manufacturer's conditions for each metal being determined. The absorbance of each sample is recorded. When very low metal concentrations are found in the sample, scale expansion can be used to increase instrument response.

9. Calibration and Standards

9.1 From each of the 1000 μg/mℓ stock metal standard solutions, prepare working standards to cover the range for each metal as indicated in the Table. All standard solutions are made 0.3 N in HCl and are stored in polyethylene bottles. The low concentration standards may deteriorate and should be remade each day.

9.2 When analyzing for any of the metals where interferences are known to occur, as is indicated in the Table, standards should be prepared according to the "Remedy" listed in the Table.

9.3 Aspirate the series of standards and record the percent absorption.

9.4 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in $\mu g/m\ell$. It is advisable to run a set of standards both before and after a sample run to insure that conditions have not changed.

10. Calculations

10.1 From the calibration curve, read the concentration ($\mu g/m\ell$) in the analysis sample.

10.2 Blank values, if any, are subtracted from each sample.

10.3 The concentration of the metal in the original sample is:

$$\mu g \text{ metal}/m\ell \text{ sample} = \mu g/m\ell \times \text{dilution factor}$$

where:

$\mu g/m\ell$ = metal concentration determined from the appropriate calibration curve (Section 10.1).

11. References

11.1 Analytical Methods for Atomic Absorption Spectrophotometry, The Perkin-Elmer Corp., Norwalk, Conn.,1971.

11.2 Methods for Emission Spectrochemical Analysis, ASTM Committee E-2, Philadelphia, 1971.

DATA TABLE FOR METALS

Element	Sensitivity (μg/mℓ)	Range of Method (μg/mℓ)	Type of Flame	Analytical Wavelengths (Å)	Interferences	Remedy
Be	0.03	0.03 – 8	reducing N_2O-C_2H_2 (rich)	2349	>500 μg/mℓ At high conc. Si + Mg	(1)
Ca	0.07	0.07 – 10	reducing Air – C_2H_2	4227	Si, Al, PO_4	(2)
Cd	0.04	0.04 – 5	oxidizing Air – C_2H_2 (lean)	2288	None	
Co	0.15	0.15 – 8	oxidizing Air – C_2H_2	2407	None	
Cr	0.2	0.2 – 10	reducing Air – C_2H_2	3579	Fe + Ni	3(a)+3(b)
Cu	0.1	0.1 – 10	oxidizing Air – C_2H_2	3247	None	
Fe	0.1	0.1 – 10	oxidizing Air – C_2H_2	2483	Ni	(4)
K	0.1	0.1 – 10	oxidizing Air – C_2H_2	7665	K is partially ionized in the Air – C_2H_2 flame	(5)
Mg	0.007	0.007– 0.7	oxidizing Air – C_2H_2	2852	Si, Al, Cu at high concentrations	(6)
Mn	0.05	0.05 – 4	oxidizing Air – C_2H_2	2795	None	
Mo	1.0	1.0 – 60	reducing N_2O-C_2H_2	3133	Ca and other ions	(7)
Na	0.02	0.02 – 5	oxidizing Air – C_2H_2	5890	Na is partially ionized in the Air – C_2H_2 flame	(8)
Ni	0.2	0.2 – 20	oxidizing Air – C_2H_2	2320	None	
Pb	0.5	0.5 – 30	oxidizing Air – C_2H_2	2170,2833	None	
Sn	5.0	5.0 –300	reducing Air – C_2H_2	2246,2354	None	
Zn	0.025	0.025– 2	oxidizing Air – C_2H_2	2139	None	

1. If these interferences are known to be present, add 500 μg/mℓ Al, Si, or Mg to all standards.
2. Add 1% La to both standards and samples.

3(a) Add 200 μg/mℓ Fe to both standards and sample solutions. 3(b) If Ni is present, use a stoichiometric flame to minimize Ni interference.

4. Add 200 μg/mℓ Ni to both standards and samples.
5. Add Na at a ratio of 2 part Na to each part K in both standards and samples.
6. Due to the high sensitivity of Mg and the effect of sample dilution, no interferences exist.
7. Add 1000 μg/mℓ Al to both standards and samples.
8. Add K at a ratio of 2 parts K to each part Na in standards and samples.

DATA TABLE FOR METALS (Continued)

Element	Sensitivity (μg/mℓ)	Range of Method (μg/mℓ)	Type of Flame	Analytical Wavelengths (Å)	Interferences	Remedy
Al	1.2	1.2 –50	reducing N_2O-C_2H_2 (rich)	3093	Fe, HCl H_2SO_4, V, Ti, $HC_2H_3O_2$ Al is partially ionized	(9)
Li	0.04	0.04– 2	oxidizing Air – C_2H_2 (lean)	6708	None	
Pd	0.4	0.4 –15	oxidizing Air – C_2H_2 (very lean)	2476	Al, Co, Ni, Pt, Rh, Ru	(10)
Si	5.0	5.0 –150	reducing N_2O-C_2H_2	2516	Fe only when using a multi-element lamp containing Fe	(11)
Ag	0.1	0.1 – 10	oxidizing Air – C_2H_2	3281	Iodate, permanganate, and tungstate H_2SO_4 and H_3PO_4 $HC_2H_3O_2$	(12)
Te	0.5	0.5 – 25	oxidizing Air – C_2H_2	2143	None	
Tl	0.5	0.5 – 20	oxidizing Air – C_2H_2	2768	None	
Ba	0.1	0.1 – 50	reducing N_2O-C_2H_4	5536	Alkali salts	(13)
As	0.5	0.5 – 50	oxidizing Air – C_2H_4	1937 (EDL)		

9. Add alkali metal salts (1000 – 2000 μg/mℓ) to sample and standard solutions.
10. Add 0.5% La or 0.01 M EDTA.
11. Use a secondary silicon resonance line of 2507, 2528, or 2524.
12. Remove interfering substances or add these to standard solutions.
13. Add 1000 μg/mℓ KCl to samples and standard solutions.

MERCURY IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Particulate Hg, Hg° and organic Hg vapors	**Method No:**	175
Matrix:	Air	**Range:**	0.001-2.5 μg Hg
Procedure:	Trapping all three forms of Hg in a three-section solid phase sampler – Flameless AA	**Precision:**	Better than ± 2% (RSD) (Analytical)
Date Issued:	12/15/73	**Classification:**	E (Proposed)
Date Revised:	1/15/74		

1. **Principle of Method**

1.1 **Particulate mercury** is collected on a membrane prefilter ahead of a two-section, solid phase sampling tube. **Organic mercury vapor** is collected on the first section of the tube and **metallic mercury vapor** is amalgamated in the second section.

1.2 The membrane filter is removed from the sampler and digested in a Teflon decomposition vessel with nitric acid. Mercury in the digested filter is reduced to metallic mercury vapor and is transferred onto a tube containing a silver coated substrate. The collected mercury is thermally desorbed from the silver through a flameless atomic absorption spectrophotometer (modified Coleman Model MAS-50 or equivalent) where the amount of mercury from the membrane is determined.

1.3 The two-section sampling tube used for absorbing organic and metallic mercury is conditioned by passing pure nitrogen gas through the tube to remove any metallic mercury which may have remained in the first section.

1.4 The two-section tube is then broken between the sections and each section is analyzed separately. The first section represents mercury collected as organic mercury vapor and the second section represents metallic mercury. Each section is analyzed by thermally desorbing the mercury through the absorption cell of the flameless atomic absorption spectrophotometer (modified Coleman Model MAS-50 or equivalent). Absorption signals at the 2537Å line are recorded by strip chart recorders.

1.5 The recorder signals are compared to standard calibration curves covering the required concentration range and the concentration of the mercury in the two sections of the tube is calculated from the signals.

2. **Range and Sensitivity**

2.1 A dual optical cell system is used to extend the range of the method. The first cell is 15.5 cm in length and is used in the 0.001 μg to 0.20 μg range. The second cell is 2.5 cm long and is used for 0.01 μg to 2.5 μg of mercury.

2.2 The range and sensitivity of the method (as Hg) is the same for the three forms of mercury since the same analytical technique is used for each form.

2.3 The sensitivity of the method using the 0 to 100% absorption scale for both optical cells is 0.001 μg (2σ above the blank reading) for the 15.5 cm cell and 0.01 μg for the 2.5 cm cell.

2.4 The range and sensitivity of the method may be extended to as low as 0.0002 μg using electronic scale expansion.

3. **Interferences**

3.1 Loading the prefilter with excess particulates will increase air flow resistance through the sampler. This may overload battery operated sampling pumps.

