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ANALYTICAL METHODS EVALUATION AND VALIDATION

ARSENIC, NICKEL, TUNGSTEN, VANADIUM, TALC, WOOD DUST

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Methods for tne sampling and analysis of arsenic (7440382) (As), nickel (7440020) (Ni), tungsten (7440337) (W), vanadium (7440622) (V), talc (14807966), and wood dust in the workplace were developed. As, Ni, W and samples were collected on a cellulose ester filter and analyzed by graphite furnace atomic absorption spectrophotometry (GFAAS) or flame atomic absorption spectrophotometry. Talc samples were collected on a polyvinyl-chloride filter and analyzed by X-ray diffraction. Wood dust samples were collected on glass fiber filters and were analyzed gravimetrically. The analytical method percent recovery of As was determined to be about 100.5 at 615 micrograms per cubic meter and in all cases collection efficiency was better than 0.939 percent. The analytical method recovery of Ni was determined to be 101.9 percent at 0.5 times the NIOSH recommended standard. The recovery was determined to be 0.963 at 1.2 milligrams per cubic meter (mg/m3) soluble W and 0.995 at 9.0mg/m3 insoluble W. The RSD for soluble W was 0.963 percent at 1.2mg/m3 and 0.995 percent at 9.0mg/m3 for insoluble W. The analytical method recovery was about 0.971 at 1.1 times the NIOSH recommended standard for soluble V and about 0.982 at 1.0 times the standard for insoluble V. The detection limit for filters containing 3.0, 19.5, and 39.0 micrograms of talc analyzed at the 002 and 006 peaks were 12 micrograms per filter for the 002 peak and 10 micrograms per filter for the 006 peak. The analytical method recovery was about 1.000 at 1.0 times the NIOSH recommended standard for wood dust with collection efficiency better than 97.5 percent in all cases. The authors conclude that the methods for Ni, W, soluble V, and wood dust were fully validated and that validation for As, insoluble W, and talc are still pending further investigation.

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ABSTRACT

Accurate, reliable information on the exposure of workers to hazardous substances in the air is essential to the maintenance of safe working conditions. Methods for the sampling and analysis of Arsenic, Nickel, Tungsten, Vanadium, Talc, and Wood Dust in the workplace environment have been developed and evaluated. For nickel, tungsten, and wood dust, fully validated methods have resulted.

All of the substances are collected on a filter in a cassette attached to a personal sampling pump. Arsenic is collected on a sodium carbonate-impregnated cellulose ester filter with cellulose backup pad; the filter-backup pad pair is digested with nitric acid-hydrogen peroxide and the residue is dissolved and analyzed by graphite furnace atomic absorption spectrophotometry. Nickel is collected on a cellulose ester filter, which is digested with nitric acid-hydrofluoric acid, and the residue is dissolved and analyzed by GFAAS. Tungsten and vanadium are each collected on a cellulose ester filter, which is then extracted for soluble species and digested for insoluble species. In each case the soluble and insoluble fractions are analyzed separately by flame AAS(W) and GFAAS(V). Talc is collected on a polyvinylchloride filter, which is radio-frequency ashed. The residue is transferred to a silver membrane filter and analyzed by x-ray diffraction. Wood dust is collected on a glass fiber filter and analyzed gravimetrically.

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INTRODUCTION

This report describes the work performed by Rockwell International - Environmental Monitoring and Services Center for the Development, Evaluation, and Validation of Methods for the Determination of Arsenic, Nickel, Tungsten, Vanadium, Talc, and Wood Dust in the air of the workplace environment, under NIOSH Contract 210-79-0060. The experiments for validation of each sampling and analytical method, as outlined in NIOSH Contract 210-79-0060, are as follows:

1. preparation and analysis of six spiked samples at each of three levels across the range of the method;

2. preparation at high humidity and analysis of six dynamically generated samples at each of three levels across the range of the method; and

3. verification of the generated concentrations by at least one independent method.

For successful validation, these criteria must be satisfied:

1. true relative standard deviation of less than 0.128 for an unbiased method;

2. minimum solid sorbent desorption efficiency of 80% and minimum filter extraction efficiency of 90%;

3. bias of no greater than $\pm$10%;

4. minimum sample time of two hours for time-weighted average concentrations;

5. stability of fourteen days of samples generated at high humidity.

In the following sections, each method is introduced, the experimental work described in detail, the sampling and analytical data presented, and the results of the efforts summarized. Table 1 briefly summarizes the methods. The work is described also in the Sampling & Analytical Method (SAM), Backup Data (BUD), and Sampling Data Sheet (SDS) for each substance.

Table 1. Synopsis of methods.

	As	Ni	W	V	Talc	Wood Dust
Species	Total Inorganic	Total Inorganic	Soluble and Insoluble	Soluble and Insoluble	Total	Total
Sampling	Base-Treated Filter	Cellulose Ester Filter	Cellulose Ester Filter	Cellulose Ester Filter	PVC Filter	Glass Fiber Filter
Digestion	HNO_3-H_2O_2	HNO_3-HF	H_2O;HNO_3-HF; HCl;HNO_3-HF	KOH;HNO_3	LTA;HCl	---
Analysis	GFAAS 193.7 nm	GFAAS 232.0 nm	AAS 255.1 nm	GFAAS 318.4 nm	XRD 002, 006 peak	Gravimetry
Existing NIOSH Method	P&CAM 286	P&CAM 298	P&CAM 271	P&CAM 290	---	---

ARSENIC

Arsenic in the workplace environment exists in both vapor and particulate form, and the OSHA standard for inorganic arsenic is 10 $\mu g/m^3$ measured as a time-weighted average for up to a ten-hour work shift in a forty-hour work week. The method developed and evaluated for arsenic involves the collection of inorganic arsenic species on a base-treated cellulose ester filter and the determination of arsenic by graphite furnace atomic absorption analysis (GFAAS). NIOSH Method P&CAM 286 (2), Particulate Arsenic, was the starting point in the development of the new method, P&CAM 346. The experiments performed for the development and evaluation of a method for the determination of inorganic arsenic in the workplace environment are described in the following sections. Experimental procedures and results are also described in the Sampling and Analytical Method, Backup Data, and Sampling Data Sheet for this substance.

EXPERIMENTAL

Reagents, laboratory glassware, equipment and instrumentation which were used throughout this effort were as follows:

Reagents

1. Arsenic Stock, 1000 µg/mL, prepared gravimetrically from reagent grade As_2O_3 in 2 mL concentrated NH_3 and diluted to 1 L
2. As Metal, Reagent grade
3. As_2O_3, Reagent grade
4. As_2O_5, Reagent grade
5. FeAs, Cerac certified
6. Cu_3As_2, Cerac certified
7. Nickel Stock, 10000 µg/mL prepared gravimetrically from reagent grade $Ni(NO_3)_2 \cdot 6H_2O$
8. Copper Stock, Baker Dilut-It
9. Chloride Stock, 1000 µg/mL, prepared gravimetrically from reagent grade NH_4Cl
10. Nitrate Stock, 1000 µg/mL, prepared gravimetrically from reagent

grade NH_4NO_3

11. Sulfate Stock, 1000 µg/mL, prepared gravimetrically from reagent grade $(NH_4)_2SO_4$
12. NBS SRM 1648, Urban Particulate
13. NBS SRM 1633a, Trace Elements in Fly Ash
14. Concentrated HNO_3, Baker Analytical Reagent Grade
15. Concentrated $HClO_4$, Baker Analytical Reagent Grade
16. Hydrogen Peroxide, 30%, Baker Analytical Reagent Grade
17. Na_2CO_3, Reagent Grade
18. Glycerol, Reagent Grade

Glassware and Equipment

1. Pipettes, volumetric class A, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0, 100.0, 1000.0-mL
2. Micropipettes, SMI, 10, 25, 50, 300-µL
3. Flasks, volumetric class A, 100.0, 1000.0-mL
4. Beakers, borosilicate glass, 50-mL
5. Filters, Millipore, 0.8-µm cellulose ester, 37-mm diameter
6. Backup pads, Millipore, cellulose, 37-mm diameter
7. Filter cassettes, Millipore, plastic, 37-mm

Instruments

1. Atomic Absorption Spectrophotometer, Perkin-Elmer Model 306 with D_2 background corrector, HGA 2100 graphite furnace, ASI autosampler, EDL power supply, and arsenic EDL
2. Recorder, Linear Instruments Corp., 10-mV full scale
3. Aerosol Generation System, described in Appendix A to this report.

