NIOSH Analytical Methods for Set N

A joint National Institute for Occupational Safety and Health (NIOSH)/Occupational Safety and Health Administration (OSHA) Standards Completion Program will complete standards for approximately 400 air contaminants presently listed in Tables Z-1, Z-2, and Z-3 of 29 CFR Part 1910.1000 by adding other requirements of a standard required under Section 6(b)(7) and 8(c)(3) of the Occupational Safety and Health Act of 1970 (PL 91-596). These completed standards will then contain, in addition to the permissible exposure limit given in 1910.1000, appropriate provisions requiring monitoring of worker exposure, engineering control, personal protection, employee training, medical surveillance, and record keeping.

As a part of the Standards Completion Program, NIOSH is engaged in a two-year study under contract CDC-99-74-45 to validate sampling and analytical procedures for use in monitoring worker exposure to substances listed in Tables Z-1, Z-2, and Z-3. These methods have been validated and are suitable for measuring airborne concentrations of these substances and thus may be used for determining compliance with the standard or the need for control, for research, or whenever there is a need to measure airborne concentrations in the workplace. These analytical methods should not be considered the only methods which may be used to evaluate worker exposure. Other methods meeting the accuracy requirements in the standard may also be used.

These analytical methods will be periodically modified as new developments in science and technology require.

Set N

Arsenic and compounds (as As)
Beryllium and Beryllium compounds (as Be)
Nickel, metal and soluble compounds (as Ni)
Tin, inorganic compounds except oxides
Barium, soluble compounds
Calcium Oxide
Tellurium
Yttrium

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Public Health Service
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Arsenic and Compounds (as As)

Analyte:	Arsenic and Compounds	Method No.:	S309
Matrix:	Air	Range:	0.198-0.903 mg/cu m
OSHA Standard:	0.5 mg/cu m	Precision ($\overline{CV}_T$):	0.058
Procedure:	Filter collection, acid digestion, flameless atomic absorption	Validation Date:	9/26/75

1. Principle of the Method (References 11.1 and 11.2)

   1.1 A known volume of air is drawn through a cellulose membrane filter to collect the analyte.

   1.2 Samples are ashed using nitric and perchloric acids to destroy the filter and other organic materials in the sample, and the arsenic (including arsenic compounds) is then solubilized in nitric acid.

   1.3 The solutions of samples and standards are pipetted into the graphite furnace of an atomic absorption spectrophotometer (AAS). An electrodeless discharge lamp for arsenic is used.

2. Range and Sensitivity

   2.1 This method was validated over the range of 0.198-0.903 mg/cu m using an 85-liter sample at an atmospheric temperature and pressure of 24.5°C and 743 mm Hg. Under the conditions of sample size (85 liters), the working range of the method is estimated to be 0.1-1.3 mg/cu m.

   2.2 The sensitivity of this method using the 100-ml final solution volume is 0.8 μg (0.008 μg/ml for a 1% absorption). The method may be expanded by adjusting the final volume.

3. Interferences

   There are no known interferences for the arsenic atomic absorption spectrophotometric assay.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range 0.198-0.903 mg/cu m is 0.058. This value corresponds to a 0.029 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.3.

4.2 A collection efficiency of 1.00 was determined for the collecting medium, thus, no bias was introduced in the sample collection step. There was also no apparent bias in the sampling and analytical method for which an analytical method recovery correction was made. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Samples collected on filters are analyzed by means of a quick, instrumental method.

5.2 This method will measure particulate arsenic and its compounds that are trapped by the mixed cellulose ester filter. Volatile arsenic compounds will not be measured.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of arsenic content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate 37-mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of $\pm$ 5% at the recommended flow rate.

6.2 Mixed cellulose ester membrane filter: 37-mm diameter, 0.8-micrometer pore size.

6.3 Atomic absorption spectrophotometer having a monochromator with a reciprocal linear dispersion of about 0.65 nm/mm in the ultraviolet region, a direct readout (or recorder output) proportional to absorbance units, a graphite furnace accessory and a background corrector accessory. The Perkin-Elmer 305B with the HGA 2000 graphite furnace and Deuterium Background Corrector is an example. The use of a background corrector is absolutely necessary in order to avoid false positive signals from molecular scatterings at the 193.7 nm wavelength.

6.3.1 Arsenic electrodeless discharge lamp.

6.3.2 High purity nitrogen.

6.3.3 Pressure reducing valve. A 2-gauge, 2-stage pressure reducing valve and appropriate hose connection are needed for the nitrogen supply tank.

6.3.4 A suitable method for measuring peak heights or areas.

6.4 Glassware, borosilicate:

6.4.1 125-ml Phillips beakers with watchglass covers.

6.4.2 Pipets, delivery or graduated, 1, 5, 10 ml.

6.4.3 100-ml volumetric flasks.

6.4.4 Eppendorf 25-µl pipettor with tips.

6.5 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Arsenic trioxide, reagent grade.

7.2 Distilled or deionized water.

7.3 Concentrated nitric acid.

7.4 Dilute nitric acid (2 ml concentrated nitric acid diluted to 100 ml with distilled or deionized water).

7.5 Perchloric acid, 60% solution.

7.6 40% sodium hydroxide.

7.7 Commercially prepared aqueous standard stock solutions; 1000 µg/ml of arsenic.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before use, all glassware should initially be soaked in a mild detergent solution to remove any residual grease or chemicals.

8.1.2 After initial cleaning, glassware must be cleaned with hot concentrated nitric acid and then rinsed thoroughly with tap water and distilled water, in that order, and then dried.

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, nitric acid and water rinses are adequate.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter cassette 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 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

8.3.2 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel. The cassette plugs are replaced after sampling.

8.3.3 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.3.4 A sample size of 90 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of $\pm$ 5%.

8.3.5 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.6 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.7 Carefully record the sample identity and all relevant sampling data.

8.3.8 With each batch of ten samples, submit one filter from the same lot of filters which was used for sample collection and which is subjected to exactly the same handling as the samples except that no air is drawn through it. Label this as a blank.

8.3.9 Shipping. The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Transfer each sample to a clean 125-ml Phillips beaker.

8.4.2 Wet Ashing. Treat the sample in each beaker with 10 ml of concentrated nitric acid and 1 ml 60% perchloric acid. Cover each beaker with a watchglass and heat it on a high temperature hot plate (400°C) in a perchloric acid fume hood until dense fumes of perchloric acid appear. Using distilled water, carefully rinse the material on the bottom of the watchglass into the beaker, rinse sides of the beaker, and allow the solution to evaporate a small volume. Do not overheat.

8.4.3 Cool each beaker and dissolve residues in 5 ml dilute nitric acid.

8.4.4 Quantitatively transfer the clear solutions to a 100-ml volumetric flask.

8.4.5 Rinse each beaker at least twice with 5 ml portions of dilute nitric acid and quantitatively transfer each rinsing to the solution in the volumetric flask. Dilute all samples to 100 ml with dilute nitric acid.

8.4.6 Pipette 25 µl of the solutions into the graphite tube using an automatic pipettor (such as the Eppendorf pipettor) with disposable plastic tips.

The instrumental parameters for graphite furnace tube source power, background corrector and furnace alignment as well as furnace parameters such as inert gas flow and time/temperature conditions for drying, charring and atomizing should be established in accord with the manufacturer's recommendations. Note, however, that the drying and charring conditions should be minimized so as to avoid premature loss of arsenic during these steps.

To obtain reliable results, samples must be frequently alternated with standards which give responses close to those of the sample. The experimental protocol recommended is as follows: inject a standard solution in duplicate, inject a sample in duplicate and reinject a standard in duplicate, ... etc.

Note: The characteristics of the graphite tubes can influence the results drastically. Careful attention must be paid to the response of the standard, i.e., if the graphite tube gives erratic results and non-reproducible peak heights or areas, it must be rejected and replaced because results so obtained are not reliable.

8.4.7 Record the absorbance at 193.7 nm. Peak heights are used for this measurement if the response is rapid and the bases of the peaks are short and reproducible. If the bases of the peaks are broadened by the presence of contaminants, the areas of the absorption peaks will give more accurate measurements. Area measurements may be made by the use of a planimeter or an electronic integrator.

8.4.8 When very low concentrations are found in the sample, the sample can be dried and rediluted to a smaller volume such as 25 or 50 ml and reinjected.