3.2 Excessive amounts of water vapor may interfere if water is condensed in the sampling tubes; however, small amounts of water are removed by purging the tubes with pure dry nitrogen gas before analysis as described.

3.3 Strong oxidizing vapors and gases, particularly chlorine, which attack silver reduce the efficiency of the sampling tube but do not interfere in the analysis of the tube. These interferences should not be a problem under normal sampling conditions.

4. **Precision and Accuracy**

4.1 Standards are prepared by injecting known amounts of mercury as standardized mercuric nitrate solution directly into tubes containing the silvered substrate followed by drying the tubes at 50°C for at least 6 hours. Radiolometric studies have indicated that all the mercury added to the tubes remains in the tubes until analysis and that the accuracy of the analytical method approaches 100%.

4.2 Radiolometric studies on the efficiency of the bubbler system used in the procedure for particulate mercury show that only 95 ±3% of the mercury in the

bubbler is transferred after 4 minutes of bubbling. A correction for bubbler efficiency must be made when analyzing for particulate mercury. This may be done by either using a correction factor or by preparing a separate calibration curve from bubbled standards.

4.3 A statistical study of precision showed a relative standard deviation of ±2% per analysis in the optimum working range of the 15.5 cm optical cell (0.01 μg to 0.1 μg) and a ±1% relative standard deviation in the optimum working range of the 2.5 cm cell (0.1 μg to 1.5 μg).

5. Advantages and Disadvantages of the Method

5.1 The main **advantage** is the convenience of the sampling procedure and the ability to analyze **particulate, metallic** and **organic** mercury.

5.1.1 The efficiency of the silvered substrate for collecting metallic mercury vapor and the efficiency of Carbosieve B for organic mercury vapor allows the use of small sampling tubes with low air flow resistance.

5.1.2 The sampling tubes contain no liquids and are easily stored and shipped without mercury losses.

5.1.3 Since each section of the sample is analyzed by the same technique, the need for separate analytical methods is eliminated.

5.1.4 Amalgamation of the metallic mercury released from each sample makes the method more selective than other methods.

5.2 The main **disadvantage** of the method is the care necessary to avoid contamination of the outer surfaces of the sampling tubes.

5.2.1 Although the method is satisfactory for total mercury below 0.001 μg, absolute separation of organic and metallic mercury becomes less certain for amounts below this level.

6. Apparatus

6.1 Preparation of Silvered Substrate

6.1.1 **Beaker**: 1000 mℓ

6.1.2 **Erlenmeyer flask**: 1000 mℓ capacity with glass stopper.

6.1.3 **Stirrer**: magnetic with stirring bar.

6.1.4 **Separatory funnel** or burette with stopcock: 125 mℓ capacity.

6.2 **Preparation of Air Sampling Tubes**

6.2.1 Glass rod

6.2.2 Gloves: white cotton

6.2.3 Thermal desorption unit: Figure 1. (Full description is given in Appendix A.)

6.3 **Preparation of Mercury Standards: Direct Addition Method**

6.3.1 **Eppendorf pipettes**: 0.025 mℓ, 0.050 mℓ, 0.075 mℓ, and 0.100 mℓ (or micropipettes with syringe).

6.3.2 **Forceps**: (tweezers), fine tip.

6.3.3 **Glass rod**: approximately 3 mm diameter.

6.3.4 Thermal desorption unit: Figure 1.

6.4 **Collection and Analysis of Air Samples**

6.4.1 **Sampling Equipment**

1. A filter unit (for particulate mercury) which consists of the filter media (Section 6.4.1.8) and cassette filter holder.

2. Two stage mercury sampling tube (Figure 2).

3. A vacuum pump suitable for delivering desired flow rates, i.e., 1 to 2 liters per minute.

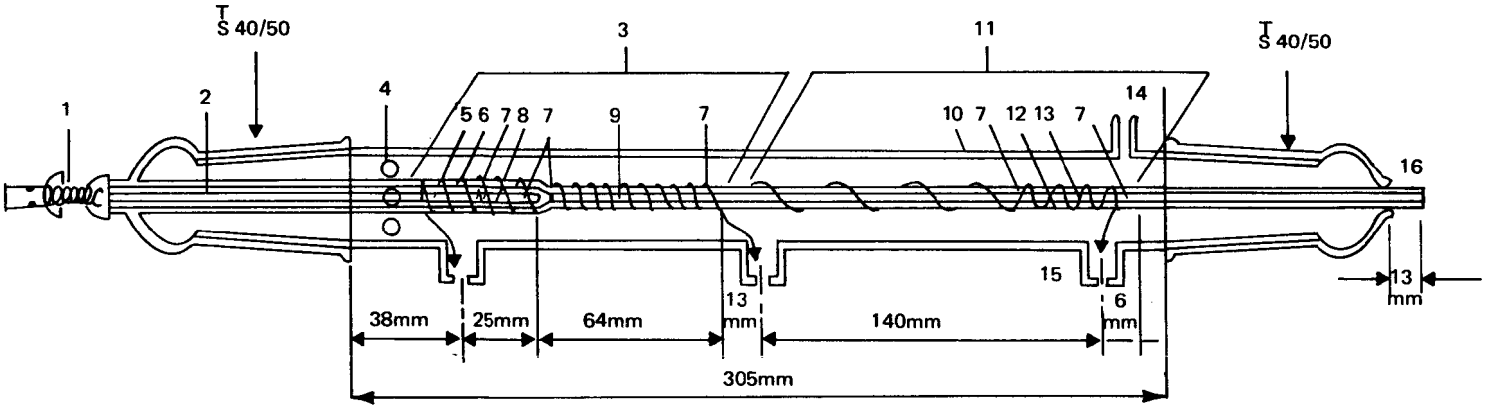
4. An integrating volume meter such as a dry gas or wet test meter.

5. Thermometer.

6. Manometer.

7. Stopwatch.

8. Membrane filter, 0.8 μ, 37 mm.



1. Loading Mechanism
2. Quartz Glass Plunger Tube
3. Sample Desorption Section
4. Cooling Air Vent Holes
5. Sampling Tube
6. Nichrome Wire Coil
7. Quartz Glass Wool Plugs
8. Sampling Tube Contents
9. Cupric Oxide (CuO)
10. Cooling Jacket
11. Second Desorption Section
12. Nichrome Wire Coils
13. Gold Section
14. Cooling Air Intake
15. Wire Holes and Solderless Conectors
16. Outlet

FIGURE 1 THERMAL DESORPTION UNIT

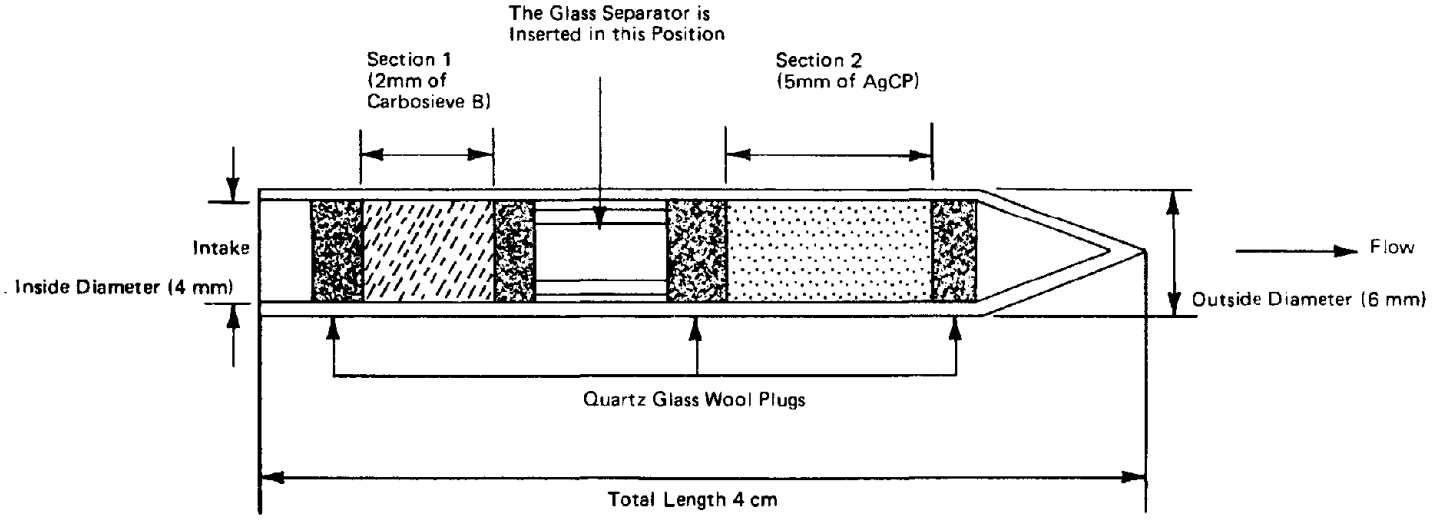


FIGURE 2 TWO STAGE MERCURY SAMPLING TUBE

6.4.2 **Analysis of Particulate Mercury**

1. **Air pump**: capable of delivering air at 1 to 2 liters/min through a bubbler flask.