Optimization of Instrumental Parameters and Determination of Instrumental Precision

Parameters examined in this study to determine the best set of experimental conditions were char temperature, atomization temperature, graphite tube type, and background matrix. Recommended parameters were: dry 100 °C (70 sec), char 1500 °C (34 sec), atomize 2700 °C (7.5 sec); background matrix 1% HNO_3 and 0.1% or 1% Ni^{++}; and non-pyrolytic graphite tubes (3). These conditions were used as a starting point for experimentation.

To ascertain the optimal char temperature, 0.04 µg/mL arsenic solutions in 1% Ni/1% HNO_3 and 0.1% Ni/1% HNO_3 were examined along with background solutions containing no arsenic. The data are presented in Figure 1. All measurements were made using non-pyrolytic graphite tubes. The optimal charring temperature is taken to be the highest temperature which can be used without significant loss of signal intensity or significant background interference. For the 0.1% nickel matrix, a plateau indicating no arsenic loss in the char cycle is observed for char temperatures between 1100 °C and 1400 °C, with background response slightly above the detection limit and constant over the range of temperatures examined. In the 1% nickel matrix, a plateau in the arsenic signal occurs between 1500 °C and 1900 °C while the background response decreases by about 50% as the char temperature increases from 1500 °C to 2100 °C. The optimal char temperature is 1400 °C in the 0.1% nickel matrix and 1900 °C in the 1.0% nickel matrix.

Analogous experiments were conducted to optimize atomization temperature, except that a 0.08 µg/mL solution was used in the 1% nickel matrix to increase instrumental response. The data are presented in Figure 2. For both the 1% and the 0.1% nickel matrices, the maximum response is observed at 2700 °C, the maximum temperature which can be reached reproducibly, and is much less at lower temperatures. The background response for the 0.1% nickel matrix is independent of atomization temperature over the range 2300 °C to 2700 °C, but for the 1% nickel matrix the background response increases with increasing atomization temperature. At 2700 °C, the 1% nickel matrix gives up to four times the background response of the 0.1% nickel matrix. The optimal atomization temperature is 2700 °C.

Experiments were conducted to compare analytical precision obtained using pyrolytically and non-pyrolytically coated graphite tubes. Solutions contained 0.04 µg/mL arsenic in 1% HNO_3 and 1% or 0.1% nickel. Graphite furnace conditions were dry 100 °C (90 sec), char 1500 °C (34 sec), atomize 2700 °C (7.5 sec). The data are presented in Table 2 and indicate that better precision is attained with non-pyrolytically coated tubes; these will be used for all future analyses.

From the data presented in Figures 1 and 2, and Table 2, it was concluded that instrumental response to arsenic is greater and background response less when the sample matrix is 1% HNO_3/0.1% Ni, so this matrix will be used for all analyses.

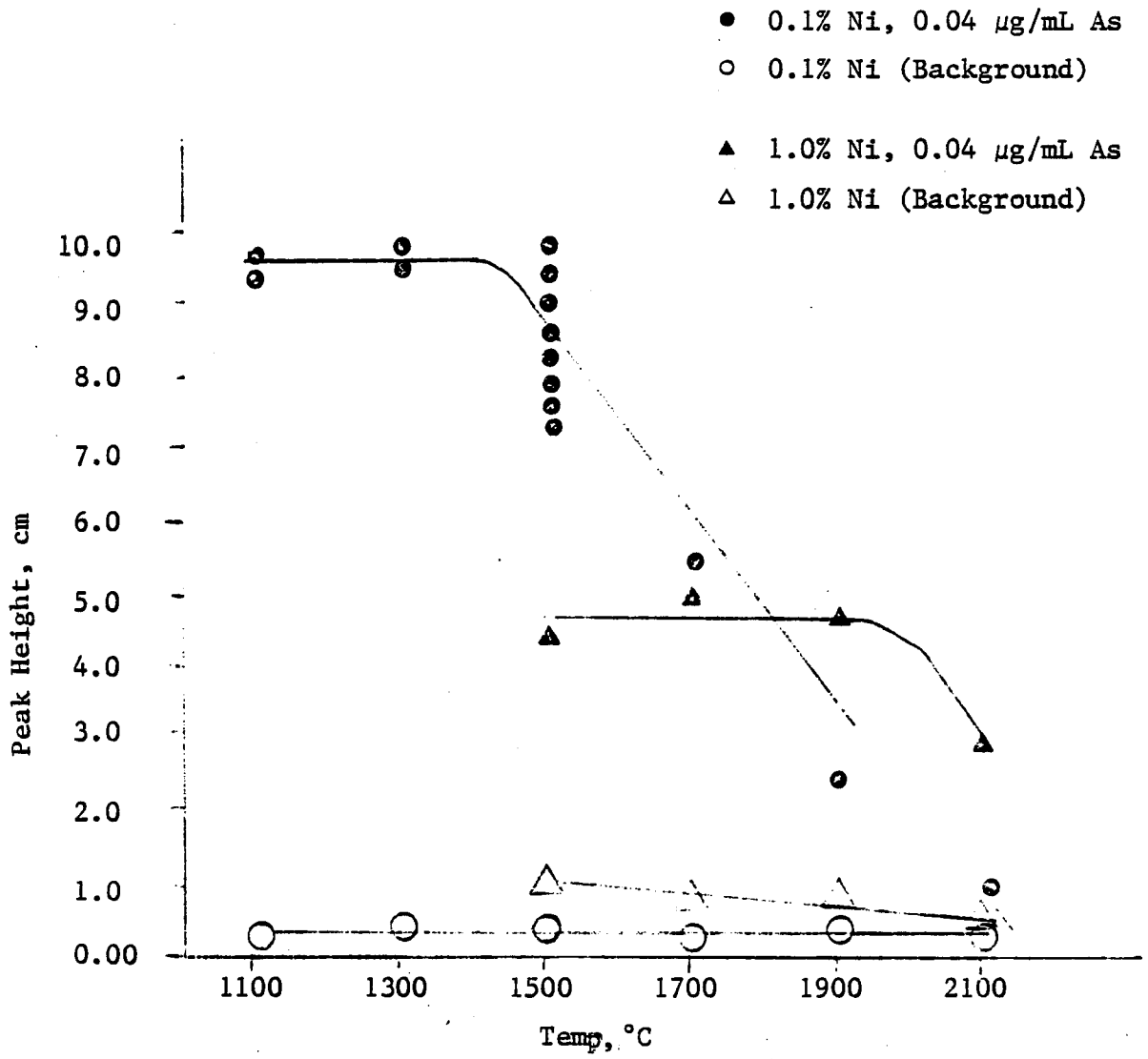

Figure 1. Instrumental response as a function of char temperature.