8.4.9 Appropriate filter blanks must be analyzed in accordance with the total procedure.

8.5 Determination of Analytical Method Recovery

8.5.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the analyte. The analytical method recovery should be determined over the concentration range of interest.

8.5.2 Procedure for determining analytical method recovery.

Six filters are spiked at each of three levels (0.5X, 1X, and 2X the OSHA standard). Appropriate amounts of arsenic trioxide are dissolved in 5 ml of 40% sodium hydroxide and diluted to 250 ml with distilled water to represent each of the three OSHA levels. Three sets of six filters are spiked with appropriate volumes of each standard solution for each of the three levels. This corresponds to the amount of arsenic collected in a 90-liter sample at the 0.5X, 1X and 2X levels, respectively. Allow the filters to dry and place each filter in a cassette filter holder, and allow to stand overnight. The filters are ashed and analyzed as described in Section 8.4. A parallel blank filter is also treated in the same manner except that no sample is added to it.

Analytical Method Recovery (A.M.R.) equals the weight in mg found divided by the weight in mg added to the filter, or

$$A.M.R. = \frac{\text{mg found}}{\text{mg added}}$$

9. Calibration and Standards

9.1 Prepare at least 4 working standards to cover the range from 15 to 80 µg/100 ml from the 1000 µg/ml stock arsenic standard solution. Make all standard solutions in dilute nitric acid and prepare fresh daily.

9.2 To determine the response, the appropriate calibration standards are alternately analyzed with the samples. This practice will minimize the effect of observed fluctuations or variations in absorbances during any given day.

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbances versus the concentration of each standard in μg/100 ml.

10. Calculations

10.1 Read the weight, in μg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on μg/100 ml.

10.2 Corrections for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

μg sample = μg found in sample filter

μg blank = μg found in blank filter

10.3 Divide the total weight by the analytical method recovery (A.M.R.) to obtain corrected μg/sample.

$$\text{Corrected } \mu g/\text{sample} = \frac{\mu g \text{ found (Section 10.2)}}{\text{A.M.R.}}$$

10.4 The concentration of the analyte in the air sample can be expressed in mg/cu m (μg/liter = mg/cu m).

$$\text{mg/cu m} = \frac{\text{Corr. } \mu g \text{ (Section 10.3)}}{\text{Air Volume Samples (liter)}}$$

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.

11.3 Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

Barium, Soluble Compounds

Analyte:	Barium, Soluble Compounds	Method No.:	S198
Matrix:	Air	Range:	0.281-1.084 mg/cu m
OSHA Standard:	0.5 mg/cu m	Precision ($\overline{CV}_T$):	0.054
Procedure:	Filter collection, hot water leaching, atomic absorption	Validation Date:	9/26/75

1. Principle of the Method (References 11.1 and 11.2)

1.1 A known volume of air is drawn through a cellulose membrane filter to collect the analyte.

1.2 Samples are leached in hot water. The soluble portion is decanted, filtered, dried, and then dissolved in dilute hydrochloric acid containing sodium chloride.

1.3 The solutions of samples and standards are aspirated into the reducing nitrous oxide-acetylene flame of an atomic absorption spectrophotometer (AAS). A hollow cathode lamp for barium is used.

2. Range and Sensitivity

2.1 This method was validated over the range of 0.281-1.084 mg/cu m using a 168-liter sample at an atmospheric temperature and pressure of 24°C and 747 mm Hg. Under the conditions of sample size (168 liters), the working range of the method is estimated to be 0.15-1.3 mg/cu m.

2.2 The sensitivity of this method using the 5-ml final solution volume is 2 µg (0.4 µg/ml for a 1% absorption). The method may be extended to higher values by dilution of the sample. Measurement of lower concentrations can be made by using longer sampling times or by scale expansion to increase instrumental response.

3. Interferences

Ionization of barium in the flame is a problem in the determination of barium by atomic absorption spectrophotometry. This can be controlled by the addition of 1000-2000 µg/ml of sodium (as sodium chloride) to the samples and standards.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range 0.281-1.084 mg/cu m is 0.054. This value corresponds to a 0.027 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.3.

4.2 A collection efficiency of 1.00 was determined for the collecting medium, thus, no bias was introduced in the sample collection step. There was no bias in the sampling and analytical method. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Samples collected on filters are analyzed by means of a quick, instrumental method.

5.2 This method measures those barium compounds as soluble if they dissolve from the collection filter in boiling water. There is a wide range of solubilities among barium compounds, and this classification may be a disadvantage in some cases.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of barium content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate 37-mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of ± 5% at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

6.2 Mixed cellulose ester membrane filter: 37-mm diameter, 0.8-micrometer pore size.

6.3 Atomic absorption spectrophotometer, having a monochomator with a reciprocal linear dispersion of about 0.65 nm/mm in the ultraviolet region. The instrument must be equipped with a nitrous oxide-acetylene burner head.

6.3.1 Barium hollow cathode lamp

6.3.2 Oxidant: nitrous oxide

6.3.3 Fuel: acetylene

6.3.4 Pressure-reducing valves, a 2-gauge, 2-stage pressure reducing valve and appropriate hose connections are needed for each compressed gas tank used.

6.4 Glassware, borosilicate:

6.4.1 125-ml Phillips beakers with watchglass covers.

6.4.2 Pipets, delivery or graduated, 1, 5, 10 ml.

6.4.3 100-ml volumetric flasks.

6.5 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Distilled or deionized water.

7.2 Concentrated nitric acid.

7.3 Dilute hydrochloric acid (5 ml concentrated hydrochloric acid diluted to 100 ml with distilled or deionized water).

7.4 Sodium chloride.

7.5 Commercially prepared aqueous standard stock solutions; 1000 μg/ml of barium.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before use, all glassware should initially be soaked in a mild detergent solution to remove any residual grease or chemicals.

8.1.2 After initial cleaning, glassware must be cleaned with hot concentrated nitric acid and then rinsed thoroughly with tap water and distilled water, in that order, and then dried.

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, nitric acid and water rinses are adequate.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter cassette 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 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

8.3.2 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel. The cassette plugs are replaced after sampling.

8.3.3 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.3.4 A sample size of 180 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of $\pm$ 5%.

8.3.5 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.6 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.7 Carefully record the sample identity and all relevant sampling data.

8.3.8 With each batch of ten samples, submit one filter from the same lot of filters which was used for sample collection and which is subjected to exactly the same handling as the samples except that no air is drawn through it. Label this as a blank.

8.3.9 Shipping. The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Transfer each sample to a clean 125-ml Phillips beaker.

8.4.2 Add 10 ml of boiling distilled water to each beaker. Leach each sample for 10 minutes with occasional swirling.

8.4.3 Decant each solution into a second clean 125-ml Phillips beaker. Wash the original beaker and filter twice with hot distilled water and add to the second beaker.

8.4.4 Repeat the leaching process on the filter, decanting and washing all solutions into the same second beaker (i.e., repeat steps 8.4.2 and 8.4.3).

8.4.5 Remove each filter with clean ivory tipped forceps and wash each side of the filter with a stream of hot distilled water into the second beaker.

8.4.6 Rinse carefully the inside of the original beaker three times with hot distilled water and add to the second beaker. Carefully filter the solutions through a Buchner funnel to thoroughly remove any insoluble barium compounds collected.

8.4.7 Add three drops of concentrated hydrochloric acid to each of the samples, and then evaporate the solution to dryness.

8.4.8 Cool each beaker and dissolve the residues in 5 ml of dilute hydrochloric acid (5 ml of concentrated hydrochloric acid diluted to 100 ml with distilled water) containing 1100 ppm of sodium added as sodium chloride (0.28 g of sodium chloride/ 100 ml of dilute hydrochloric acid).

8.4.9 After the residue is dissolved, aspirate the solutions into a reducing nitrous oxide-acetylene flame and record the absorbance at 553.6 nm. The absorbance is proportional to the barium concentration and can be determined from the appropriate calibration curve. When very low concentrations are found in the sample, scale expansion can be used to increase the instrument response.

Note: Follow instrument manufacturer's recommendations for specific AAS operating parameters.

8.4.10 Appropriate filter blanks must be analyzed in accordance with the total procedure.

9. Calibration and Standards

9.1 Prepare at least 4 working standards to cover the range from 40 to 200 µg/5 ml from the 1000 µg/ml stock barium standard solution. Make all standard solutions in dilute hydrochloric acid containing 1100 ppm of sodium added as sodium chlorice and prepare fresh daily.