2. **Bubbler flask**: 300 mℓ BOD bottle as supplied with Coleman MAS-50 or equivalent.

3. **Connecting tubing** – minimum lengths of either glass or Tygon.

4. **Decomposition vessels**: Teflon, 20 mℓ capacity, Uni-Seal Ltd. (P.O. Box 9463, Haifa 31094, Israel) or equivalent.

5. Midget impinger.

6. Oven.

6.4.3 **Analysis of Metallic and Organic Mercury**

1. Analysis system: (see Figure 3).

2. **Flow meters** with needle valves: 0-2 liters/min and 0-25 liters/min.

3. **Purge gas**: pure, compressed dry nitrogen gas.

4. Thermal desorption unit (full description in Appendix A).

5. Vacuum pump.

6.4.4 **Absorption cell #1**: 15.5 cm length, made of Pyrex glass with quartz glass windows for Coleman MAS-50, 1.2 cm inside diameter.

6.4.5 **Absorption cell #2**: 2.5 cm length, made of Pyrex glass with quartz glass windows, 1.2 cm inside diameter.

6.4.6 **Flameless atomic absorption mercury analyzers**: Coleman Mercury Analysis System (MAS-50), or equivalent.

7. **Reagents**

All reagents used should be ACS Reagent Grade or better.

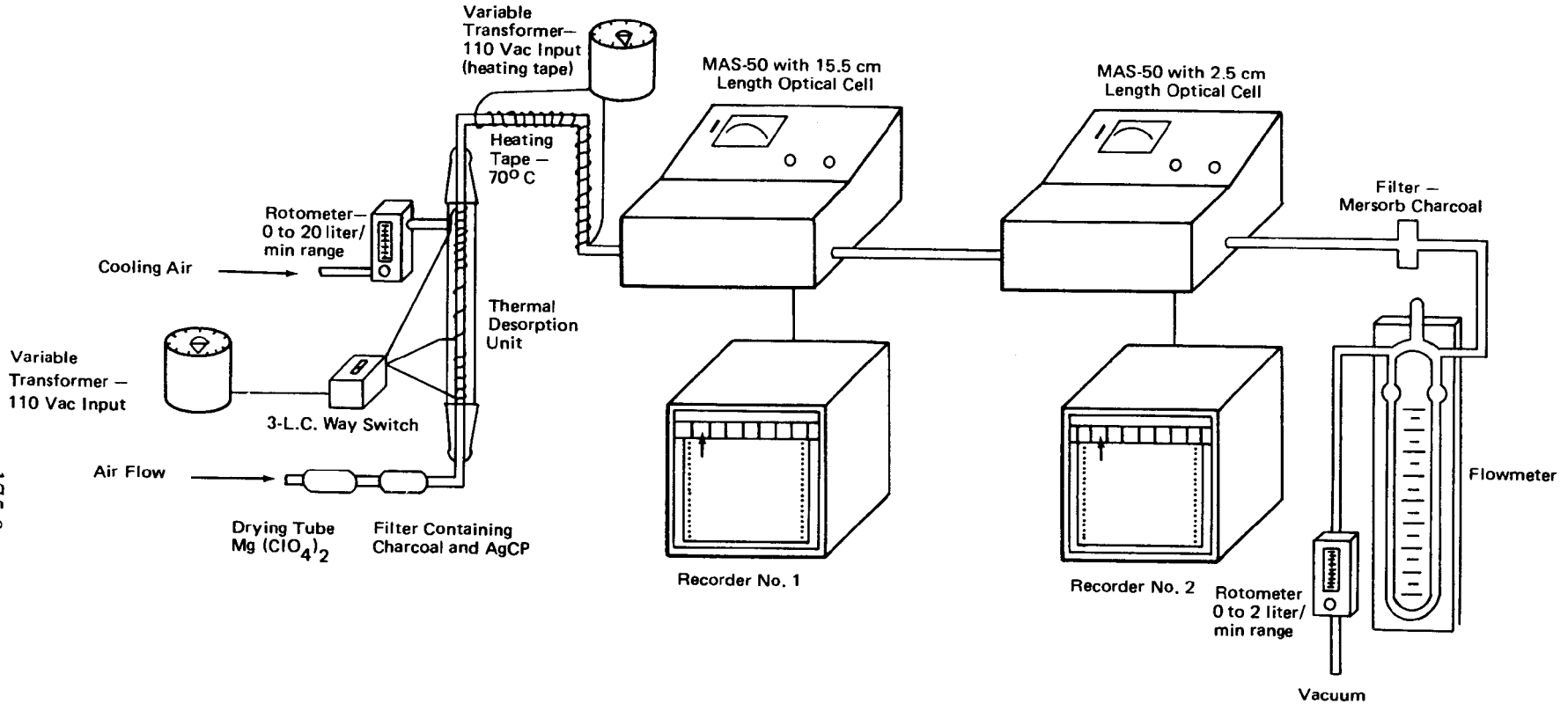


FIGURE 3 MERCURY ANALYSIS SYSTEM

7.1 **Preparation of Silvered Substrate**

7.1.1 **Ammonium hydroxide** (NH_4OH): concentrated

7.1.2 **Chromosorb P**: non-acid washed, sieved to 30/60 mesh. (Johns-Manville)

7.1.3 **Dextrose**: powder.

7.1.4 **Potassium hydroxide** (KOH)

7.1.5 **Silver nitrate** ($AgNO_3$): crystals.

7.2 **Preparation of Air Sampling Tubes**

7.2.1 **Carbosieve B**: 45/60 mesh (Supelco, Inc.)

7.2.2 **Glass tubes**: Pyrex, 4 mm ID, 4 cm length, flame sealed at one end.

7.2.3 **Glass separators**: 1 cm glass tubes, approximately 3 mm O.D.

7.2.4 Quartz glass wool.

7.2.5 **Silvered Chromosorb P** (AgCP): see Section 8.2.

7.2.6 **Pure nitrogen gas**: filtered through AgCP.

7.3 **Preparation of Mercury Standards: Direct Addition Method**

7.3.1 **Silver Chromosorb P** (AgCP) tubes: prepared as described in 8.3.1 and 8.3.2 but containing a 15 mm section of AgCP.

7.3.2 **Stock solution**: 100 μg Hg/mℓ prepared by dissolving 100 mg of metallic mercury in 50 mℓ concentrated nitric acid in a 1000 mℓ Pyrex volumetric flask and diluting to volume with double distilled H_2O. The solution may be stored in the flask for as long as 6 months.

7.3.3 **Standard working solution A**: 1 μg/mℓ prepared by diluting 1.00 mℓ of the standard stock solution to 100 mℓ with 1 mℓ concentrated HNO_3 and double distilled water. Prepare fresh dilutions every 5 days.

7.3.4 **Standard working solution B**: 2 μg/mℓ, prepared as above except with 2 mℓ of stock solution. Prepare fresh dilutions every 5 days.

7.4 **Analysis of Air Samples**

7.4.1 Double distilled water.

7.4.2 **Nitric acid**, HNO_3 : concentrated.

7.4.3 **Standard working solutions A and B**: previously described.

7.4.4 **Stannous chloride solution**: 20% w/v in 6 N HCl – freshly prepared.

8. **Procedure**

8.1 **Cleaning of Equipment.** Acid clean all glassware and Teflon before use.

8.1.1 Wash in detergent tap water solution and follow with tap water.

8.1.2 Soak in concentrated HNO_3 for 30 minutes, and follow with tap, distilled and double distilled water rinses.

8.2 **Preparation of Silvered Substrate**

8.2.1 Dissolve 20 g $AgNO_3$ in 300 mℓ of distilled water (Solution A) in a 1000 mℓ beaker.

8.2.2 Place a magnetic stirring bar in the solution and stir on a magnetic stirrer.

8.2.3 Slowly add concentrated NH_4OH until a dark brown precipitate of Ag_2O forms.

8.2.4 While stirring, add concentrated NH_4OH dropwise until the solution just clears. Disregard any small specks which may form.

8.2.5 Take another 2 g of $AgNO_3$ and dissolve in 30 mℓ distilled water in a separatory funnel (Solution B). Then add this solution dropwise to the mixture in the 1000 mℓ beaker (Section 8.2.4) until the solution turns straw yellow.