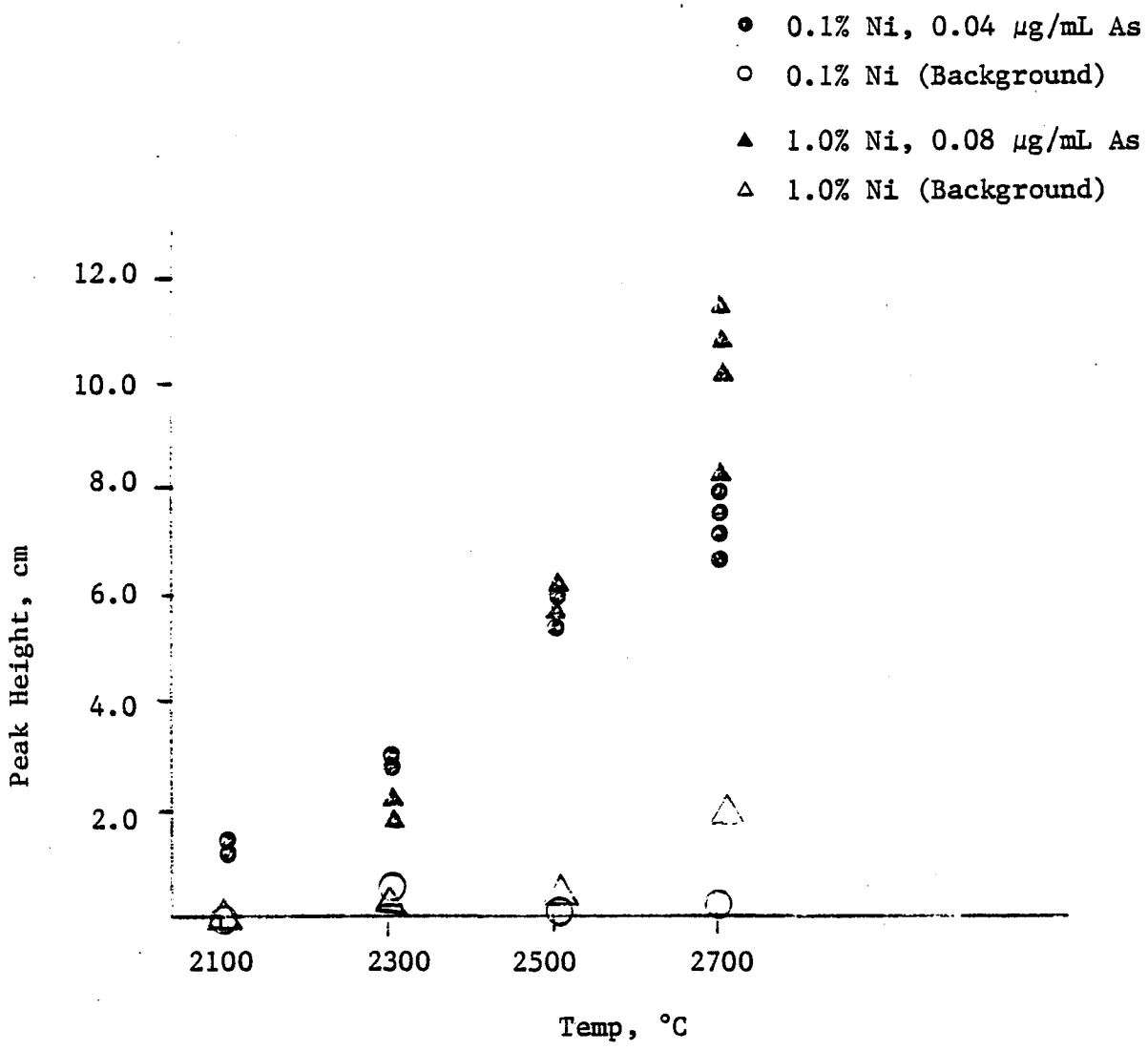

Figure 2. Instrumental response as a function of atomization temperature.

Table 2. Instrumental precision obtained using pyrolytic and non-pyrolytic graphite tubes for arsenic analysis*.

Graphite Tube Type	Matrix	Peak Height in cm**	Mean ± SD
pyrolytic	0.1% Ni	8.60*** 8.25 6.83 10.10	8.45 ± 1.34
pyrolytic	1.0% Ni	1.00 5.20 6.65 7.10	4.99 ± 2.8
non-pyrolytic	0.1% Ni	9.10 9.15 9.20 9.05	9.12 ± 0.06
non-pyrolytic	1.0% Ni	7.50 7.40 6.30 6.75	6.99 ± 0.57

* solution contained 0.04 µg/mL As.

** 0.0131 absorbance units/cm.

*** instrumental conditions were Dry 100 °C (90 sec), char 1500 °C (34 sec), atomize 2700 °C (7.5 sec).

Optimized instrumental conditions for the analysis of arsenic using a Perkin-Elmer 306 were:

Wavelength	143.7
Slit width	4 nm
Scale expansion	3x
Argon flow setting	20 cc/min
Dry	100 °C (90 sec)
Char	1400 °C (30 sec)
Atomize	2700 °C (7.5 sec)
Injection volume	10, 50 µL
Sample matrix	1% HNO_3, 0.1% Ni^{++}
Sample tube	non-pyrolytic

Experiments were then conducted to evaluate instrumental precision under the optimized instrumental conditions. Both 0.1% and 1% nickel matrices were examined. Calibration curves, each consisting of a background matrix sample and arsenic standards at five concentrations, were analyzed repetitively. The data were pooled and a linear least squares fit performed; data are presented in Tables 3 (0.1% Ni) and 4 (1% Ni). These data support the choice of the 0.1% nickel matrix and demonstrate that in this matrix, under the optimized instrumental conditions, X, the arsenic concentration at which 10% analytical precision is attained, is below 0.02 µg/mL.

Evaluation of Interferences

Solutions containing arsenic at a concentration of 0.026 µg/mL in 1% HNO_3 and 0.1% Ni and interference concentrations of 0.025 µg/mL (1x), 0.25 µg/mL (10x), and 1.25 µg/mL (50x) were prepared and analyzed. Interferences examined were chloride, nitrate, sulfate, and copper. For copper, a higher concentration, 4.00 µg/mL (160x), was examined. The results are presented in Table 5. Copper is the only species which interferes in the analysis of arsenic, causing negative interference only when present in very large excess (160x).

Optimization of Digestion Variables

Both wet ashing and low temperature ashing were considered for the digestion of filters exposed to arsenic. The following variables and possibilities were examined:

1. Concentration of HNO_3 in initial digestion
2. Use of perchloric acid
3. Time of ashing
4. Concentration of nitric acid for solubilization
5. HF treatment of silicates.

Table 3. Instrumental precision for the analysis of As.

matrix: 1% HNO_3/0.1% Ni conditions: Dry 100 °C (90 sec), char 1500 °C (30 sec), atomize 2700 °C (7.5 sec) tube: non-pyrolytic

Arsenic, taken (µg/mL)	As found (µg/mL) 1	2	3	4	5	Mean ± SD	% Recovery	%RSD
0.02	0.01832	0.01969	0.02106	0.02146	0.01246	0.02040 ± 0.0014	102.0	6.86
0.04	0.03754	0.04029	0.04049	0.03951	0.04206	0.03998 ± 0.0016	99.9	4.00
0.06	0.05246	0.05716	0.06266	0.06403	0.06325	0.05991 ± 0.0050	98.8	8.35
0.08	0.07875	0.07894	0.08130	0.08502	0.08718	0.08224 ± 0.0037	102.8	4.49
0.10	0.08738	--	--	--	--	-- --	--	--
					Mean ± SD		100.9% ±	5.92

intercept = 0.001053

slope = 0.003924

SD = 0.004343

coefficient of correlation = 0.9710

Table 4. Instrumental precision for the analysis of As.

matrix: 1% HNO_3/1.0% Ni conditions: Dry 100 °C (90 sec), char 1500 °C (30 sec), atomize 2700 °C (7.5 sec)
tube: non-pyrolytic

Arsenic, taken (µg/mL)	As found (µg/mL) 1	2	3	4	5	Mean	±	SD	% Recovery	%RSD
0.02	0.02472	0.02178	0.01968	0.02304	0.01926	0.02170	±	0.0023	108.5	10.6
0.04	0.03859	0.04111	0.04030	0.04195	0.04321	0.04103	±	0.0017	102.6	4.14
0.06	0.05582	0.05497	0.06128	0.06464	0.05918	0.05917	±	0.0040	98.6	6.76
0.08	0.07766	0.07556	0.06464	0.08061	0.08229	0.07626	±	0.0071	95.3	9.31
0.10	0.10414	0.09741	0.10119	0.10414	0.10287	0.10195	±	0.0028	101.9	2.75
					Mean ± SD				101.4	± 6.71

intercept = 0.007149

slope = 0.008404

SD = 0.004357

coefficient of correlation = 0.9782

Table 5. Interferences in the analysis of arsenic.

Species Studied	Conc. level in µg/mL	Concentration of As in µg/mL		% Recoverv ± SD
		Taken	Found ± SD	
Cl^-	0.025	0.0257	0.0259 ± 0.0004	100.8 ± 1.4
	0.25	0.0257	0.0260 ± 0.0001	101.2 ± 0.6
	1.25	0.0257	0.0257 ± 0.0006	100.0 ± 2.3
NO_3^-	0.025	0.0257	0.0258 ± 0.0005	100.4 ± 2.0
	0.25	0.0257	0.0266 ± 0.0010	103.5 ± 3.8
	1.25	0.0257	0.0262 ± 0.0009	101.9 ± 3.6
SO_4^{-2}	0.025	0.0257	0.0260 ± 0.0011	101.2 ± 3.8
	0.25	0.0257	0.0266 ± 0.0006	103.5 ± 1.8
	1.25	0.0257	0.0267 ± 0.0003	103.9 ± 0.9
Cu^{+2}	0.025	0.0273	0.0273 ± 0.0006	100.0 ± 2.1
	0.25	0.0273	0.0273 ± 0.0002	100.0 ± 0.9
	1.25	0.0273	0.0272 ± 0.0004	99.6 ± 1.4
	4.00	0.0200	0.0165 ± 0.0002	82.5 ± 1.2

During the literature evaluation, some insights were gained. Arsenic will react with the halogens to form the trihaldes, which are generally low boiling point materials. The halides can also be formed by the reaction of halogens with arsenic compounds. Thus, As_2O_3 will react with chlorine to give $AsCl_3$. This clearly has to be avoided in the analysis of As_2O_3, since the halide is volatile and highly poisonous. Also, losses of As are noted for a HNO_3, H_2SO_4, $HClO_4$ digestion and for a HNO_3, H_2SO_4 digestion. It would, therefore, be advantageous to avoid these combinations of acids if possible (4,5).