9.2 Aspirate each of the standard samples and record the absorptions.

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in µg/5 ml. It is advisable to run standards both before and after the analysis of a series of samples to insure that conditions have not changed.

10. Calculations

10.1 Read the weight, in μg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on μg/5 ml.

10.2 Corrections for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

μg sample = μg found in sample filter

μg blank = μg found in blank filter

10.3 The concentration of the analyte in the air sample can be expressed in mg/cu m (μg/liter = mg/cu m).

$$\text{mg/cu m} = \frac{\mu g \text{ (Section 10.2)}}{\text{Air Volume Sampled (liter)}}$$

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.

11.3 Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

Beryllium and Beryllium Compounds (as Be)

Analyte:	Beryllium and Beryllium Compounds	Method No.: S339
Matrix:	Air	Range: 2.68-11.84 µg/cu m
OSHA Standard:	5 µg/cu m - Ceiling 25 µg/cu m - Peak 2 µg/cu m - T.W.A.	Precision ($\overline{CV}_T$): 0.064
Procedure:	Filter collection, acid digestion, flameless atomic absorption	Validation Date: 9/26/75

1. Principle of the Method (References 11.1 and 11.2)

   1.1 A known volume of air is drawn through a cellulose membrane filter to collect the analyte.

   1.2 Samples are ashed using nitric, sulfuric and perchloric acids to destroy the filter and any organic material, and the beryllium (including beryllium compounds) is then solubilized in dilute hydrochloric acid.

   1.3 The solutions of samples and standards are pipetted into the graphite furnace of an atomic absorption spectrophotometer (AAS). A hollow cathode lamp for beryllium is used.

2. Range and Sensitivity

   2.1 This method was validated over the range of 2.68-11.84 µg/cu m using a 40-liter sample at an atmospheric temperature and pressure of 23.5°C and 749 mm Hg. Under the conditions of sample size (40 liters), the working range of the method is estimated to be 1.5-15 µg/cu m.

   2.2 The sensitivity of this method using the 10-ml final solution volume is 3.5 ng of Be (0.35 ng/ml for a 1% absorption). The method may be expanded by adjusting the final volume.

3. Interferences

   There are no known interferences for the beryllium atomic absorption spectrophotometric assay.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 2.68-11.84 µg/cu m is 0.064. This value corresponds to a 0.32 ug/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.3.

4.2 A collection efficiency of 1.00 was determined for the collecting medium, thus, no bias was introduced in the sample collection step. There is also no bias in the sampling and analytical method for which an analytical method recovery correction was made. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Samples collected on filters are analyzed by means of a quick, instrumental method.

6. Apparatus

6.1 Sampling Equipment - The sampling unit for the collection of personal air samples for the determination of beryllium content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate 37-mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump - A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at the recommended flow rate.

6.2 Mixed cellulose ester membrane filter: 37-mm diameter, 0.45 micrometer pore size.

6.3 Atomic absorption spectrophotometer having a monochromator with a reciprocal linear dispersion of about 0.65 nm/mm in the ultraviolet region, a direct readout (or recorder output) proportional to absorbance units, a graphite furnace accessory and a background corrector accessory. The Perkin-Elmer 305B with HGA 2000 Graphite Furnace and Deuterium Background Corrector is an example. The use of a background corrector is absolutely necessary in order to avoid false positive signals from molecular scattering at the 234.9 nm wavelength.

6.3.1 Beryllium hollow cathode lamp.

6.3.2 High purity nitrogen.

6.3.3 Pressure reducing valves, a 2-gauge, 2-stage pressure reducing valve and appropriate hose connections are needed for the nitrogen supply tank.

6.3.4 A suitable method for measuring peak heights or areas.

6.4 Glassware, borosilicate:

6.4.1 125-ml Phillips beakers with watchglass covers.

6.4.2 Pipets, delivery or graduated, 1, 5, 10 ml.

6.4.3 100-ml volumetric flasks and other convenient sizes for preparation of standards.

6.4.4 Eppendorf 25-µl pipettor with tips.

6.5 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Beryllium metal, reagent grade.

7.2 Distilled or deionized water.

7.3 Concentrated nitric acid.

7.4 3 M hydrochloric acid (25 ml concentrated hydrochloric acid diluted to 100 ml with distilled or deionized water).

7.5 6 M hydrochloric acid.

7.6 Perchloric acid, 60% solution.

7.7 Concentrated sulfuric acid.

7.8 Commercially prepared aqueous standard stock solutions; 1000 µg/ml of beryllium.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before use, all glassware should initially be soaked in a mild detergent solution to remove any residual grease or chemicals.

8.1.2 After initial cleaning, glassware must be cleaned with hot concentrated nitric acid and then rinsed thoroughly with tap water and distilled water, in that order, and then dried.

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, nitric acid and water rinses are adequate.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter cassette 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 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

8.3.2 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel. The cassette plugs are replaced after sampling.

8.3.3 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.3.4 To determine if the concentration of interest exceeds the ceiling OSHA standard, a sample size of 45 liters is recommended. Sample for 30 minutes at a flow rate of 1.5 liter per minute.

8.3.5 To determine if the concentration of interest exceeds the T.W.A. OSHA standard, a sample size of 90 liters is recommended. Sample at a flow rate of 1.5 liters per minute for one hour.

8.3.6 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.7 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.8 Carefully record the sample identity and all relevant sampling data.

8.3.9 With each batch of ten samples, submit one filter from the same lot of filters which was used for sample collection and which is subjected to exactly the same handling as the samples except that no air is drawn through it. Label this as a blank.

8.3.10 Shipping. The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Transfer each sample to a clean 125-ml Phillips beaker.

8.4.2 Wet Ashing: Treat the sample in each beaker with 10 ml of concentrated nitric acid, 1 ml concentrated sulfuric acid, and 1 ml 60% perchloric acid. Cover each beaker with a watchglass and heat it on a high temperature hot plate (400°C) in a perchloric acid fume hood until dense fumes of perchloric acid appear. Using distilled water, carefully rinse the material on the bottom of the watchglass into the beaker, rinse sides of beaker, and allow the solution to evaporate just to dryness. Remove the beaker immediately.

8.4.3 Beryllium and beryllium compounds are soluble in dilute hydrochloric acid and no special precaution is needed to solubilize the beryllium.

8.4.4 Cool each beaker and dissolve residues in 10 ml 3 M hydrochloric acid. An attempt to make a quantitative transfer into a 10-ml volumetric flask is not recommended, and the dilution is carried out in the beaker. Therefore, the addition of 10 ml of 3 M hydrochloric acid (Section 7.4) must be quantitative.

8.4.5 Pipette 25 µl of the solutions into the graphite tube using an automatic pipettor (such as the Eppendorf pipettor) with disposable plastic tips.

The instrumental parameters for the graphite furnace tube source power, background corrector and furnace alignment as well as furnace parameters such as inert gas flow and time/temperature conditions for drying, charring and atomizing should be established in accord with the manufacturer's recommendations. Note, however, that the drying and charring conditions should be minimized so as to avoid premature loss of beryllium during these steps.

To obtain reliable results, samples must be frequently alternated with standards which give responses close to those of the sample. The experimental protocol recommended is as follows: inject a standard solution in duplicate, inject a sample in duplicate and reinject a standard in duplicate,...etc.

Note: The characteristics of the graphite tubes can influence the results drastically. Careful attention must be paid to the response of the standard, i.e., if the graphite tube gives erratic results and non-reproducible peak heights or areas, it must be rejected and replaced because results so obtained are not reliable.

8.4.6 Record the absorbance at 234.9 nm. Peak heights are used for this measurement if the response is rapid and the bases of the peaks are short and reproducible. If the bases of the peaks are broadened by the presence of contaminants, the areas of the absorption peaks will give more accurate measurements. Area measurements may be made by the use of a planimeter or an electronic integrator.

8.4.7 When very low concentrations are found in the sample, the sample can be dried and rediluted to a smaller volume of 5 ml and reinjected. Before following this procedure, caution must be taken to take a minimal amount of aliquots from the original sample.

8.4.8 Appropriate filter blanks must be analyzed in accordance with the total procedure.

8.5 Determination of Analytical Method Recovery

8.5.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the analyte. The analytical method recovery should be determined over the concentration range of interest.