CAUTION: Use face shield and rubber gloves.

8.2.6 Slowly add 100 mℓ of KOH solution (14 g KOH in 100 mℓ of H_2O) while constantly stirring.

8.2.7 Add concentrated NH_4OH dropwise until the solution in 1000 mℓ beaker just clears.

8.2.8 Add more Solution B until a thin straw yellow or light brown precipitate forms. Again disregard any small specks.

8.2.9 Remove the 1000 mℓ beaker from the stirrer and filter the solution (Solution C) through glass wool.

8.2.10 Dissolve 7.8 g dextrose in 120 mℓ of distilled H_2O in a 1000 mℓ Erlenmeyer flask and add 40 grams of Chromosorb P to the dextrose solution.

8.2.11 Swirl the Chromosorb P in the dextrose solution until the surfaces are wet and then carefully decant any excess dextrose solution.

8.2.12 Slowly add the silver solution (Solution C – Section 8.2.9) to the Chromosorb P, stopper the flask and shake vigorously until all the surfaces come in contact with the silver solution.

8.2.13 Decant and discard the excess silver solution.

8.2.14 Rinse and decant the silvered Chromosorb P (AgCP) three times with distilled water.

8.2.15 Dry the AgCP in a drying oven at 60°C.

Note: Dry in an atmosphere free of sulfides.

8.3 **Preparation of Air Sampling Tubes**

8.3.1 Insert a glass wool plug into the open end of a glass tube and lightly pack the plug at the other end of the tube with the glass rod.

8.3.2 Add enough AgCP to the tube to make a 5 mm section of AgCP and pack lightly with a second glass wool plug (Figure 2).

8.3.3 Insert a glass separator on top of the second wool plug and lightly pack a third quartz glass wool plug over the separator.

8.3.4 Add enough Carbosieve B to make a 2 mm section and pack the Carbosieve with a fourth glass wool plug (Figure 2).

8.3.5 Break the sealed end of the tube and place the tube inside the thermal desorption unit.

8.3.6 Purge the tube in the desorption unit with pure air at a flow rate of approximately 1 liter/minute and heat the tube to 700°C for 15 seconds.

8.3.7 Remove the tube from the thermal desorption unit and allow to cool.

CAUTION: The tubes are hot on removal from the desorption unit and should be dropped directly into a small glass stoppered volumetric flask or vial for cooling and storage.

8.3.8 Seal and store the sampling tube in the bottle or vial until used.

8.4 **Collection of Air Samples**

8.4.1 After the sampling tubes have been prepared and stored, they should be stable indefinitely. White gloves should be used when removing the tubes from the storage vials and when inserting the tube into the sampler at the sampling site.

8.4.2 The sampler should be equipped with a holder for a 37 mm diameter, 0.8 μ membrane filter preceding the sampling tube to collect particulate mercury.

8.4.3 Draw air through the filter and sampling tube at the appropriate flow rate for the necessary length of time. Measure the flow rate, time, and/or volume as accurately as possible.

8.4.4 Remove the sampling tube from the sampler, and replace inside the glass vial. Once again, gloves should be used when handling the sampling tube.

8.4.5 Either remove the filter from the holder and place in another glass vial or submit the entire holder with the filter to the analyst.

8.4.6 Appropriate "blank" samples should be handled and submitted together with the samples.

8.5 **Analysis of Filters for Particulate Mercury**

8.5.1 Remove the filter from the holder or glass vial and place inside the decomposition vessel.

8.5.2 Add 5 mℓ of concentrated HNO_3 and cap the vessel securely.

8.5.3 Place the vessel in an oven at 150°C for 1.5 hours.

8.5.4 Remove the vessels from the oven and cool to room temperature in a water bath.

8.5.5 Open the vessel and quantitatively transfer the contents into a bubbler flask with double distilled water.

8.5.6 Bring the total volume of liquid in the flask to 75 mℓ with double distilled water.

8.5.7 Connect a blank sampling tube containing a single section of AgCP to the outlet end of the bubbler system.

8.5.8 Add one mℓ of stannous chloride solution to the contents of the bubbler flask and immediately connect the flask to the bubbler system.

8.5.9 Turn on the pump and bubble the contents of the flask for 4 min at 1 to 2 liters/min.

8.5.10 Turn off the pump and remove the AgCP tube from the bubbler system.

8.5.11 Purge the AgCP tube for 2 min at 5 liters/min with pure, dry nitrogen gas and analyze the contents of the tube using the procedure for metallic mercury. (Section 8.6.13, including 8.6.3 to 8.6.7.)

8.5.12 The signals obtained from this AgCP tube represent total particulate mercury.

NOTE: Since the efficiency of the bubbler system is only 95 ±3%, the amount of mercury found in the AgCP tube represents this percent of the total mercury originally present in the filter. This error may be corrected by using a correction factor or by preparing a separate calibration curve from bubbled standards. These standards are prepared by adding the appropriate amount of Solution A or B to 5 mℓ of the concentrated HNO_3 in the bubbler flask and proceeding with steps 8.5.6 through 8.5.11.

8.6 **Analysis of Air Sampling Tubes for Organic and Metallic Mercury**

8.6.1 All operations requiring the handling of the sample tubes should be done using clean white cotton gloves.

8.6.2 Remove the sample from the glass storage vial, wipe the outer surface, and pass pure, dry nitrogen through the tube from the intake end for 2 min at room temperature at a flow rate of 5 liters/min.

8.6.3 Adjust the cooling air through the thermal desorption unit to 25 liters/min, using the needle valve.

8.6.4 Adjust the air flow through the desorption section of the thermal desorption unit to approximately 1.0 liter/min using the small needle valve.

NOTE: The optimum flow rate setting through the desorption unit is determined by analyzing standards until the best signal is obtained. However, once the optimum setting is found, it must be exactly the same for each set of analyses to assure reproducibility.

8.6.5 Turn on the MAS-50's and adjust the recorders to give 0 divisions at the 100% T setting and 100 divisions at the 0% T setting. A warm-up period may be necessary to stabilize the MAS-50's. This period will vary with individual instruments.

8.6.6 Clean the thermal desorption unit by heating section 1 of the unit for 30 seconds (30 volts) and then heating section 2 for 30 seconds (30 volts).

8.6.7 Repeat step 8.6.6 until no mercury signal is obtained on the recorders.

8.6.8 Cut the purged sampling tube between the 2nd and 3rd glass wool plug and separate the two tube sections.

8.6.9 Place the Carbosieve B section of the sampling tube in the thermal desorption unit and heat the tube for 30 seconds at 700°C (30 volts) in section 1 of the desorption unit.

8.6.10 Immediately desorb the mercury from section 2 of the desorption unit by heating at 700°C (30 volts) for 30 seconds.

8.6.11 Allow a 60 second cooling period between samples.

8.6.12 The signals obtained for the Carbosieve B section of the sampling tube represent total organic mercury.

8.6.13 Repeat steps 8.6.9 and 8.6.11, using the AgCP section of the air sampling tube. The signals obtained for this section represent total metallic mercury.

9. Calibration

9.1 Remove the glass wool plug from the open end of a blank AgCP tube using gloved hands and tweezers.

9.2 Inject the required amount of mercury solution directly on top of the exposed AgCP using an Eppendorf pipette while holding the tube in the upright position. (No more than 0.1 mℓ volume.)

9.3 Replace the glass wool plug and repack the tube using a glass rod.

9.4 Place the wet tubes upright in a small beaker and dry the tubes for at least 6 hours at 50°C in a drying oven.

9.5 When the tubes are dry, break the sealed end of the tube and place in the thermal desorption unit for analysis.

9.6 The signals obtained from the standard tubes are used to prepare a calibration curve.

10. Calculations

10.1 To determine total micrograms of mercury as particulate, organic and metallic mercury, the absorption signals for the filters and sampling tubes are compared with the appropriate calibration curve.

10.2 Calculate the mercury concentration in micrograms per cubic meter ($\mu g\ Hg/m^3$) for each type of mercury,

$$\mu g\ Hg/m^3 = \frac{\mu g\ Hg}{V_s} \quad \text{(from Section 10.1)}$$

where:

V_s = volume of air sampled in cubic meter at standard conditions of 25°C and 760 mm Hg. (1000 ℓ = 1 m^3); volume = flow rate x time.

10.3 The total amount of mercury in the sample may be obtained by adding the mercury found in each section of the sampler; i.e., particulate + organic + metallic.

10.4 If large amounts of metallic mercury are found in the second section of the sampling tube (above 0.1 μg), a correction must be made for the organic section. This is done by subtracting 2% of the metallic mercury content from the amount found for organic mercury.