Reagents for the digestion of filters containing arsenic were limited also because the final acid matrix concentration must be as low as possible for optimum flameless AAS graphite tube stability, and because volatile arsenic species may be lost in the charring step of flameless analysis. Since arsenic species in the (III) state are much more volatile than arsenic species in the (V) state, the digestion procedure should be sufficiently oxidizing to convert As(III) to As(V), but the oxidant used should not interfere in the graphite furnace analysis. Of the techniques reported in the literature, a nitric acid-hydrogen peroxide digestion most nearly achieves the above goals. It was expected that nitric acid-hydrogen peroxide would dissolve all arsenic species to be determined except silicates.

The work done to optimize the instrumental conditions showed that a final matrix of 1% HNO_3-0.1% Ni would give the best response for arsenic. With these facts in mind, the following procedure was developed and tested.

The exposed filter is transferred to a clean 50-mL beaker and 5 mL concentrated HNO_3 added. The beaker is covered with a watchglass and placed on a hotplate at 150 °C. Digestion is allowed to proceed until the volume is reduced to 1-2 mL; the beaker is then removed from the hotplate and the solution allowed to cool. The watchglass is rinsed and removed, 2 mL 30% hydrogen peroxide is added, and the beaker again placed on the steam bath. The solution is then taken to dryness and cooled. Ten mL 1% HNO_3-0.1% Ni is added; the beaker is covered with parafilm and sonicated for 30 minutes. The solution is then analyzed by GFAAS.

A series of experiments was conducted to test the proposed digestion procedure:

1. Spiked filters (As_2O_3) were digested with concentrated nitric acid with and without hydrogen peroxide

2. Experiment 1 was repeated, with no intentional changes

3. Experiment 1 was repeated with a larger quantity of arsenic spiked onto the filters.

The data are presented in Table 6. In experiment 1, recovery was high and precision poor when HNO_3 alone was used for digestion. Both were improved when HNO_3-H_2O_2 was used. In experiment 2, the repetition of experiment 1,

Table 6. Determination of arsenic using different digestion procedures.

	Digestion Mixture	Concentration of As in µg/mL		% Recovery ± % SD
		Taken	Found ± SD	
1.**	A. 5 mL con. HNO_3	0.062*	0.077 ± 0.022	124 ± 28
	B. 5 mL con. HNO_3 2 mL 30% H_2O_2	0.062*	0.065 ± 0.006	105 ± 9.2
2.**	A. 5 mL con. HNO_3	0.062*	0.077 ± 0.008	124 ± 10
	B. 5 mL con. HNO_3 2 mL 30% H_2O_2	0.062*	0.068 ± 0.009	110 ± 13
3.***	A. 5 mL con. HNO_3	0.257	0.237 ± 0.015	92 ± 6.3
	B. 5 mL con. HNO_3 2 mL 30% H_2O_2	0.257	0.248 ± 0.007	96 ± 2.8

All solutions were 1% HNO_3 - 0.1% Ni.

*The filter samples were prepared by spiking cellulose ester filters with 25 µL of 2.5 µg/mL As solution with a micropipette.

**dry 100 °C, 90 sec; char 1400 °C, 30 sec; atomize 2700 °C, 10 sec; 50-µl injection.

***dry 100 °C, 30 sec; char 1400 °C, 15 sec; atomize 2700 °C, 7.5 sec; 10-µl injection.

precision was better, but recovery still high for HNO_3 alone, suggesting that the high recovery is reproducible. At the higher spike level of experiment 3, both recoveries and precisions were improved, but were still better for HNO_3-H_2O_2.

The digestion was now tested on other arsenic-containing species, including As metal, As_2O_3, As_2O_5, $NaAsO_2$, FeAs, Cu_3As_2, NBS SRM 1632 (trace elements in coal fly ash), and NBS SRM 1648 (urban particulates). The data are presented in Table 7. In each case recovery and precision were satisfactory.

As part of the digestion experiments, work was done to determine the oxidation state of the arsenic at various times in the analysis. Under NIOSH Contract No. 210-77-0134 (1), an analytical technique for determining organoarsenicals was developed. By using the procedures and equipment developed for that contract, it was possible to separate and analyze As(III) and As(V).

Spiked and blank filters were analyzed before and after digestion with and without the addition of hydrogen peroxide to determine in what oxidation state the arsenic exists at various points in the digestion.

Spiked non-digested filters were analyzed and showed that no change in oxidation state took place on the filter. However, all the As(III) was converted to As(V) on the spiked digested filters. This was the case regardless of the presence of hydrogen peroxide. Five mL of concentrated nitric acid was enough by itself to complete this oxidation (5).

Blank filters digested with and without hydrogen peroxide were analyzed by Dionex ion chromatography to determine any background NO_3^-, $SO_4^=$, and Cl^- levels. In the course of this analysis, it became apparent that the filters digested with nitric-acid hydrogen peroxide had considerably less organic anion present. It appears that the peroxide reduces the amount of organic material left in solution after digestion, as well as oxidizing the As(III) to As(V). This might also account for the better precision and accuracy of the nitric acid-hydrogen peroxide digested filters. With less organic material present, the nitric acid-hydrogen peroxide digested filters would have a matrix closer to that of the standards. Ion chromatograms are shown in Figure 3.

The method was tested by a Youden-Steiner test of variables (6), shown in Table 8. The digestion experiments and the Youden-Steiner variable study indicate that the technique is reasonably reproducible. The only critical factor is that the hydrogen peroxide be added before the digested filter goes to dryness. The digestion technique gives good recoveries.

The effect of perchloric acid in the digestion of As_2O_3 on cellulose ester filters was investigated. Each of four cellulose ester filters was spiked with As_2O_3 solution and placed in a 50-mL beaker. Five mL of concentrated HNO_3 was added to each beaker; the beakers were covered with a watchglass and placed on a 160 °C hotplate. The volume of the solution was reduced to approximately 2 mL. The beaker was removed from the hotplate and allowed to cool. After cooling, 2 mL concentrated ultrapure $HClO_4$ was pipetted into the

Table 7. Determination of arsenic in various materials.

Material	Weight of Material (gm) Dissolved in 25 mL	Amount (gm) of Arsenic in the material		% Recovery ± SD
		Taken	Found	
As metal	0.1012	0.1012	0.1084	102.9 ± 3.5
	0.1008	0.1008	0.1009	
	0.1060	0.1060	0.1077	
As_2O_3	0.1451	0.10990	0.1046	99.2 ± 3.5
	0.0998	0.07559	0.0759	
	0.1023	0.07748	0.07895	
As_2O_5	0.1424	0.08613	0.07637	96.3 ± 7.6
	0.1125	0.06530	0.06319	
	0.1023	0.05937	0.06137	
$NaAsO_2$	0.0994	0.05732	0.05545	98.6 ± 2.7
	0.1016	0.05859	0.05953	
	0.1057	0.06096	0.05940	
CuAs	0.1044	0.02945	0.03059	94.2 ± 0.90
	0.1015	0.02863	0.02540	
	0.1000	0.02821	0.02558	
NBS SRM 1633a (μgAs/gm)	0.2552	3.70×10^{-6}	3.73×10^{-6}	100.3 ± 0.72
	0.2515	3.65×10^{-6}	3.63×10^{-6}	
	0.2502	3.63×10^{-6}	3.65×10^{-6}	
NBS SRM 1648 115 μg/gm	0.1001	11.51	11.668	100.5 ± 0.95
	0.1020	11.73	11.668	
	0.1219	14.02	14.086	