8.5.2 Procedure for determining analytical method recovery. Six filters are spiked at each of the three levels (0.5X, 1X, and 2X the OSHA standard) using a stock solution of 112.5 mg beryllium in 20 ml of 6M hydrochloric acid and diluting to 250 ml with distilled water. Three sets of six filters are spiked with appropriate volumes of the stock solution. This corresponds to the amount of beryllium collected in a 45-liter sample at the 0.5X, 1X, and 2X levels, respectively. Allow the filters to dry and place each filter in a cassette filter holder and allow to stand overnight. The filters are ashed and analyzed as described in Section 8.4. A parallel blank filter is also treated in the same manner except that no sample is added to it.

Analytical Method Recovery (A.M.R.) equals the weight in mg found divided by the weight in mg added to the filter, or,

$$\text{A.M.R.} = \frac{\text{mg found}}{\text{mg added}}$$

9. Calibration and Standards

9.1 Prepare at least four working standards to cover the range from 0.1 to 0.5 µg/10 ml from the 1000 µg/ml standard beryllium solution (Section 7.8). Make all standard solutions in 3 M hydrochloric acid and prepare fresh daily.

9.2 To determine the response, the appropriate calibration standards are alternately analyzed with the samples. This practice will minimize the effect of observed fluctuations or variations in absorbances during any given day.

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbances versus the concentration of each standard in µg/10 ml, or if a smaller sample volume is used, make an appropriate calibration curve.

10. Calculations

10.1 Read the weight, in µg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on µg/10 ml.

10.2 Corrections for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

μg sample = μg found in sample filter

μg blank = μg found in blank filter

10.3 Divide the total weight by the analytical method recovery (A.M.R.) to obtain corrected µg/sample.

$$\text{Corrected } \mu g/\text{sample} = \frac{\mu g \text{ found (Section 10.2)}}{\text{A.M.R.}}$$

10.4 The concentration of the analyte in the air sample can be expressed in µg/cu m.

$$\mu g/\text{cu m} = \frac{\text{Corr. } \mu g \text{ (Section 10.3) X 1000 liter/cu m}}{\text{Air Volume Sampled (liter)}}$$

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.

11.3 Documentation of NIOSH Validation Tests, Contract No. CDC-99-74-45.

Calcium Oxide

Analyte:	Calcium Oxide	Method No.:	S205
Matrix:	Air	Range:	2.6-10.16 mg/cu m
OSHA Standard:	5 mg/cu m	Precision (CV_T):	0.063
Procedure:	Filter collection, acid digestion, atomic absorption	Validation Date:	9/26/75

1. Principle of the Method (References 11.1 and 11.2)

   1.1 A known volume of air is drawn through a cellulose membrane filter to collect the analyte.

   1.2 Samples are ashed using nitric and perchloric acids to destroy the filter and any organic material, and the calcium oxide is then solubilized in hydrochloric acid.

   1.3 The solutions of samples and standards are aspirated into the oxidizing air-acetylene flame of an atomic absorption spectrophotometer (AAS). A hollow cathode lamp for calcium is used.

2. Range and Sensitivity

   2.1 This method was validated over the range of 2.6-10.16 mg/cu m using an 85-liter sample at an atmospheric temperature and pressure of 23.5°C and 744.5 mm Hg. Under the conditions of sample size (85 liters), the working range of the method is estimated to be 1-20 mg/cu m.

   2.2 The sensitivity of this method using the 100-ml final solution volume is 10 μg of calcium (0.1 μg/ml for a 1% absorption). The method may be extended to higher values by dilution of the sample. Measurement of lower concentrations can be made by using smaller final solution volumes, by longer sampling times, or by scale expansion to increase instrumental response. To maintain a linear calibration curve over the range of 10-20 mg/cu m of calcium, an alternate calcium line (239.9 nm), sample dilution, burner repositioning, or other suitable means must be employed.

3. Interferences

3.1 Interferences to the calcium atomic absorption spectrophotometric assay include Si, Al and PO_4^{-3}, which are controlled by the addition of La at 1% (1 g/100 ml) to both standards and samples.

3.2 Alkali type metals such as sodium, potassium, lithium, and magnesium suppress ionization, thus enhancing the response to calcium, and cause a positive interference.

3.3 Calcium compounds other than calcium oxide will also be measured as the oxide, resulting in a high reading.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range 2.6-10.16 mg/cu m is 0.063. This value corresponds to a 0.32 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.3.

4.2 A collection efficiency of 1.00 was determined for the collecting medium, thus, no bias was introduced in the sample collection step. There was also no bias in the sampling and analytical method. Thus, CV_T is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Samples collected on filters are analyzed by means of a quick, instrumental method.

5.2 This method is not specific for calcium oxide. Other calcium compounds which are collected on the filter will be measured.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the collection of personal air samples for the determination of calcium oxide content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate 37-mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of ± 5% at the recommended flow rate.

6.2 Mixed cellulose ester membrane filter; 37-mm diameter, 0.8-micrometer pore size.

6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 0.65 nm/mm in the ultraviolet region. The instrument must be equipped with an air-acetylene burner head.

6.3.1 Calcium hollow cathode lamp

6.3.2 Oxidant: compressed air

6.3.3 Fuel: acetylene

6.3.4 Pressure-reducing valves, a 2-gauge, 2-stage pressure reducing valve and appropriate hose connections are needed for each compressed gas tank used.

6.4 Glassware, borosilicate:

6.4.1 125-ml Phillips beakers with watchglass covers

6.4.2 Pipets, delivery or graduated, 1, 5, 10 ml

6.4.3 25 and 100-ml volumetric flasks

6.5 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Double distilled water

7.2 Concentrated nitric acid

7.3 Dilute hydrochloric acid (5 ml concentrated hydrochloric acid diluted to 100 ml with distilled or deionized water) containing 1% La (1 g La/100 ml)

7.4 Perchloric acid, 60% solution

7.5 Commercially prepared aqueous standard stock solutions; 1000 µg/ml of calcium (1400 µg/ml calcium oxide).

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before use, all glassware should initially be soaked in a mild detergent solution to remove any residual grease or chemicals.

8.1.2 After initial cleaning, glassware must be cleaned with hot concentrated nitric acid and then rinsed thoroughly with tap water and distilled water, in that order, and then dried.

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, nitric acid and water rinses are adequate.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter cassette 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 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

8.3.2 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel. The cassette plugs are replaced after sampling.

8.3.3 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.3.4 A sample size of 85 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of $\pm$ 5%.

8.3.5 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.6 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.7 Carefully record the sample identity and all relevant sampling data.

8.3.8 With each batch of ten samples, submit one filter from the same lot of filters which was used for sample collection and which is subjected to exactly the same handling as the samples except that no air is drawn through it. Label this as a blank.

8.3.9 Shipping. The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples.

8.4.1 Transfer each sample to a clean 125-ml Phillips beaker.

8.4.2 Wet Ashing. Treat the sample in each beaker with 5 ml of concentrated nitric acid to destroy the filter. Cover each beaker with a watchglass and heat on a hot plate (140°C) in a fume hood until most of the acid has evaporated. Add 2 ml concentrated nitric acid and 1 ml 60% perchloric acid. Cover each beaker with a watchglass and heat it on a high temperature hot plate (400°C) in a perchloric acid fume hood until dense fumes of perchloric acid appear. Using distilled water, carefully rinse the material on the bottom of the watchglass into the beaker, rinse sides of the beaker, and allow the solution to evaporate to dryness.

8.4.3 Cool each beaker and dissolve residues in 5 ml dilute hydrochloric acid containing 1% La. Calcium and its compounds are soluble in hydrochloric acid and no special precaution is needed to solubilize the calcium compounds.

8.4.4 Quantitatively transfer the clear solutions to a 100-ml volumetric flask.

8.4.5 Rinse each beaker at least twice with 5 ml portions of dilute hydrochloric acid (containing 1% La) and quantitatively transfer each rinsing to the volumetric flask. Dilute all samples to 100 ml with dilute hydrochloric acid (containing 1% La).

8.4.6 Aspirate the solutions into an oxidizing air-acetylene flame and record the absorbance at 422.7 nm. The absorbance is proportional to the calcium oxide concentration and can be determined from the appropriate calibration curve. When very low concentrations are found in the sample, scale expansion can be used to increase instrument response or the solution can be evaporated to a small volume and diluted to a volume such as 25 or 50 ml before aspiration. In such a case use no more acid solution in 8.4.5 than is necessary to effect a quantitative transfer.