11. References

11.1 Campbell, E.E., Trujillo, P.E., and Wood, G.O., Los Alamos Scientific Laboratory, Quarterly Report No. LA-S 340-PR, "Development of a Multistage Tandem Air Sampler for Mercury," Los Alamos, March 31, 1973.

VINYL CHLORIDE IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Vinyl Chloride (Chloroethene, Chloroethylene)	Method No.:	P&CAM #178
Matrix:	Air	Range:	0.2-1500 ng per injection
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC		
Date Issued:	9/3/74	Precision:	Unknown
Date Revised:	10/15/74	Classification:	D (Operational)

1. Principle of the Method

   1.1 A known volume of air is drawn through a charcoal tube to trap the vinyl chloride present.

   1.2 The charcoal in the tube is transferred to a small vial containing carbon disulfide where the vinyl chloride is desorbed.

   1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

   1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

   2.1 The minimum detectable amount of vinyl chloride was found to be 0.2 nanograms per injection at a 1 x 1 attenuation on a gas chromatograph.

   2.2 At the recommended sampling flow rate of 50 ml/min, the total volume to be sampled should not exceed 5.0 liters. This value is the volume of air containing 200 ppm of vinyl chloride which can be sampled before a significant amount of vinyl chloride is found on the backup section. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethan foam. (See Section 6.2.1) If a particular atmosphere

is suspected of containing a high concentration of contaminants and/or a high humidity is suspected, the sampling volume should be reduced by 50%.

3. Interferences

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped. Preliminary experiments indicate that high humidity severely decreases the capacity of the charcoal for organic vapors.

3.2 When two or more substances are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample since these compounds may interfere with the analysis for vinyl chloride.

3.3 It must be emphasized that any compound which has the same retention time as vinyl chloride at the operation conditions described in this method is an interference. Hence, retention time data on a single column, or even on a number of columns, cannot be considered as proof of chemical identity. For this reason it is important that a sample of the bulk material be submitted at the same time so that identity(ies) can be established by other means.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

The precision and accuracy of the total sampling and analytical method have not been determined.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more components suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 20% of that found on the front section, the possibility of sample loss exists. During sample storage, volatile compounds such as vinyl chloride will migrate throughout the tube until equilibrium is reached. At this time, 33% of these compounds will be found in the backup section. This may lead to some confusion as to whether sample loss has occurred. This migration effect can be considerably decreased by shipping and storing the tubes at -20°.

5.3 The precision of the overall method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 An approved and calibrated personal sampling pump for personal and area samples whose flow can be determined accurately at 50 milliliters per minute.

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated coconut charcoal separated by a 2-mm portion of urethan foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing to remove material possibly absorbed on charcoal. The primary absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethan foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 ℓ/min.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Stainless steel column (20 ft x 1/8 in) packed with 10% SE-30 on 80/100 mesh Chromosorb W (acid washed, silanized with dimethyldichlorosilane). Other columns capable of performing the required separations may be used.

6.5 A mechanical or electronic integrator or a recorder and some method for determining peak area.

6.6 Two-ml vials which can be sealed with caps containing teflon-lined silicone rubber septa.

6.7 Microliter syringes: 10-μℓ, and convenient sizes for making standards.

6.8 Gas-tight syringes: 1-mℓ, with open/close valve.

6.9 Pipets: 0.5-mℓ delivery pipets or 1.0-mℓ type graduated in 0.1-mℓ increments.

6.10 Volumetric flasks: 10-mℓ or convenient sizes for making standard solutions. It is preferable to have plastic stoppers for the volumetric flasks.

7. Reagents

7.1 Spectroquality carbon disulfide.

7.2 Vinyl chloride, lecture bottle, 99.9% minimum purity.

7.3 Toluene, chromatographic quality.

7.4 Bureau of Mines Grade A helium.

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, the ends of the tube are broken to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a backup and is positioned nearest the sampling pump.

8.3.3 The charcoal tube is placed in a vertical position during sampling to prevent "channelling" of the charcoal.

8.3.4 Air being sampled is not to be passed through any hose or tubing before entering the charcoal tube.

8.3.5 Bulk air samples (i.e., samples of 10-20 liters of the air in the environment) are taken along with personal samples.

8.3.6 The flow, time, and/or volume must be measured as accurately as possible. The sample is taken at a flow rate of 50 ml/min. The maximum volume to be sampled should not exceed 5.0 liters (See Section 2.2).

8.3.7 The temperature and pressure of the atmosphere being sampled is measured and recorded.

8.3.8 The charcoal tubes are capped with the supplied plastic caps immediately after sampling. Under no circumstances are rubber caps to be used.

8.3.9 One tube is handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube is labeled as a blank.

8.3.10 Capped tubes are packed tightly before they are shipped to minimize tube breakage during transport to the laboratory. If the samples will spend a day or more in transit, cooling (e.g., with dry ice) is necessary to minimize migration of vinyl chloride to the backup section.

8.3.11 Samples received at the laboratory are logged in and immediately stored in a freezer (around -20°) until time for analysis. Samples may be stored in this manner for long periods of time with no appreciable loss of vinyl chloride (2 months). Even around -20°C, vinyl chloride will equilibrate between the two sections of charcoal, i.e., will migrate to the backup section. This phenomenon is observable after two weeks and may be confused with sample loss after 1 to 2 months.

8.4 Analysis of Samples

8.4.1 Preparation and Desorption of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a small vial containing 1 ml of carbon disulfide. (Note: the addition to the CS_2 is important.) The vial is topped with a

septum cap (See Section 6.6). The separating section of foam is removed and discarded; the second section is transferred to another small vial containing 1 ml of CS_2. These two sections are analyzed separately. Tests indicate that desorption is complete in 30 minutes if the sample is agitated occasionally during this period. In any case samples should be analyzed within 60 minutes after addition to CS_2.

8.4.2 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 40 cc/min (80 psig) helium carrier gas flow
2. 65 cc/min (20 psig) hydrogen gas flow to detector
3. 500 cc/min (50 psig) air flow to detector
4. 230°C injector temperature
5. 230°C manifold temperature (detector)
6. 60°C isothermal column temperature (oven).

8.4.3 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blowback or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µℓ syringe is first flushed with solvent several times to wet the barrel and plunger. Two microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent and the plunger is pulled back about 0.4 µℓ to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µℓ aliquot is withdrawn to the 7.4 µℓ mark (2 µℓ solvent + 0.4 µℓ air + 5 µℓ sample = 7.4 µℓ). After the needle is removed from the sample and prior to injection the plunger is pulled back a short distance to minimize evaporation of the sample from the tip of the needle. Duplicate injections of each sample and standard are made. No more than a 3% difference in area is to be expected.

8.4.4 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of vinyl chloride that is removed in the

desorption process. Desorption efficiency should be determined on the same batch of charcoal tubes used in sampling. Results indicate that desorption efficiency varies with loading (total vinyl chloride on the tube), particularly at lower values, i.e., 2.5 µg.

8.5.2 Procedure for determining desorption efficiency. Charcoal tubes from the same batch as that used in obtaining samples are used in this determination. A measured volume of vinyl chloride gas is injected into a bag containing a measured volume of air. The bag is made of Tedlar (or a material which will retain the vinyl chloride and not absorb it) and should have a gas sampling valve and a septum injection port. The concentration of the bag may be calculated knowing room temperature and pressure. A measured volume is then sampled through a charcoal tube with a calibrated sampling pump. At least five tubes are prepared in this manner. These tubes are desorbed and analyzed in the same manner as the samples (See Section 8.4). Samples taken with a gas tight syringe from the bag are also injected into the GC. The concentration in the bag is compared to the concentration obtained from the tubes.

The desorption efficiency equals the amount of vinyl chloride desorbed from the charcoal divided by the quantity of vinyl chloride contained in the volume of synthetic atmosphere sampled, or

$$\frac{\text{quantity vinyl chloride from charcoal}}{\text{concentration vinyl chloride in atmosphere} \times \text{volume atmosphere sampled}}$$

9. Calibration and Standards

CAUTION: Laboratory Operations Involving Carcinogens

Vinyl chloride has been identified as a human carcinogen and appropriate precautions must be taken in handling this gas. The Occupational Safety and Health Administration has promulgated regulations for the use and handling of vinyl chloride. They may be found in 29 CFR 1910.93q (Section 1910.93q in Title 29 of the Code of Federal Regulations available in the Federal Register, Vol. 39, No. 194, Friday, October 4, 1974, pp. 35890-35898).

A series of standards, varying in concentration over the range of interest, are prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in µg/1.0 mℓ versus peak area. There are two methods of preparing standards and as long as highly purified vinyl chloride is used, both are comparable.