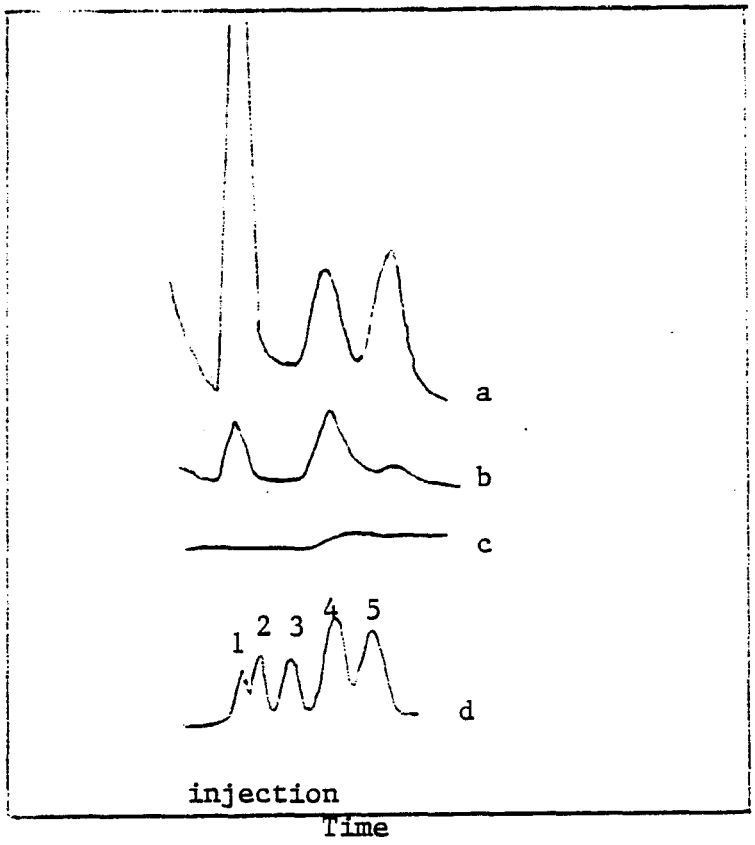

Figure 3. Ion chromatographic analysis of cellulose ester filters. All four chromatograms were run under the same instrumental conditions. Each represents the following: (a) filter digested with 5 mL concentrated HNO_3, evaporated to dryness and dissolved in 10.0 mL of the IC eluents; (b) filter digested with 5 mL concentrated HNO_3 and 2 mL 30% H_2O_2, evaporated to dryness and dissolved in 10.0 mL of IC eluent; (c) 5 mL concentrated HNO_3, evaporated to dryness and dissolved in 10.0 mL of IC eluents (no filter); (d) mixed standard solution containing 5 μg/mL F^-, 10 μg/mL Cl^- (2), 50 μg/mL $PO_4^{\equiv}$ (3), 50 μg/mL NO_3^- (4), and 50 μg/mL $SO_4^{\equiv}$ (5).

Table 8. Youden-Steiner ruggedization for arsenic.

Effects of variables in the digestion of filters loaded with arsenic

EXPERIMENT	A	B	C	D	E	F	G
Concentration of As, µg/mL	0.179 0.214	0.259 0.260	0.161 0.208	0.259 0.253	0.251 0.253	0.264 0.264	0.220 0.190
Effect of Variable	-0.026 -0.012	0.022 0.016	-0.049 -0.047	-0.013 -0.009	-0.040 0.002	0.002 0.019	0.007 -0.020
Average Effect of Variable	-0.019	0.019	-0.048	-0.011	-0.019	0.011	-0.006

At the 95% probability level (1.18s), variables greater than 0.024 are significant: C = -0.048. All others insignificant.

A	Amount of concentrated HNO_3	2 mL vs 5 mL
B	Temperature of hotplate	150 °C vs 250 °C
C	When peroxide is added	before dryness vs after dryness
D	Amount of peroxide	2 mL vs 5 mL
E	Time of solubilization	5 min vs 30 min
F	Dummy	
G	Dummy	

beaker. The beaker was placed on the hotplate and the solution was brought close to dryness. The watchglass was rinsed with a small amount of water and removed, and the beaker was placed on a steam bath. The solution was evaporated to dryness. Ten mL of 1% HNO_3/0.1% Ni^{++} was pipetted into the beaker, it was covered with Parafilm and ultrasonically agitated for 30 minutes.

The experimental data are presented in Table 9. Losses of about 50% may be attributed to the formation of volatile arsenic chloride. Therefore, the digestion method using HNO_3-H_2O_2 is the preferred method for the analysis of arsenic.

In the course of collection efficiency experiments, discussed later in this report, it became clear that in order to collect arsenic vapors, base-treated filters were necessary. In addition, arsenic would reside on both the filter and backup pad. Therefore, for the quantification of total arsenic, it was necessary to digest both filter and backup pad. Experiments were then conducted to test the digestion efficiency of the filter-backup pad pair.

Two sets of six Na_2CO_3-glycerol treated filter-backup pad pairs were spiked with As_2O_3 solution. The pressure drop across the Na_2CO_3-glycerol treated filters was determined and compared to the pressure drop across an untreated filter. The data are presented in Table 10. Pressure drops for the treated filters are acceptably low.

Six filter-backup pad pairs were ashed in a plasma asher for 12 hours at 100 watts RF power. Six were acid digested with the following modifications to the normal procedure: 15 mL of concentrated HNO_3 was used instead of 5 mL, and 6 mL of 30% hydrogen peroxide was used instead of 2 mL.

Table 11 gives the data from this experiment. The data demonstrate good recoveries from the spiked filter-backup pad pairs when wet digestion is used. In the plasma ashing experiments, much residue from the filter-backup pad pair remained even after twelve hours. So, plasma ashing was unsatisfactory for digestion of the filter- backup pad pair and wet digestion was the satisfactory method.

Determination of Collection Efficiency

Six plastic cassettes, one containing one filter-backup pad pair and five containing two filter-backup pad pairs, each pair separated by a spacer, were loaded with As_2O_3 vapor in the vapor generation system. Each filter and backup pad was digested and analyzed for arsenic. The data are presented in Table 12.

Arsenic trioxide is clearly penetrating the first filter, and in some cases it also penetrates the backup pad. The same phenomenon has been observed with Teflon filters; in these experiments no backup pads were used and arsenic was found in the bubbler. Clearly the 0.8-μm cellulose ester filter results in poor collection efficiency for the As_2O_3 vapor (7-9).

Table 9. Effect of $HClO_4$ treatment of spiked filters on the recovery of arsenic.

	Amount of Arsenic in µg/filter		
Filter #	Taken	Found	% Recovery
1	0.101	0.05	50
2	0.101	0.05	50
3	0.101	0.06	60
4	0.101	0.05	50
	Mean ± SD		53 ± 5

Table 10. Pressure drops across filter-backup pad pairs.

Treatment	Filter	First Reading	Second Reading	Third Reading
		Inches of H_2O	Inches of H_2O	Inches of H_2O
10% glycerol 90% 1 M Na_2CO_3	A	5.1	4.9	4.9
	B	5.0	5.0	5.0
	C	5.0	5.0	4.9
	D	5.0	4.8	4.8
	E	4.5	4.4	4.4
Untreated	0	3.9	4.0	3.9

Table 11. Digestion of spiked treated filter-backup pad pairs*.

Filter #	As µg		% Recovery
	Taken	Found	
1	0.489	0.4917	100.5
2	0.489	0.5074	103.8
3	0.489	0.4989	102.0
4	0.489	0.5379	110.0
5	0.489	0.4964	101.5
6	0.489	0.4498	92.0
Mean		0.4970	101.6
SD		± 0.0284	± 5.7

*HNO_3-H_2O_2 was used for digestion.

Table 12. Collection efficiency for arsenic using cellulose ester filters.

Experiment # (*)	Oven Temp. °C	Dilution Flow L/min	Total Flow L/min	Sampling Rate cc/min	µg/filter
1 Filter #1**	100°	1.2	10.0	1500	0.06
Backup Pad #1					∿0.10
2 Filter #1	200°	1.2	5.0	1500	0.27
Backup Pad #1					0.23
Filter #2					0.06
Backup Pad #2					0.18
3 Filter #1	125°	1.2	8.0	1500	0.08
Backup #1					0.48
Filter #2					0.09
Backup #2					0.02
4 Filter #1	125°	1.2	8.0	1500	0.08
Backup #1					0.08
Filter #2					0.08
Backup #2					0.02
5 Filter #1	150°	1.2	8.0	1500	0.264
Backup #1					0.194
Filter #2					0.020
Backup #2					0.010
6 Filter #1	150°	1.2	8.0	1500	0.508
Backup #1					0.138
Filter #2					0.020
Backup #2					0.010

*A bubbler with 0.1N NaOH was behind each filter holder. Analysis of these bubblers showed no detectable arsenic levels.

**0.8 µm pore size cellulose ester filters; cellulose backup pads.

Experiments were performed to evaluate chemically treated filters for the quantitative collection of both particulate and gaseous As_2O_3. The collection efficiencies of 0.8-µm cellulose ester filters treated with Na_2CO_3-glycerol solution, $(C_4H_9)_4NOH$-glycerol solution, or NaOH-glycerol solution were examined. Data from these experiments are presented in Table 13.

The Na_2CO_3-glycerol treated filters appear to be collecting arsenic trioxide vapor most efficiently. In Table 14, data from the Na_2CO_3-glycerol treated filter experiments are rearranged and presented again to illustrate percentage recoveries. In each case the first filter- backup pad pair collected greater than 90% of the total arsenic. Filter pairs will be digested and analyzed together in the final method.