Note: The lanthanum is added to prevent formation of calcium oxide molecules in the flame and to prevent interference from Si, Al, and $PO_4^{\equiv}$. Follow the instrument manfacturer's recommendations for specific AAS operating parameters.

8.4.7 Appropriate filter blanks must be analyzed in accordance with the total procedure.

9. Calibration and Standards

9.1 Prepare at least four working standards to cover the range from 100 to 1500 µg/100 ml calcium from the 1000 µg/ml stock calcium standard solution (140 to 2100 µg/100 ml of calcium oxide). Make all standard solutions in dilute hydrochloric acid (containing 1% La). Prepare fresh working standards each day.

9.2 Aspirate each of the standards and record the absorptions.

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in µg/100 ml of calcium oxide. It is advisable to run standards both before and after the analysis of a series of samples to insure that conditions have not changed.

10. Calculations

10.1 Read the weight, in µg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on µg/100 ml.

10.2 Corrections for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where

μg sample = µg found in sample filter

μg blank = µg found in blank filter

10.3 Calculate the µg of calcium oxide by multiplying the µg of calcium found (Section 10.2) by 1.40, which is a conversion factor to convert µg calcium to µg calcium oxide.

10.4 The concentration of the analyte in the air sample can be expressed in mg/cu m (µg/liter = mg/cu m).

$$\text{mg/cu m} = \frac{\mu g \text{ (Section 10.2)}}{\text{Air Volume Sampled (liter)}}$$

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.

11.3 Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

Nickel, Metal and Soluble Compounds (as Ni)

Analyte:	Nickel	Method No.:	S206
Matrix:	Air	Range:	0.447-2.075 mg/cu m
OSHA Standard:	1 mg/cu m	Precision ($\overline{CV}_T$):	0.057
Procedure:	Filter collection, acid digestion, atomic absorption	Validation Date:	9/26/75

1. Principle of the Method (References 11.1 and 11.2)

   1.1 A known volume of air is drawn through a cellulose membrane filter to collect the analyte.

   1.2 Samples are ashed using nitric and perchloric acids to destroy the filter and other organic materials in the sample, and the nickel (including nickel compounds) is then dissolved in nitric acid.

   1.3 The solutions of samples and standards are aspirated into the oxidizing air-acetylene flame of an atomic absorption spectrophotometer (AAS) using a hollow cathode lamp for nickel.

2. Range and Sensitivity

   2.1 This method was validated over the range of 0.447-2.075 mg/cu m using an 85-liter sample at an atmospheric temperature and pressure of 26.5°C and 745 mm Hg. Under the conditions of sample size (85 liters), the working range of the method is estimated to be 0.4-8 mg/cu m.

   2.2 The sensitivity of this method using the 25-ml final solution volume is 2.5 μg (0.1 μg/ml for a 1% absorption). The method may be extended to higher values by dilution of the sample. Measurement of lower concentrations can be made by using smaller final solution volumes, by longer sampling times, or by scale expansion to increase instrumental response.

3. Interferences

   There are no known interferences for the nickel atomic absorption spectrophotometric assay.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range 0.447-2.075 mg/cu m is 0.057. This value corresponds to a 0.057 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.3.

4.2 A collection efficiency of 1.00 was determined for the collecting medium, thus, no bias was introduced in the sample collection step. There was also no apparent bias in the sampling and analytical method. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Samples collected on filters are analyzed by means of a quick, instrumental method.

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 37-mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump. A calibrated personal sampling pump whose flow can be determined to an accuracy of + 5% at the recommended flow rate. The pump must be calibrated with a representative filter holder and filter in the line.

6.2 Mixed cellulose ester membrane filter; 37-mm diameter, 0.8-micrometer pore size.

6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 0.65 nm/mm in the ultraviolet region. The instrument must be equipped with an air-acetylene burner head.

6.3.1 Nickel hollow cathode lamp

6.3.2 Oxidant: compressed air

6.3.3 Fuel: acetylene

6.3.4 Pressure-reducing valves, a 2-gauge, 2-stage pressure reducing valve and appropriate hose connections are needed for each compressed gas tank used.

6.4 Glassware, borosilicate:

6.4.1 125-ml Phillips beakers with watchglass covers.

6.4.2 Pipets, delivery or graduated, 1, 5, 10 ml.

6.4.3 25 and 100-ml volumetric flasks.

6.5 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Distilled or deionized water.

7.2 Concentrated nitric acid.

7.3 Dilute nitric acid (5 ml concentrated nitric acid diluted to 100 ml with distilled or deionized water).

7.4 Perchloric acid, 60% solution.

7.5 Commercially prepared aqueous standard stock solutions; 1000 μg/ml of nickel.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before use, all glassware should initially be soaked in a mild detergent solution to remove any residual grease or chemicals.

8.1.2 After initial cleaning, glassware must be cleaned with hot concentrated nitric acid and then rinsed thoroughly with tap water and distilled water, in that order, and then dried.

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, nitric acid and water rinses are adequate.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter cassette 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 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

8.3.2 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel. The cassette plugs are replaced after sampling.

8.3.3 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.3.4 A sample size of 90 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of $\pm$ 5%.

8.3.5 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.6 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.7 Carefully record the sample identity and all relevant sampling data.

8.3.8 With each batch of ten samples, submit one filter from the same lot of filters which was used for sample collection and which is subjected to exactly the same handling as the samples except that no air is drawn through it. Label this as a blank.

8.3.9 Shipping. The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Transfer each sample to a clean 125-ml Phillips beaker.

8.4.2 Wet Ashing. Treat the sample in each beaker with 5 ml of concentrated nitric acid to destroy the filter. Cover each beaker with a watchglass and heat on a hot plate (140°C) in a fume hood until most of the acid has evaporated.

Add 2 ml concentrated nitric acid and 1 ml 60% perchloric acid. Cover each beaker with a watchglass and heat it on a high temperature hot plate (400°C) in a perchloric acid fume hood until dense fumes of perchloric acid appear. Using distilled water, carefully rinse the material on the bottom of the watchglass into the beaker, rinse the sides of the beaker, and allow the solution to evaporate to dryness.

8.4.3 Nickel and its compounds are soluble in nitric acid and no special precaution is needed to solubilize the nickel.

8.4.4 Cool each beaker and dissolve residues in 5 ml dilute nitric acid.

8.4.5 Quantitatively transfer the clear solutions to a 25-ml volumetric flask.

8.4.6 Rinse each beaker at least twice with 5-ml portions of dilute nitric acid and quantitatively transfer each rinsing to the solution in the volumetric flask. Dilute all samples to 25 ml with dilute nitric acid.

8.4.7 Aspirate the solutions into an oxidizing air-acetylene flame and record the absorbance at 232.0 nm. The absorbance is proportional to the sample concentration and can be determined from the appropriate calibration curve. When very low concentrations are found in the sample, scale expansion can be used to increase instrument response or the sample can be dried and rediluted to some smaller volume such as 5 or 10 ml before aspiration. In such a case use no more acid solution in 8.4.6 than is necessary to effect a quantitative transfer.

Note: Follow instrument manufacturer's recommendations for specific AAS operating parameters.

8.4.8 Appropriate filter blanks must be analyzed in accordance with the total procedure.

9. Calibration and Standards

9.1 Prepare at least 4 working standards to cover the range from 12.5 to 250 µg/25 ml from the 1000 µg/ml stock nickel standard solution. Make all standard solutions in dilute nitric acid and prepare fresh daily.

9.2 Aspirate each of the standard samples and record the absorptions.

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in µg/25 ml. It is advisable to run standards both before and after the analysis of a series of samples to insure that conditions have not changed.

10. Calculations

10.1 Read the weight, in μg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on μg/25 ml.

10.2 Corrections for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

μg sample = μg found in sample filter

μg blank = μg found in blank filter

10.3 The concentration of the analyte in the air sample can be expressed in mg/cu m (μg/liter = mg/cu m).

$$\text{mg/cu m} = \frac{\mu g \text{ (Section 10.2)}}{\text{Air Volume Sampled (liter)}}$$

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.