NOTE: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of day-to-day variations of the FID response.

9.1 Standard Preparation

Gravimetric Method - Vinyl chloride is slowly bubbled into a tared 10-ml volumetric flask containing approximately 5 ml of toluene. After 3 minutes, the flask is again weighed. A weight change of 100-300 mg is usually observed. The solution is diluted to exactly 10 ml with carbon disulfide and is used to prepare other standards by removal of aliquots with different sized syringes. Subsequent dilution of these aliquots with carbon disulfide results in a series of points that are linear from the range of 0.2 nanograms per injection, the minimum detectable amount of vinyl chloride, to 1.5 micrograms per injection.

Volumetric Method - A 1-ml gas sample of pure vinyl chloride is drawn into a gas-tight syringe and the tip of the needle is inserted into a 10-ml volumetric flask containing approximately 5 ml of CS_2. The plunger is withdrawn slightly to allow the CS_2 to enter the syringe. The action of the vinyl chloride dissolving in the CS_2 creates a vacuum and the syringe becomes filled with the solvent. An air bubble (~2%) is present and was found to be due to the void volume in the needle of the syringe. The solution is returned to the flask and the syringe is rinsed with clean CS_2 and the washings added to the volumetric. The volumetric is then filled to the mark with CS_2. Other standards are then prepared from this stock solution.

Standards are stored in a freezer at -20°C and are found to be stable at this temperature for three days. Tight-fitting plastic tops on the volumetrics seem to retain the vinyl chloride better than ground glass stoppers.

10. Calculations

10.1 The weight, in µg, correspondong to each peak area is read from the standard curve for vinyl chloride. No volume corrections are needed, because the standard curve is based on µg/1.0 mℓ CS_2 and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank are made for each sample.

$$\mu g = \mu g_s - \mu g_b$$

where:

μg_s = µg found in front section of sample tube
μg_b = µg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 These values are further corrected for the desorption efficiency at the level of vinyl chloride measured.

$$\text{Corrected } \mu g = \frac{\mu g}{\text{desorption efficiency}}$$

10.4 The corrected amounts present in the front and backup sections of the same sample tube are added to determine the total amount of vinyl chloride in the sample.

10.5 The concentration of the vinyl chloride in the air sampled is expressed in mg/m^3, which is numerically equal to µg/liter of air

$$mg/m^3 = \mu g/\ell = \frac{\text{total } \mu g \text{ (Section 10.4)}}{V}$$

where: V is the volume of air sampled

10.6 Another method of expressing concentration is ppm, defined as µℓ of vinyl chloride gas/liter of air

$$ppm = \mu g/\ell \times \frac{24.45}{62.5} \times \frac{760}{P} \times \frac{T+273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (ℓ/mole) at 25°C and 760 mm Hg
62.5 = molecular weight (g/mole) of vinyl chloride
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

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11.2 White, L.D., D. G. Taylor, P.A. Mauer, and R.E. Kupel, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Am. Ind. Hyg. Assn.J., 31, 225 (1970).

APPENDIX A

DESCRIPTION, INSTALLATION, AND OPERATION OF THE TWO STAGE THERMAL DESORPTION UNIT FOR THE DETERMINATION OF MERCURY

Introduction

The thermal desorption unit described here was designed for the determination of mercury collected on 4 mm ID sampling tubes containing silvered Chromosorb P (AgCP) and/or Carbosieve B. Sampling tubes are inserted into the first section of the desorption unit where the mercury is thermally desorbed and transferred to a second section. The second section contains gold granules which amalgamate all the mercury released by the first section and allow impurities to pass. Mercury is then thermally desorbed from the second section and passed into a flameless atomic absorption spectrophotometer where the amount of desorbed mercury is determined.

Description

With the exception of the electrical components and the loading spring, the entire thermal desorption unit is made of either quartz or Pyrex glass. A diagram of the unit giving the critical dimensions is shown in Figure 1A. Each important part of the thermal desorption unit is numbered in the diagram and the numbers represent the following:

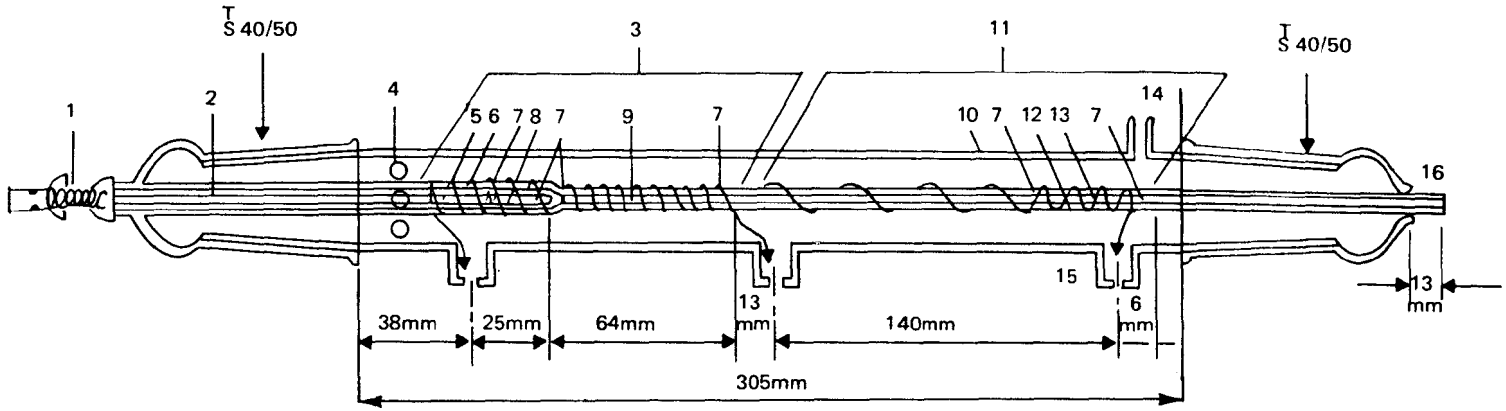
1-2. Loading mechanism (Figure 2A) – Made from an $18/7 female glass joint with a steel spring (#1), and a plunger tube (3 mm or 4 mm OD quartz glass – #2). The length of the plunger is cut to reach the sample desorption section.

3. Sample desorption section – Made from 8 mm ID and 5 mm ID quartz tubing. The junction between the two sizes of tubing is tapered on the inside so that sampling tube tips fit snugly against the junction.

4. Cooling vent holes – About seven 4 mm holes are placed around the outer jacket of the unit to allow cooling air to flow from the second heating coil to the first coil.

5. Sampling tube – Sampling tubes are positioned inside the first desorption section during mercury desorption. The spring on the loading mechanism is adjusted to press the sampling tubes lightly in place.

6. Nichrome wire coils – Twenty-eight coils of 18 gauge nichrome wire are wrapped around the first desorption section to heat the sampling tubes during the thermal desorption step.



1. Loading Mechanism
2. Quartz Glass Plunger Tube
3. Sample Desorption Section
4. Cooling Air Vent Holes
5. Sampling Tube
6. Nichrome Wire Coil
7. Quartz Glass Wool Plugs
8. Sampling Tube Contents
9. Cupric Oxide (CuO)
10. Cooling Jacket
11. Second Desorption Section
12. Nichrome Wire Coils
13. Gold Section
14. Cooling Air Intake
15. Wire Holes and Solderless Conectors
16. Outlet

FIGURE 1A THERMAL DESORPTION UNIT

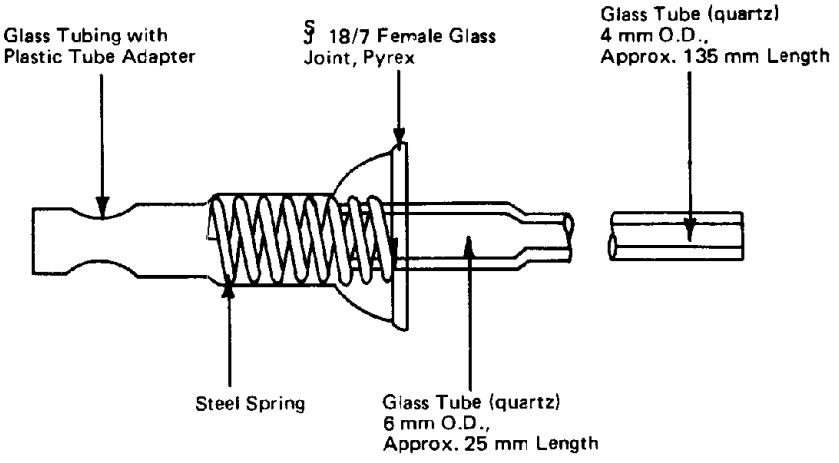


FIGURE 2A LOADING MECHANISM

7. Quartz glass wool plugs – Quartz wool glass plugs are used to separate each section. Although the plugs should be large enough to hold the materials, they should not be packed too tightly.