To test the loading capacity of the treated filter-backup pad pairs for arsenic, filters were loaded at ten times the OSHA standard for arsenic; samples were collected for 4 hours at 1.6 to 1.9 liters per minute. The pairs were digested and analyzed according to the established procedure. The data from this experiment are presented in Table 15.

From Table 15 it is clear that at a total arsenic concentration exceeding ten times the OSHA standard, breakthrough of less than 1% occurs from the treated filter-backup pad pair.

Procedure for Preparation of Treated Filter-Backup Pad Pairs

Because it was shown to be necessary to treat cellulose ester filters with base to ensure collection of all airborne inorganic arsenic species, a standard procedure for the preparation of treated filter-backup pad pairs was developed.

A 0.8-µm pore size cellulose ester filter with cellulose backup pad is placed in a plastic filter cassette and closed firmly. The top plug of the cassette is removed and 300 µL of 9:1 1M Na_2CO_3:glycerol is injected onto the filter. The plug is replaced, the cassette is rotated gently, and the filter is allowed to dry overnight before use.

Treated filters may be prepared by this procedure up to one week before use.

Determination of the LAQL

Six treated filters were spiked at each of three concentration levels, 2X, 20X, and 200X, where X is the level at which ten percent instrumental precision is attained. The filters were digested and analyzed for arsenic, and the results are presented in Table 16.

The LAQL for arsenic is less than 0.49 µg per filter, which is less than one tenth of the OSHA standard.

Table 13. Collection efficiency for arsenic of base-treated filters.

Na_2CO_3-Glycerol							
Date Generated	Sampling Port	Experiment # (*)	Oven Temp °C	Dilution Flow L/min	Total Flow L/min	Sampling Rate cc/min	µg/filter**
6/24/80	1	Filter #1 Backup Pad #1	150	0.54	8.0	1500	19.88 ± 0.00 0.222 ± 0.003
	7	Filter #1 Backup #1	150	0.54	8.0	1500	10.82 ± 0.49 0.345 ± 0.005
6/25/80	1	Filter #1 Backup #1 Filter #2 Backup #2	150	0.54	8.0	1500	16.55 ± 0.37 1.135 ± 0.048 0.061 ± 0.003 0.063 ± 0.013
	7	Filter #1 Backup #1 Filter #2 Backup #2	150	0.54	8.0	1500	5.399 ± 0.043 0.166 ± 0.009 0.059 ± 0.008 not detected
6/26/80	1	Filter #1 Backup #1 Filter #2 Backup #2	150	0.54	8.0	1500	9.579 ± 0.060 0.524 ± 0.003 0.135 ± 0.000 0.082 ± 0.005
	7	Filter #1 Backup #1 Filter #2 Backup #2	150	0.54	8.0	1500	1.641 ± 0.019 0.052 ± 0.003 0.063 ± 0.005 not detected

The detection limit is 0.06 µg/filter. No arsenic was detected in the treated filter-backup pad pair blank.

*A bubbler with 0.1N NaOH was behind each filter holder. Analysis of these bubblers showed no detectable arsenic levels.

**The LAQL for this system has been determined to be less than 0.49 µg/filter.

(continued)

Table 13. Collection efficiency for arsenic of base-treated filters.

NaOH-Glycerol

Date Generated	Sampling Port	Experiment # (*)	Oven Temp °C	Dilution Flow L/min	Total Flow L/min	Sampling Rate cc/min	µg/filter**
6/30/80	1	Filter #1	150	0.54	8.0	1500	10.21 ± .11
		Backup #1					0.312 ± 0.00
		Filter #2					0.159 ± 0.007
		Backup #2					0.076 ± 0.066
	7	Filter #1	150	0.54	8.0	1500	0.843 ± 0.024
		Backup #1					0.073 ± 0.002
		Filter #2					0.058 ± 0.000
		Backup #2					not detected
7/1/80	1	Filter #1	150	0.54	8.0	1500	4.789 ± 0.067
		Backup #1					0.1313± 0.0056
		Filter #2					not detected
		Backup #2					not detected
	7	Filter #1	150	0.54	8.0	1500	2.757 ± 0.061
		Backup #1					0.1366± 0.0030
		Filter #2					not detected
		Backup #2					not detected

The detection limit is 0.06 µg/filter. No arsenic was found in the treated filter-backup pad pair blank.

*A bubbler with 0.1N NaOH was behind each filter holder. Analysis of these bubblers showed no detectable arsenic levels.

**The LAQL for this system has been determined to be less than 0.49 µg/filter.

(continued)

Table 13. Collection efficiency for arsenic of base-treated filters.

	$(C_4H_9)_4NOH$-Glycerol						
Date Generated	Sampling Port	Experiment # (*)	Oven Temp °C	Dilution Flow L/min	Total Flow L/min	Sampling Rate cc/min	µg/filter**
7/3/80	1	Filter #1	150	0.54	8.0	1500	6.489 ± 0.120
		Backup #1					1.290 ± 0.054
		Filter #2					not detected
		Backup #2					not detected
	7	Filter #1	150	0.54	8.0	1500	3.813 ± 0.054
		Backup #1					0.687 ± 0.008
		Filter #2					not detected
		Backup #2					not detected
7/7/80	1	Filter #1	150	0.54	8.0	1500	11.447 ± 0.08
		Backup #1					4.076 ± 0.063
		Filter #2					not detected
		Backup #2					not detected
	7	Filter #1	150	0.54	8.0	1500	7.482 ± 0.370
		Backup #1					3.062 ± 0.054
		Filter #2					not detected
		Backup #2					not detected

The detection limit is 0.06 µg/filter. No arsenic was found in the treated filter-backup pad pair blank.

*A bubbler with 0.1N NaOH was behind each filter holder. Analysis of these bubblers showed no detectable arsenic levels.

**The LAQL for this system has been determined to be less than 0.49 µg/filter.

Table 14. Percentage recoveries of arsenic from Na_2CO_3-glycerol treated filters.

Date Generated	Sampling Port	Wt. of Arsenic (μg)/% of Total Arsenic				Total Arsenic* Found (μg)
		Filter #1	Backup Pad #1	Filter #2	Backup Pad #2	
6/25	1	16.55 μg 92.9%	1.135 μg 6.4%	0.061 μg 0.3%	0.063 μg 0.4%	17.809 μg
	7	5.399 μg 95.2%	0.166 μg 2.9%	0.059 μg 1.0%	0.050 μg 0.9%	5.674 μg
6/26	1	9.579 μg 92.8%	0.524 μg 5.1%	0.135 μg 1.3%	0.082 μg 0.8%	10.320 μg
	7	1.641 μg 90.9%	0.052 μg 2.9%	0.063 μg 3.5%	0.050 μg 2.8%	1.806 μg

*No arsenic was found in a 0.1 N NaOH bubbler downstream of the cassette.

Table 15. Loading capacity of treated filter-backup pad pairs for arsenic.

Top Filtering Pair		Bottom Filtering Pair	
Filter #	As $\mu g/m^3$ found	Filter #	As $\mu g/m^3$ found
1A	65.2	1B	0.230
2A	68.5	2B	0.291
3A	73.5	3B	0.179
4A	71.7	4B	0.235
5A	68.9	5B	0.311
6A	75.7	6B	0.305
Mean	70.6	Mean	0.258

Table 16. LAQL for arsenic.

As taken µg/filter	As found µg/filter	% Recovery ± SD
0.490 (2X)	0.449	91.7 ± 4.4
4.900 (20X)	5.782	118.0 ± 3.7
49.00 (200X)	55.08	112.4 ± 6.8

Evaluation of the Stability of Loaded Filters

Fourteen treated filter-backup pad pairs were loaded by spiking with As_2O_3. Seven filters were analyzed the next day and seven were analyzed fourteen days later. The results of the study are presented in Table 17. The filters were stable over a fourteen-day period at the 95% confidence level.

Eighteen treated filter-backup pad pairs were loaded with arsenic in the aerosol generation system. During generation the humidity in the system was maintained at 85%. On days one, seven and fourteen, six filters were digested and analyzed for arsenic. The results are presented in Table 18. At the 95% confidence level, the filters were stable over a fourteen-day period.

Evaluation of the Method

The analytical method was evaluated with filter-backup pad pairs spiked with arsenic at three concentration levels, 0.528 µg/filter, 2.62 µg/filter, and 10.50 µg/filter. Each filter pair was analyzed for arsenic and the recoveries and their standard deviations calculated. The results are presented in Table 19. Evaluation of the analytical method was successful; all recoveries and their standard deviations are satisfactory.