11.3 Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

Tellurium

Analyte:	Tellurium	Method No.:	S204
Matrix:	Air	Range:	0.0495-0.240 mg/cu m
OSHA Standard:	0.1 mg/cu m	Precision (CV_T):	0.055
Procedure:	Filter collection, Acid digestion, Atomic absorption	Validation Date:	9/26/75

1. Principle of the Method (References 11.1 and 11.2)

   1.1 A known volume of air is drawn through a cellulose membrane filter to collect the analyte.

   1.2 Samples are ashed using nitric and perchloric acids to destroy the filter and other organic materials in the sample, and the tellurium is then dissolved in dilute nitric acid solution.

   1.3 The solutions of samples and standards are aspirated into the oxidizing air-acetylene flame of an atomic absorption spectrophotometer (AAS). An electrodeless discharge lamp for tellurium is used.

2. Range and Sensitivity

   2.1 This method was validated over the range of 0.0495-0.240 mg/cu m using a 670-liter sample at an atmospheric temperature and pressure of 22.5°C and 746 mm Hg. Under the conditions of sample size (670 liters), the working range of the method is estimated to be 0.02-0.4 mg/cu m.

   2.2 The sensitivity of this method using the 5-ml final solution volume is 2.5 micrograms (0.5 microgram/ml for 1% absorption). The method may be extended to higher values by dilution of the sample. Measurement of lower concentrations can be made by scale expansion to increase instrumental response.

3. Interferences

   There are no known interferences for the tellurium AAS assay.

4. Precision and Accuracy

4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 0.0495-0.240 mg/cu m is 0.055. This value corresponds to a 0.006 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.3.

4.2 A collection efficiency of 1.00 was determined for the collecting medium, thus, no bias was introduced in the sample collection step. There was also no bias in the sampling and analytical method. Thus, CV_T is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages of the Method

The sampling device is small, portable, and involves no liquids. Samples collected on filters are analyzed by means of a quick, instrumental method.

6. Apparatus

6.1 Sampling Equipment - The sampling unit for the collection of personal air samples for the determination of tellurium content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate 37-mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump - A calibrated personal sampling pump whose flow can be determined to an accuracy of ±5% at the recommended flow rate.

6.2 Mixed cellulose ester membrane filter; 37-mm diameter, 0.8-micrometer pore size.

6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 0.65 nm/mm in the ultraviolet region. The instrument must be equipped with an air-acetylene burner head.

6.3.1 Tellurium electrodeless discharge lamp.

6.3.2 Oxidant: compressed air.

6.3.3 Fuel: acetylene.

6.3.4 Pressure-reducing valves, a 2-gauge, 2-stage pressure reducing valve and appropriate hose connections are needed for each compressed gas tank used.

6.4 Glassware, borosilicate:

6.4.1 125-ml Phillips beakers with watchglass covers.

6.4.2 Pipets, delivery or graduated, 1, 5, 10 ml.

6.4.3 100-ml volumetric flasks.

6.5 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Distilled or deionized water.

7.2 Concentrated nitric acid.

7.3 Dilute nitric acid (10 ml concentrated nitric acid diluted to 100 ml with distilled or deionized water).

7.4 Perchloric acid, 60% solution.

7.5 Commercially prepared aqueous standard stock solutions; 1000 micrograms Te/ml.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before use all glassware should initially be soaked in a mild detergent solution to remove any residual grease or chemicals.

8.1.2 After initial cleaning, glassware must be cleaned with hot concentrated nitric acid and then rinsed thoroughly with tap water and distilled water, in that order, and then dried.

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, nitric acid and water rinses are adequate.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter cassette 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 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

8.3.2 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel. The cassette plugs are replaced after sampling.

8.3.3 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.3.4 A sample size of 670 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of $\pm$5%.

8.3.5 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.6 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.7 Carefully record the sample identity and all relevant sampling data.

8.3.8 With each batch of ten samples, submit one filter from the same lot of filters which was used for sample collection and which is subjected to exactly the same handling as the samples, except that no air is drawn through it. Label this as a blank.

8.3.9 Shipping. The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Transfer each sample to a clean 125-ml Phillips beaker.

8.4.2 Wet Ashing: Treat the sample in each beaker with 5 ml of concentrated nitric acid to destroy the filter. Cover each beaker with a watch glass and heat on a hot plate (140°C) in a fume hood until most of the acid has evaporated.

Add 2 ml concentrated nitric acid and 1 ml 60% perchloric acid. Caution must be taken when using perchloric acid to destroy the filter. Cover each beaker with a watchglass and heat on a high temperature hot plate (400°C) in a perchloric acid fume hood until dense fumes of perchloric acid appear. Using distilled water, rinse the material on the bottom of the watchglass into the beaker, rinse sides of beaker, and allow the solution to evaporate to dryness.

8.4.3 The tellurium compounds are soluble in nitric acid and no special precaution is needed to solubilize them.

8.4.4 Cool each beaker and quantitatively add 5 ml of dilute nitric acid.

8.4.5 After the samples are dissolved aspirate the solutions into an oxidizing air-acetylene flame and record the absorbance at 214.3 nm. The absorbance is proportional to the tellurium concentration which can be determined from the appropriate calibration curve. When very low concentrations are found in the sample, scale expansion can be used to increase instrument response.

Note: Follow instrument manufacturer's recommendations for specific AAS operating parameters.

8.4.6 Appropriate filter blanks must be analyzed in accordance with the total procedure.

9. Calibration and Standards

9.1 Prepare at least four working standards to cover the range from 20-400 micrograms/5 ml from the 1000 micrograms/ml stock tellurium standard solution. All standard solutions are made in dilute nitric acid and are prepared fresh daily.

9.2 Aspirate each of the standard solutions and record the absorptions.

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in microgram/5 ml. It is advisable to run standards both before and after the analysis of a series of samples to insure that conditions have not changed.

10. Calculations

10.1 Read the weight, in microgram, corresponding to the total absorbance, from the standard curve. No volume corrections are needed, because the standard curve is based on microgram/5 ml.

10.2 Corrections for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

μg sample = μg found in sample filter

μg blank = μg found in blank filter

10.3 The concentration of the analyte in the air sampled can be expressed in mg/cu m (μg/liter = mg/cu m).

$$\text{mg/cu m} = \frac{\mu g \text{ (Section 10.2)}}{\text{Air Volume Sampled (liter)}}$$

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.

11.3 Documentation of NIOSH Validation Tests, Contract No. CDC-99-74-45.

Tin, Inorganic Compounds Except Oxides

Analyte:	Tin	Method No.:	S183
Matrix:	Air	Range:	0.939-4.32 mg/cu m
OSHA Standard:	2 mg/cu m	Precision ($\overline{CV}_T$):	0.055
Procedure:	Filter collection, acid digestion, atomic absorption	Validation Date:	9/26/75

1. Principle of the Method (References 11.1 and 11.2)

   1.1 A known volume of air is drawn through a cellulose membrane filter to collect the analyte.

   1.2 Samples are ashed using nitric and sulfuric acids to destroy the filter and any organic material, and the tin, including tin inorganic compounds, is then solubilized in dilute hydrochloric acid.

   1.3 The solutions of samples and standards are aspirated into the reducing air-acetylene flame of an atomic absorption spectrophotometer (AAS). An electrodeless discharge for tin is used.

2. Range and Sensitivity

   2.1 This method was validated over the range of 0.939-4.32 mg/cu m using a 250-liter sample at an atmospheric temperature and pressure of 22.7°C and 747 mm Hg. Under the conditions of sample size (250 liters), the working range of the method is estimated to be 0.5-6 mg/cu m.

   2.2 The sensitivity of this method using the 5-ml final solution volume is 10 micrograms of tin (2 micrograms/ml for a 1% absorption). The method may be extended to higher values by dilution of the sample. Measurement of lower atmospheric concentrations can be made, by longer sampling times, or by scale expansion to increase instrumental response.

3. Interferences

   Any tin compound which is collected on the filter will be measured.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range of 0.939-4.32 mg/cu m is 0.055. This value corresponds to a 0.11 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.3.

4.2 A collection efficiency of 1.00 was determined for the collecting medium, thus, no bias was introduced in the sample collection step. There is also no bias in the sampling and analytical method for which an analytical method recovery correction was made. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Samples collected on filters are analyzed by means of a quick, instrumental method.

5.2 This method is not specific for inorganic tin compounds. Any tin compound which is collected on the MCEF filter will be measured and will be an interference.

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 37-mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump - A calibrated personal sampling pump whose flow can be determined to an accuracy of +5% at the recommended flow rate.

6.2 Mixed cellulose ester membrane filter; 37-mm diameter, 0.8-micrometer pore size.

6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 0.65 nm/mm in the ultraviolet region. The instrument must be equipped with an air-acetylene burner head.