8. Sampling tube contents – The material in the sampling tube may be Carbosieve B, AgCP, or both, depending on what type of analysis is required.

9. Cupric oxide (CuO) – A 40 mm section of rod shaped CuO is placed just downstream from the sampling tubes. When heated, the CuO oxidizes organic vapors desorbed from the sampling tube. The CuO is held by a quartz glass wool plug which fits against a crimp in the glass tubing.

10. Cooling jacket – The Pyrex glass outer covering not only directs the flow of cooling air, but also acts as electrical insulation for the heating coils.

11. Second desorption section – This section is made from the 5 mm ID quartz glass tubing extending from the first desorption section. The contents are held in place by a crimp in the glass tube.

12. Nichrome wire coils – Thirty coils of size 20 nichrome wire are wrapped around the second desorption section. The coils are wrapped to allow most of the generated heat to concentrate over the gold granules of the second desorption section.

13. Gold section – This section consists of a 25 mm length of 35/50 mesh granular gold mixed one-to-one with 20/40 mesh sea sand. The sand is added to the gold to prevent fusing of the gold granules and to allow better air flow through the section.

14. Cooling air intake – A 6 mm ID piece of glass tubing is used for connecting plastic tubing from the cooling air supply.

15. Wire holes and solderless connectors – Wires to the heating coils enter the cooling jacket through 5 mm holes at the ends of glass nipples on the side of the jacket. The solderless connectors between the wires and the coils are placed inside the jacket to prevent exposing uninsulated wire outside the cooling jacket. The insulated wires to the connectors are sealed in place with a heat resistant sealer.

16. Outlet – The outlet from the desorption unit is butt connected with a Tygon overseal to a glass tube which leads to a flameless atomic absorption spectrophotometer (MAS-50). The end of the quartz tube slides through an opening at the end of the cooling jacket. The opening is kept to a minimum to limit the escape of cooling air.

Installation

A diagram of the installed thermal desorption unit system is shown in Figure 3A.

1. Power connections – The wires to the heating coils should be heavy enough to carry the current necessary to heat the coils (about #12). Power to the heating coils is controlled by a three position switch with an off position, an on position for coil #1 and an on position for coil #2. Power to the switch comes from a 120 Vac input, 20 A variable transformer set at 30 Vac.

2. Air supply – The air which passes through the heated sections of the thermal desorption unit is drawn from the room by a vacuum pump. The pump is attached to a ballast tank to prevent fluctuations in air flow.

   Before entering the desorption unit, room air passes through a drying tube containing anhydrous $Mg(ClO_4)_2$. The dimensions of the drying tube and all subsequent filters may vary but should not interfere with the air flow through the system. The $Mg(ClO_4)_2$ should be changed periodically depending on the humidity of the work area. The dried air passes through a filter containing activated charcoal and 30/60 mesh silvered Chromosorb P to remove organic vapors and metallic mercury.

   The dry, filtered air then passes by a shutoff valve, through the thermal desorption unit, through the flameless atomic absorption optical cells and into a filter containing Mersorb charcoal which collects any mercury desorbed by the desorption unit. Air from this charcoal filter then passes through a flowmeter and into the ballast tank of the vacuum pump. The flowmeter covers a 0 to 5 ℓ/min range and controls the flow of air through the system.

3. Cooling air – Cooling air for the heating coils is supplied by an air compressor. A flowmeter controls the flow rate at 15 ℓ/min. The air enters the desorption unit from a plastic tube into the air intake near the second desorption section.

4. Detection system – Mercury desorbed from the gold section of the thermal desorption system enters the optical cell of a flameless atomic absorption spectrophotometer through a glass tube. The glass tube connecting the desorption unit with the optical cell is maintained at 70°C using a heating tape. Power for the heating tape is supplied by a 120 Vac, 8 A variable transformer.

   Any reliable flameless atomic absorption spectrophotometer or mercury analysis system set to absorb the 2537Å wavelength of mercury may be used to detect the mercury vapor released from the desorption unit. A dual optical cell system made from two modified Coleman Mercury Analyzer Systems (MAS-50) is shown. The first MAS-50 contains a 15.5 cm optical cell made of Pyrex glass with quartz glass

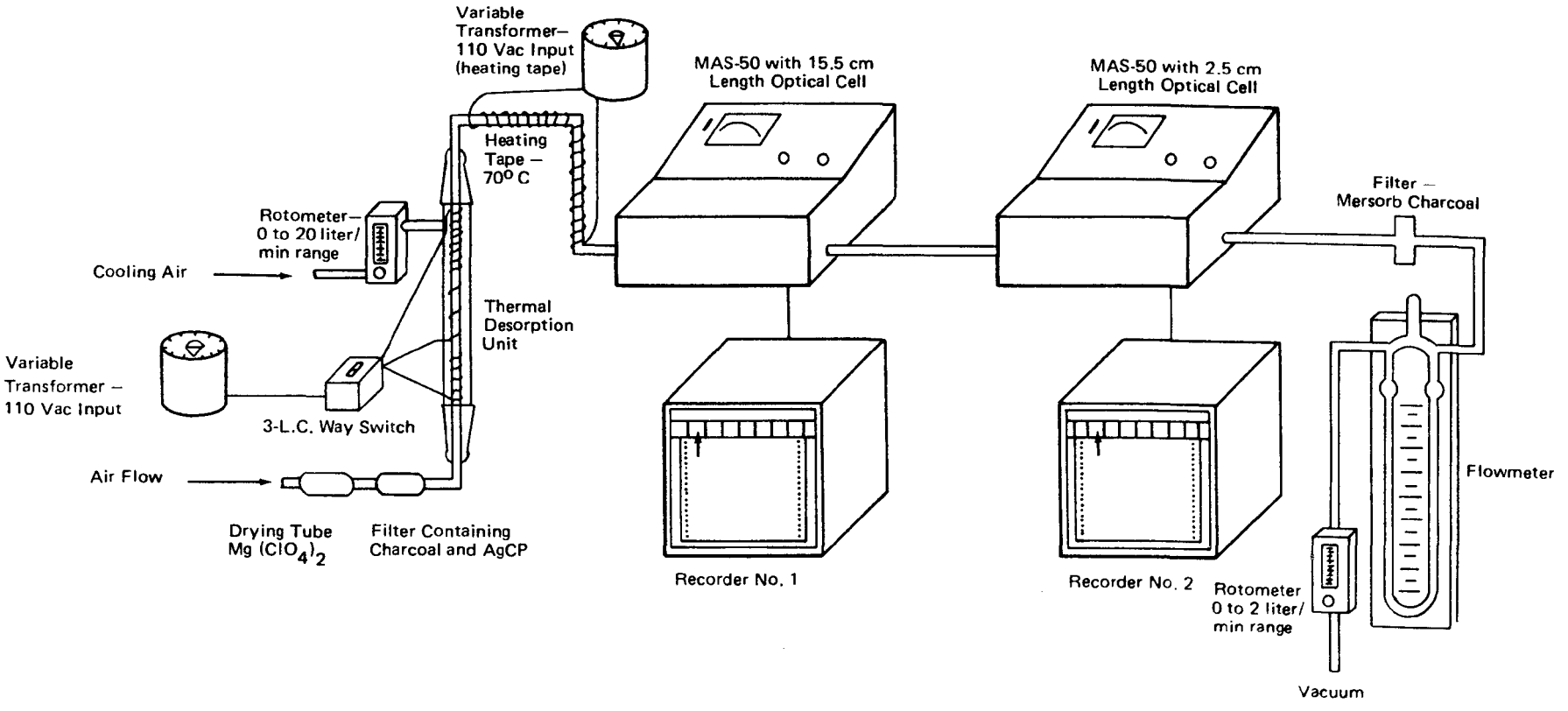


FIGURE 3A MERCURY ANALYSIS SYSTEM

windows. The output signal from the first instrument is displayed on a 0-10 mV recorder. After the mercury vapor is detected by the first MAS-50 the vapor passes directly into the optical cell of a second modified MAS-50. This MAS-50 contains a 2.5 cm glass optical cell with quartz glass windows. Signals from the second MAS-50 are displayed by a second recorder. (A dual pen recorder may be used, if available.) The tubing in both the MAS-50's was changed to glass and was rerouted to bypass the air pumps which came with the MAS-50's. Both air pumps were turned off and not used.