The sampling and analytical method was evaluated with filter-backup pad pairs loaded with arsenic in the aerosol generation system. Humidity was maintained at 85% during the course of the experiments. The data are presented in Table 20. All of the measured relative standard deviations are satisfactory.

Filter-backup pad pairs loaded with arsenic were analyzed by neutron activation analysis for comparison. The results of these analyses are presented in Table 21. Two sets of analyses by neutron activation were conducted. In the first set, the NAA data are significantly higher than the AAS, but in the second set they are significantly lower. This does not indicate bias in the method, but rather a problem in the analyses. The data do not satisfy the final criterion for validation.

An attempt to conduct alternate analysis for validation using polarography was unsuccessful because of interference by nitrate ion, present in the residue from digestion of the loaded filters.

SUMMARY AND CONCLUSIONS

A method has been developed and evaluated for the determination of inorganic arsenic in the air of the workplace environment. Samples are collected on a Na_2CO_3-treated 0.8-µm cellulose ester filter-cellulose backup pad pair, digested with nitric acid-hydrogen peroxide, and analyzed by graphite furnace atomic absorption spectrophotometry. This method will appear in the NIOSH manual of analytical methods as P&CAM 346.

Table 17. The stability of treated filter-backup pad pairs spiked with arsenic.

DAY 1				DAY 14			
Filter #	As, µg/filter			Filter #	As, µg/filter		
	Taken	Found	%Recovery		Taken	Found	%Recovery
1	0.587	0.5620	95.7	8	0.587	0.5286	90.1
2	0.587	0.5844	99.6	9	0.587	0.5768	98.3
3	0.587	0.5723	97.5	10	0.587	0.5638	96.0
4	0.587	0.6106	104.0	11	0.587	0.5388	91.8
5	0.587	0.5555	94.6	12	0.587	0.5768	98.3
6	0.587	0.5751	98.0	13	0.587	0.5499	93.7
7	0.587	0.5256	89.5	14	0.587	0.5638	96.0
Mean ± SD		97.0 ± 4.5				94.9 ± 3.2	

Table 18. The stability of generated filter-backup pad pairs containing arsenic.

DAY 1		DAY 7		DAY 14	
Filter #	As, $\mu g/m^3$	Filter #	As, $\mu g/m^3$	Filter #	As, $\mu g/m^3$
1	1.159	7	1.066	13	1.112
2	1.159	8	1.031	14	1.035
3	1.143	9	1.206	15	1.122
4	1.018	10	1.243	16	1.108
5	1.106	11	1.066	17	1.144
6	1.204	12	1.292	18	1.129
Mean ± SD	1.132 ± 0.064		1.151 ± 0.10		1.108 ± 0.038

Table 19. Validation of the arsenic method: spiked filters.

	Filter #	As, µg/filter Taken	Found	%Recovery
LAQL	1	0.528	0.512	97.0
	2	0.528	0.520	98.5
	3	0.528	0.492	93.2
	4	0.528	0.494	93.6
	5	0.528	0.546	103.4
	6	0.528	0.514	97.3
mean ± SD				97.2 ± 3.7
% RSD				3.8
5xLAQL	7	2.62	2.72	103.8
	8	2.62	2.56	97.7
	9	2.62	2.64	100.8
	10	2.62	2.64	100.8
	11	2.62	2.60	99.2
	12	2.62	2.64	100.8
mean ± SD				100.5 ± 2.0
% RSD				2.0
20xLAQL	13	10.50	10.82	103.0
	14	10.50	9.92	94.5
	15	10.50	10.98	104.6
	16	10.50	10.46	99.6
	17	10.50	10.15	96.7
	18	10.50	10.04	95.6
mean ± SD				99.0 ± 4.1
% RSD				4.2

Table 20. Generated filters for the validation of the arsenic method.

	Filter #	As, $\mu g/m^3$		Filter #	As, $\mu g/m^3$		Filter #	As, $\mu g/m^3$
0.06 x OSHA Std.	1	0.6552	OSHA Std.	7	10.990	3 x OSHA Std.	13	33.63
	2	0.6682		8	9.555		14	32.67
	3	0.6803		9	9.471		15	31.44
	4	0.6155		10	10.213		16	32.90
	5	0.7067		11	10.093		17	32.52
	6	0.6943		12	9.847		18	29.78
Mean ± SD		0.6700 ± 0.0323			10.03 ± 0.553			32.16 ± 1.36
% RSD		4.82			5.52			4.24

Table 21. Comparison of AAS and NAA for the analysis of arsenic.

	AAS $\mu g/m^3$	NAA $\mu g/m^3$
Set 1	6.90	
	7.45	
	6.77	
	7.82	
	7.37	
	7.85	
Mean ± S.D.	7.36 ± 0.45	
		9.56
		9.00
		8.08
Mean ± S.D.		8.88 ± 0.75
Set 2	10.99	
	9.56	
	9.47	
	10.21	
	10.09	
	9.85	
Mean ± S.D.	10.03 ± 0.55	
		9.12*
		9.05*
		8.36*
		8.84 ± 0.42

*corrected for difference in standards

NICKEL

The NIOSH proposed standard for inorganic nickel in the workplace environment is 15 $\mu g/m^3$ measured as a time-weighted average for up to a ten-hour work shift in a forty-hour work week (NIOSH, 1977). The method developed, evaluated, and validated for nickel involves the determination of nickel by graphite furnace atomic absorption analysis. NIOSH Method P&CAM 298, Particulate Nickel and Compounds (10), was examined carefully and used in the development of the new method. The experiments performed for the development, evaluation, and validation of a method for determination of inorganic nickel in the workplace environment are described in the following sections. Experimental procedures and results are also described in the Sampling and Analytical Method, Backup Data, and Sampling Data Sheet for this substance.

EXPERIMENTAL

Reagents, laboratory glassware, equipment, and instrumentation which were used throughout this effort were as follows:

Reagents:

1. Nickel Stock, Titrisol Dilut-It
2. Nickel Metal, A.D. MacKay, 99.9% pure
3. Nickel Nitrate, Baker Reagent Grade
4. Copper Stock, Baker Dilut-It
5. Molybdenum Stock, Fisher Reference Standard
6. Iron Stock, Titrisol Dilut-It
7. Calcium Stock, Baker Dilut-It
8. Nitrate Stock, Prepared gravimetrically from reagent grade NH_4NO_3
9. Sulfate Stock, Prepared gravimetrically from reagent grade $(NH_4)_2SO_4$
10. Concentrated $HClO_4$, Baker Ultrapure
11. Concentrated HF, Baker Analytical Reagent Grade
12. Concentrated HNO_3, Baker Analytical Reagent Grade

13. Concentrated HCl, Baker Analytical Reagent Grade

14. National Bureau of Standards, Standard Reference Materials

132b	Tool Steel
672	Nickel Oxide #2
339	Stainless Steel
1648	Urban Particulate
1633a	Coal Fly Ash

Glassware and Equipment:

1. Pipettes, volumetric class A, 1, 2, 3, 4, 5, 6, 8, 10, 15, 20, 25-mL

2. Micropipettes, SMI, 25, 50-µL

3. Flasks, volumetric class A, 10, 25, 50, 100, 250, 1000-mL

4. Beakers, borosilicate glass, 50-mL

5. Beakers, Teflon, 100-mL

6. Filters, Millipore, 0.8-µm cellulose ester, 37-mm diameter

7. Backup pads, Millipore, cellulose, 37-mm diameter

8. Filter cassettes, Millipore, plastic, 37-mm

Instruments

1. Atomic Absorption Spectrophotometer, Perkin-Elmer Model 306 with D_2 background corrector, HGA 2100 graphite furnace, AS-1 autosampler, and nickel hollow cathode lamp

2. Recorder, Linear Instruments Corp., 10mV full scale

3. Aerosol Generating System, described in Appendix A to this report.

Optimization of Instrumental Parameters and Determination of Instrumental Precision

To determine the best set of conditions for the analysis, parameters including char and atomization temperatures and background matrix were examined. Solutions containing 0.005-0.04 µg/mL nickel in 1% HNO_3 and in 1% HCl were prepared. Optimal char and atomization temperatures were determined for the 0.03 µg/mL nickel solution in 1% HCl and in 1% HNO_3. Figure 4 presents the effect of the char temperature on response, and Figure 5 presents the effect of atomization temperature on response.