6.3.1 Tin electrodeless discharge lamp.

6.3.2 Oxidant: compressed air.

6.3.3 Fuel: acetylene.

6.3.4 Pressure-reducing valves, a 2-gauge, 2-stage pressure reducing valve and appropriate hose connections are needed for each compressed gas tank used.

6.4 Glassware, borosilicate:

6.4.1 125-ml Phillips beakers with watchglass covers.

6.4.2 Pipets, delivery or graduated, 1,5, 10 ml.

6.4.3 Volumetric flasks of appropriate sizes.

6.5 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

6.6 Muffle furnace capable of controlling temperature at 200°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Stannous chloride, reagent grade.

7.2 Distilled or deionized water.

7.3 Concentrated nitric acid.

7.4 Dilute hydrochloric acid (10 ml concentrated hydrochloric acid diluted to 100 ml with distilled or deionized water).

7.5 Concentrated hydrochloric acid.

7.6 Concentrated sulfuric acid.

7.7 Commercially prepared aqueous standard stock solutions; 1000 micrograms/ml of tin.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before use, all glassware should initially be soaked in a mild detergent solution to remove any residual grease or chemicals.

8.1.2 After initial cleaning, glassware must be cleaned with hot concentrated nitric acid and then rinsed thoroughly with tap water and distilled water, in that order, and then dried.

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, nitric acid and distilled water rinses are adequate.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter cassette 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 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

8.3.2 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel. The cassette plugs are replaced after sampling.

8.3.3 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.3.4 A sample size of 250 liters is recommended. Sample at a flow rate of 1.5 liters per minute.

8.3.5 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.6 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.7 Carefully record the sample identity and all relevant sampling data.

8.3.8 With each batch of ten samples, submit one filter from the same lot of filters which was used for sample collection and which is subjected to exactly the same handling as the samples except that no air is drawn through it. Label this as a blank.

8.3.9 Shipping. The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Transfer each sample to a clean 125-ml Phillips beaker.

8.4.2 Wet Ashing: Treat the sample in each beaker with 1 ml of concentrated sulfuric acid and 5 ml of concentrated nitric acid. Cover each beaker with a watchglass and heat on a hot plate (140°C) in a fume hood until fumes of sulfuric acid appear. If any black suspension remains, add a few drops of concentrated nitric acid and fume again until a clear solution is obtained. Cool the beaker. Using distilled water, carefully rinse the material on the bottom of the watchglass into the beaker, rinse sides of beaker. Return the beaker to the hot plate and heat until all the sulfuric acid fumes disappear. To remove the last traces of sulfuric acid, heat the beaker in a muffle furnace at a temperature of 200°C for about 1 hour.

8.4.3 Cool each beaker and dissolve residues in 5 ml (pipetted) dilute hydrochloric acid (Section 7.4). The addition of the dilute hydrochloric acid must be quantitative. Swirl to wash down sides of the beaker and mix thoroughly.

8.4.4 Aspirate the solutions into a reducing air-acetylene flame and record the absorbance at 224.6 nm. The absorbance is proportional to the sample concentration and can be determined from the appropriate calibration curve. When very low concentrations are found in the sample, scale expansion can be used to increase instrument response.

Note: Follow instrument manufacturer's recommendations for specific AAS operating parameters.

8.4.5 Appropriate filter blanks must be analyzed in accordance with the total procedure.

8.5 Determination of Analytical Method Recovery

8.5.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the analyte. The analytical method recovery should be determined over the concentration range of interest.

8.5.2 Procedure for determining analytical method recovery. Six filters are spiked at each of the levels (0.5X, 1X, and 2X the OSHA standard). Appropriate amounts of stannous chloride are dissolved in 25 ml concentrated HCl and diluted to 250 ml with distilled water to represent each of the three levels. Three sets of six filters are spiked with appropriate volumes of each standard solution for each

of the three levels. This corresponds to the amount of tin collected in a 250-liter sample at the 0.5X, 1X, and 2X levels, respectively.

Allow the filters to dry and place each filter in a cassette filter holder, and allow to stand overnight. The filters are ashed and analyzed as described in Section 8.4. A parallel blank filter is also treated in the same manner except than no sample is added to it.

Analytical Method Recovery (A.M.R.) equals the weight in mg found divided by the weight in mg added to the filter, or,

$$\text{A.M.R.} = \frac{\text{mg found}}{\text{mg added}}$$

9. Calibration and Standards

9.1 Prepare at least four working standards to cover the range from 150 to 1500 micrograms/5 ml from the 1000 micrograms/ml stock tin standard solution. Make all standard solutions in dilute hydrochloric acid and prepare fresh daily.

9.2 Aspirate each of the standard samples and record the absorptions.

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in microgram per 5 ml. It is advisable to run standards both before and after the analysis of a series of samples to insure that conditions have not changed.

10. Calculations

10.1 Read the weight, in µg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on microgram/5 ml.

10.2 Corrections for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

µg sample = µg found in sample filter

µg blank = µg found in blank filter

10.3 Divide the total weight by the analytical method recovery (A.M.R.) to obtain corrected microgram/sample.

$$\text{Corrected } \mu g/\text{sample} = \frac{\mu g \text{ found (Section 10.2)}}{\text{A.M.R.}}$$

10.4 The concentration of the analyte in the air sample can be expressed in mg/cu m (μg/liter = mg/cu m).

$$\text{mg/cu m} = \frac{\mu\text{g (Section 10.3)}}{\text{Air Volume Sampled (liter)}}$$

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.

11.3 Documentation of NIOSH Validation Tests, Contract No. CDC-99-74-45.

Yttrium

Analyte:	Yttrium	Method No.:	S200
Matrix:	Air	Range:	0.529-2.211 mg/cu m
OSHA Standard:	1 mg/cu m	Precision ($\overline{CV}_T$):	0.054
Procedure:	Filter collection, acid digestion, atomic absorption	Validation Date:	9/26/75

1. Principle of the Method (References 11.1 and 11.2)

   1.1 A known volume of air is drawn through a cellulose membrane filter to collect the analyte.

   1.2 Samples are ashed using nitric and perchloric acids to destroy the filter and other organic materials in the sample, and the yttrium is then dissolved in hydrochloric acid.

   1.3 The solutions of samples and standards are aspirated into the reducing nitrous oxide-acetylene flame of an atomic absorption spectrophotometer (AAS). A hollow cathode lamp for yttrium is used.

2. Range and Sensitivity

   2.1 This method was validated over the range of 0.529-2.211 mg/cu m using a 500-liter sample at an atmospheric temperature and pressure of 24.5°C and 745 mm Hg. Under the conditions of sample size (500 liters), the working range of the method is estimated to be 0.15-5 mg/cu m.

   2.2 The sensitivity of this method using the 5-ml final solution volume is 10 μg (2 μg/ml for a 1% absorption). The method may be extended to higher values by dilution of the sample. Measurement of lower concentrations can be made by longer sampling times, or by scale expansion to increase instrumental response.

3. Interferences

   The presence of aluminum, potassium, and phosphoric acid in the flame are known to depress the absorbance by yttrium. Also yttrium is partially ionized in the nitrous oxide-acetylene flame. These effects can be overcome by the addition of 1000 ppm sodium (as NaCl) to samples and standards.

4. Precision and Accuracy

4.1 The Coefficient of Variation ($\overline{CV}_T$) for the total analytical and sampling method in the range 0.529-2.211 mg/cu m is 0.054. This value corresponds to a 0.054 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.3.

4.2 A collection efficiency of 1.00 was determined for the collecting medium, thus, no bias was introduced in the sample collection step. There was also no apparent bias in the sampling and analytical method for which an analytical method recovery correction was made. Thus, $\overline{CV}_T$ is a satisfactory measure of both accuracy and precision of the sampling and analytical method.

5. Advantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Samples collected on filters are analyzed by means of a quick, instrumental method.

6. Apparatus

6.1 Sampling Equipment - The sampling unit for the collection of personal air samples for the determination of yttrium content has the following components:

6.1.1 The filter unit, consisting of the filter media (Section 6.2) and appropriate 37-mm 3-piece cassette filter holder.

6.1.2 Personal Sampling Pump - A calibrated personal sampling pump whose flow can be determined to an accuracy of + 5% at the recommended flow rate.