Operation

1. Turn on both MAS-50 analyzers and allow to stabilize.

   Note: The time required for stabilization varies with the individual instruments.

2. Turn on the heating tape.

3. After the MAS-50's have stabilized, turn on the vacuum pump and open the shutoff valve.

4. Use the flowmeter to adjust the flowrate through the system to the desired setting (approximately 1.0 ℓ/min).

   Note: The desired flowrate setting is obtained initially by analyzing standards and determining which setting gives the optimum recorder responses. Once the setting is optimized, it is used for all subsequent analyses.

5. Turn on the cooling air and adjust cooling air flowmeter to 15 ℓ/min.

6. Turn on the recorders and allow to stabilize.

7. Adjust the MAS-50's and recorders to the desired 0 and 100% T settings.

8. Purge the system before analyzing samples by heating the first desorption section of the desorption unit for 30 seconds and then immediately heating the second section for 30 seconds.

9. Allow the desorption unit to cool for one minute before analyzing samples.

10. Remove the clamp between the loading mechanism and desorption unit and insert the sampling tube.

11. Push the sampling tube into the first desorption section of the desorption unit using the plunger of the loading mechanism and replace the clamp.

12. Turn on the first section of the thermal desorption unit and heat the sampling tube for the required time (usually a timed 30 seconds).

13. After the first section is heated, immediately switch the 3-way power switch to heat the second desorption section of the thermal desorption unit. This section is usually heated for about 25 seconds.

    Note: At this time both recorders (or the dual recorder) will record the absorption signal of any mercury desorbed from the sampling tube.

14. Turn the 3-way switch to the off position.

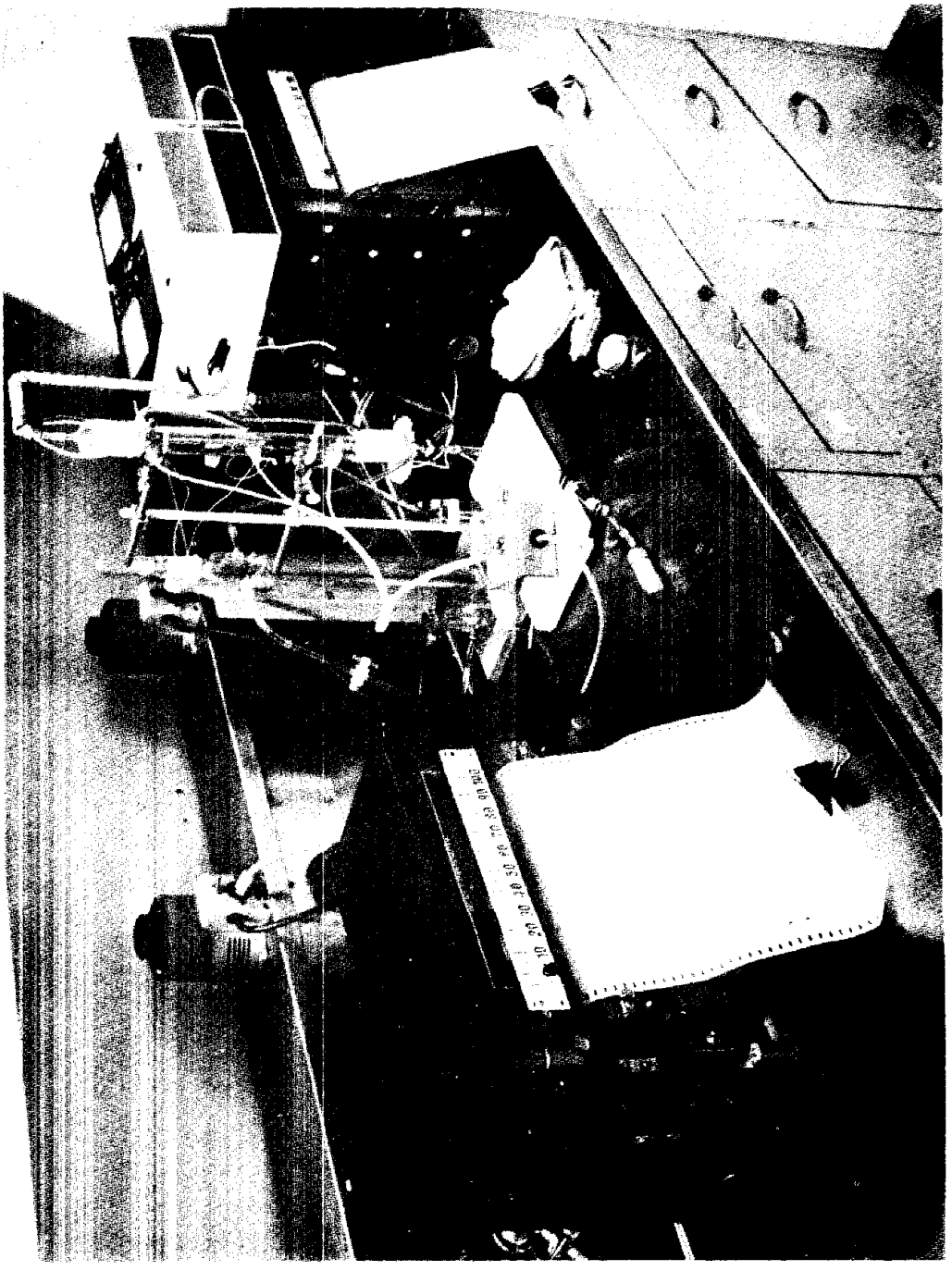
15. Allow the thermal desorption unit to cool for about 30 seconds and open the clamp on the loading mechanism to unload the used sampling tube.

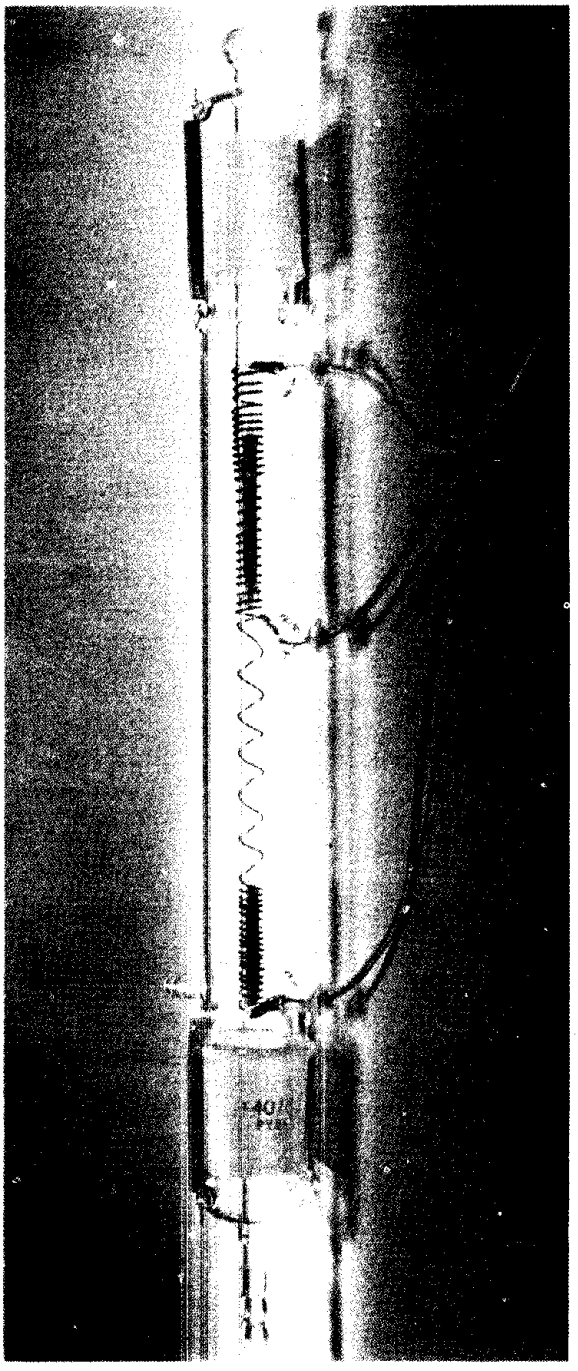
    Note: If the used sampling tube does not drop when the plunger is removed, turn off the air flow through the desorption unit using the shutoff valve and remove the tube with a metal rod.

    Caution: The sampling tube is *very hot* when it comes out of the desorption unit. Do not touch the tube with bare hands. Drop the hot tube into a dry beaker to cool.

16. Make sure the shutoff valve is reopened and then reload the desorption unit with another sampling tube.

17. Repeat steps #11 through #17 for each analysis.





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