6.2 Mixed cellulose ester membrane filter; 37-mm diameter, 0.8-micrometer pore size.

6.3 Atomic absorption spectrophotometer, having a monochromator with a reciprocal linear dispersion of about 0.65 nm/mm in the ultraviolet region. The instrument must be equipped with a nitrous oxide-acetylene burner head.

6.3.1 Yttrium hollow cathode lamp

6.3.2 Oxidant: nitrous oxide

6.3.3 Fuel: acetylene

6.3.4 Pressure-reducing valves, a 2-gauge, 2-stage pressure reducing valve and appropriate hose connections are needed for each compressed gas tank used.

6.4 Glassware, borosilicate:

6.4.1 125-ml Phillips beakers with watchglass covers.

6.4.2 Pipets, delivery or graduated, 1, 5, 10 ml.

6.4.3 100-ml volumetric flasks.

6.5 Adjustable thermostatically controlled hot plate capable of reaching 400°C.

7. Reagents

All reagents used must be ACS Reagent Grade or better.

7.1 Yttrium metal, reagent grade.

7.2 Distilled or deionized water.

7.3 Concentrated nitric acid.

7.4 0.6 M hydrochloric acid (5 ml concentrated hydrochloric acid diluted to 100 ml with distilled or deionized water). To this solution add 250 mg of NaCl. The HCl solution will contain 1000 ppm of sodium.

7.5 6 M hydrochloric acid.

7.6 Perchloric acid, 60% solution.

7.7 Commercially prepared aqueous standard stock solutions; 1000 µg/ml of yttrium.

8. Procedure

8.1 Cleaning of Equipment

8.1.1 Before use, all glassware should initially be soaked in a mild detergent solution to remove any residual grease or chemicals.

8.1.2 After initial cleaning, glassware must be cleaned with hot concentrated nitric acid and then rinsed thoroughly with tap water and distilled water, in that order, and then dried.

8.1.3 For glassware which has previously been subjected to the entire cleaning procedure, nitric acid and water rinses are adequate.

8.2 Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative filter cassette 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 Assemble the filter in the three-piece filter cassette holder and close firmly to insure that the center ring seals the edge of the filter. The cellulose membrane filter is held in place by a cellulose backup pad.

8.3.2 Remove the cassette plugs and attach to the personal sampling pump tubing. Clip the cassette to the worker's lapel. The cassette plugs are replaced after sampling.

8.3.3 Air being sampled should not pass through any hose or tubing before entering the filter cassette.

8.3.4 A minimum sample size of 500 liters is recommended. Sample at a flow rate of 1.5 liters per minute. The flow rate should be known with an accuracy of $\pm$5%.

8.3.5 Turn the pump on and begin sample collection. Since it is possible for a filter to become plugged by heavy particulate loading or by the presence of oil mists or other liquids in the air, the pump rotameter should be observed frequently, and the sampling should be terminated at any evidence of a problem.

8.3.6 Terminate sampling at the predetermined time and note sample flow rate, collection time and ambient temperature and pressure. If pressure reading is not available, record the elevation.

8.3.7 Carefully record the sample identity and all relevant sampling data.

8.3.8 With each batch of ten samples, submit one filter from the same lot of filters which was used for sample collection and which is subjected to exactly the same handling as the samples except that no air is drawn through it. Label this as a blank.

8.3.9 Shipping. The cassettes in which the samples are collected should be shipped in a suitable container, designed to prevent damage in transit.

8.4 Analysis of Samples

8.4.1 Transfer each sample to a clean 125-ml Phillips beaker.

8.4.2 Wet Ashing: Treat the sample in each beaker with 5 ml of concentrated nitric acid to destroy the filter. Cover each beaker with a watchglass and heat on a hot plate (140°C) in a fume hood until most of the acid has evaporated. Add 2 ml concentrated nitric acid and 1 ml 60% perchloric acid. Cover each beaker with a watchglass and heat it on a high temperature hot plate (400°C) in a perchloric acid fume hood until dense fumes of perchloric acid appear. Using distilled water, carefully rinse the material on the bottom of the watchglass into the beaker, rinse sides of the beaker, and allow the solution to evaporate to dryness.

8.4.3 Yttrium nitrate and perchlorate are soluble in hydrochloric acid and no special precaution is needed to solubilize the yttrium.

8.4.4 Cool each beaker and dissolve residues in 5 ml 0.6 M hydrochloric acid which contains 1000 ppm sodium. The addition of the hydrochloric acid must be quantitative.

8.4.5 When the residue is completely dissolved, aspirate the solutions into a reducing nitrous oxide-acetylene flame and record the absorbance at 410.2 nm. The absorbance is proportional to the yttrium concentration and can be determined from the appropriate calibration curve.

Note: Follow instrument manufacturer's recommendations for specific AAS operating parameters.

8.4.6 Appropriate filter blanks must be analyzed in accordance with the total procedure.

8.5 Determination of Analytical Method Recovery

8.5.1 Need for Determination. To eliminate any bias in the analytical method, it is necessary to determine the recovery of the analyte. The analytical method recovery should be determined over the concentration range of interest.

8.5.2 Procedure for determining analytical method recovery. Six filters are spiked at each of three levels (0.5X, 1X, and 2X the OSHA standard). Appropriate amounts of yttrium metal are dissolved in 25 ml of 6 M HCl and 2-3 drops of concentrated nitric acid and diluted to 100 ml with distilled water to represent each of the three levels. Three sets of six filters are spiked with appropriate volumes of each standard solution for each of the three levels. This corresponds to the amount of yttrium collected in a 500-liter sample at the 0.5X, 1X, and 2X levels, respectively. Allow the

filters to dry and place each filter in a cassette filter holder, and allow to stand overnight. The filters are ashed and analyzed as described in Section 8.4. A parallel blank filter is also treated in the same manner except that no sample is added to it.

Analytical Method Recovery (A.M.R.) equals the weight in mg found divided by the weight in mg added to the filter, or

$$\text{A.M.R.} = \frac{\text{mg found}}{\text{mg added}}$$

9. Calibration and Standards

9.1 Prepare at least 4 working standards to cover the range from 150 to 1500 µg/5 ml from the 1000 µg/ml stock yttrium standard solution. Make all standard solutions in 0.6M hydrochloric acid containing 1000 ppm sodium. Prepare fresh working standards daily.

9.2 Aspirate each of the standard samples and record the absorptions.

9.3 Prepare a calibration curve by plotting on linear graph paper the absorbance versus the concentration of each standard in µg/5 ml. It is advisable to run standards both before and after the analysis of a series of samples to insure that conditions have not changed.

10. Calculations

10.1 Read the weight, in µg, corresponding to the total absorbance from the standard curve. No volume corrections are needed, because the standard curve is based on µg/5 ml.

10.2 Corrections for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

µg sample = µg found in sample filter
µg blank = µg found in blank filter

10.3 Divide the total weight by the analytical method recovery (A.M.R.) to obtain corrected µg/sample.

$$\text{Corrected } \mu g/\text{sample} = \frac{\mu g \text{ found (Section 10.2)}}{\text{A.M.R.}}$$

10.4 The concentration of the analyte in the air sample can be expressed in mg/cu m (µg/liter = mg/cu m).

$$\text{mg/cu m} = \frac{\text{Corr. } \mu g \text{ (Section 10.3)}}{\text{Air Volume Sampled (liter)}}$$

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.

11.3 Documentation of NIOSH Validation Tests, NIOSH Contract CDC-99-74-45.

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15. Supplementary Notes

16. Abstracts

Industrial Hygiene sampling and analytical monitoring methods validated under the joint NIOSH/OSHA Standards Completion Program for Set N are contained herein. Monitoring methods for the following compounds are included:

Arsenic and compounds (as As)
Beryllium and Beryllium compounds (as Be)
Nickel, metal and soluble compounds (as Ni)
Tin, inorganic compounds except oxides
Barium, soluble compounds
Calcium Oxide
Tellurium
Yttrium

17. Key Words and Document Analysis. 17a. Descriptors

Chemical analysis
Sampling

*Arsenic and compounds (as As)
*Beryllium and Beryllium compounds (as Be)
*Nickel, metal and soluble compounds (as Ni)
*Tin, inorganic compounds except oxides
*Barium, soluble compounds
*Calcium oxide
*Tellurium
*Yttrium

17b. Identifiers/Open-Ended Terms

17c. COSATI Field/Group 6,7, & 14

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