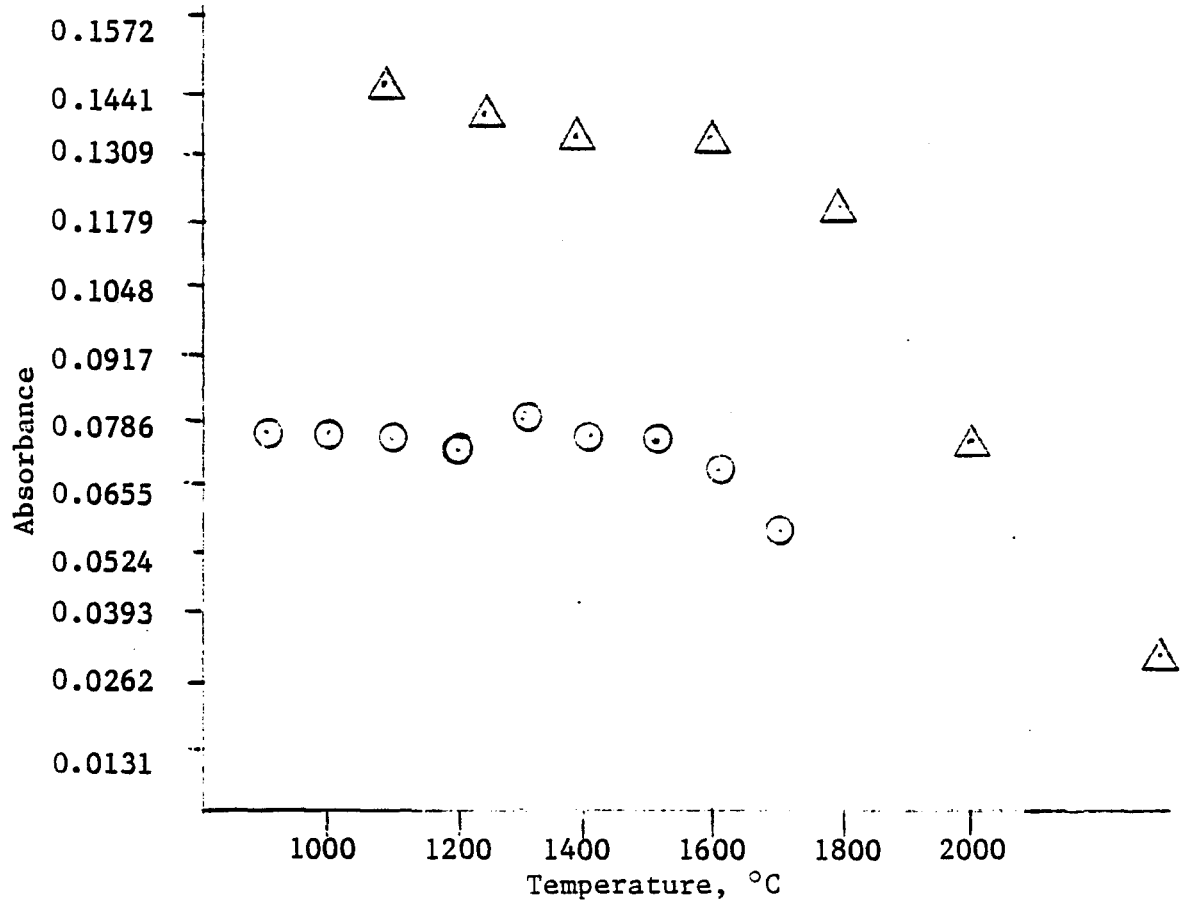

Figure 4. **Instrumental response** of 0.03 μg/mL nickel in 1% HNO_3 as a function of the charring temperature; each point represents the average of three measurements.

drying = 150 °C (50 sec)
atomization = 2700 °C (10 sec)

▲ 1% HCl matrix

● 1% HNO_3 matrix

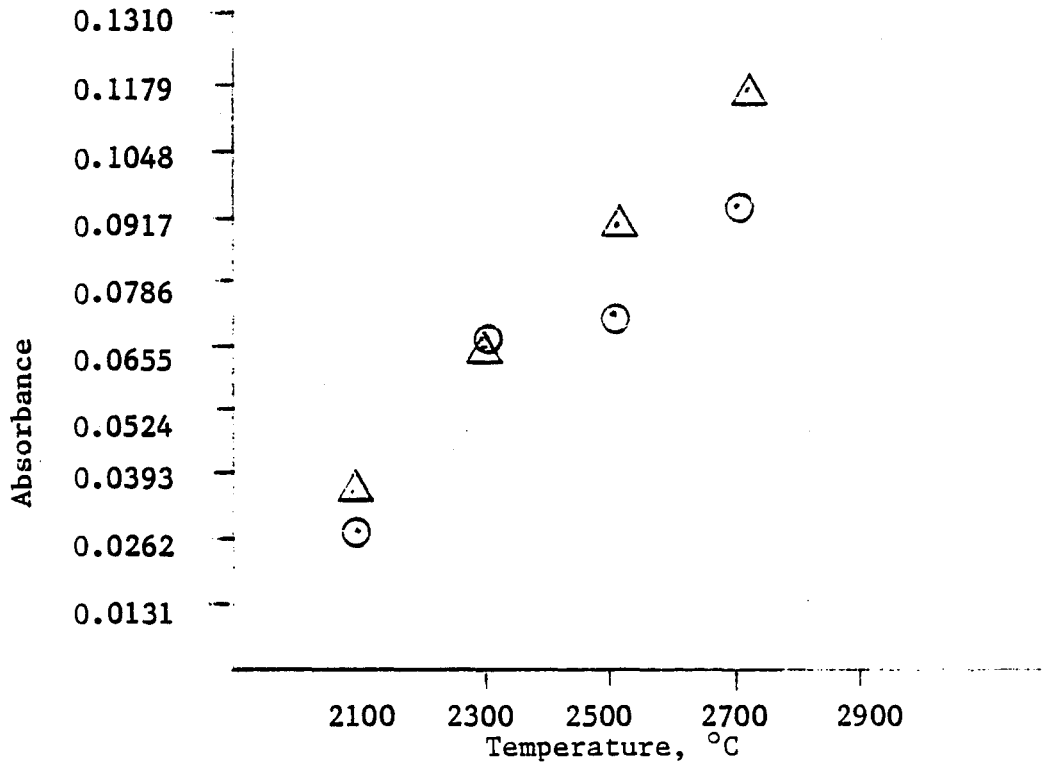

Figure 5. Instrumental response of 0.03 µg/mL Nickel in 1% HNO_3 as a function of atomization temperature.

drying = 150 °C (50 sec)

charring = 1300 °C (10 sec)

▲ 1% HCl

● 1% HNO_3

The optimal charring temperature is taken to be the highest temperature which can be used without loss of signal intensity. In both the 1% HCl and 1% HNO_3 matrices, the optimal charring temperature is 1300 °C. The optimal atomization temperature, too, is taken to be the highest temperature which can be used without loss of signal intensity. In both acid matrices, the optimal atomization temperature is 2700 °C.

Next, to determine the preferred matrix, the instrumental response to nickel solutions in the concentration range 0.005–0.04 µg/mL was measured in both acid matrices under the optimized conditions. The results are presented in Figure 6. In 1% HCl, both the instrumental response and the linear range are greater, making 1% HCl the preferred matrix.

Optimized instrumental conditions for the analysis of nickel using a Perkin-Elmer 306 were:

Wavelength	232.0 nm
Slit width	3 (0.2 nm)
Scale expansion	3x
Argon flow setting	30
Drying	150 °C (50 sec)
Charring	1300 °C (10 sec)
Atomization	2700 °C (10 sec)
Injection volume	10, 50 µL
Sample matrix	1% HCl

Finally, instrumental precision was examined, and the data are presented in Table 22. The level, X, at which 10% precision is attained, is approximately 0.002 µg/mL.

Evaluation of Interferences

Solutions containing nickel at a concentration of 0.020 µg/mL in 1% HCl and interference concentrations of 0.020 µg/mL (1x), 0.20 µg/mL (10x), 1.00 µg/mL (50x), and 4.00 µg/mL (200x) were prepared and analyzed. Interferences examined were nitrate, sulfate, copper, iron, molybdenum, and calcium (11). The results are presented in Table 23. Iron is the only species which interferes with the analysis of nickel and this interference becomes significant when the concentration of iron is about 100 times that of nickel.

Several sets of experiments were conducted to investigate and minimize the interference of iron.

1. Effect of Char Time on the Interference of Iron in Nickel Analysis.

Char times of 10 sec (standard), 60 sec, and 120 sec were used in an effort to remove iron as the volatile $FeCl_3$. Decrease in interferences by iron was not eliminated with increased char time, as is demonstrated in Table 24.

2. Analysis of NBS 1648 (Urban Particulate) and NBS 1633a (Coal Fly Ash) for Nickel; Matrix Modification

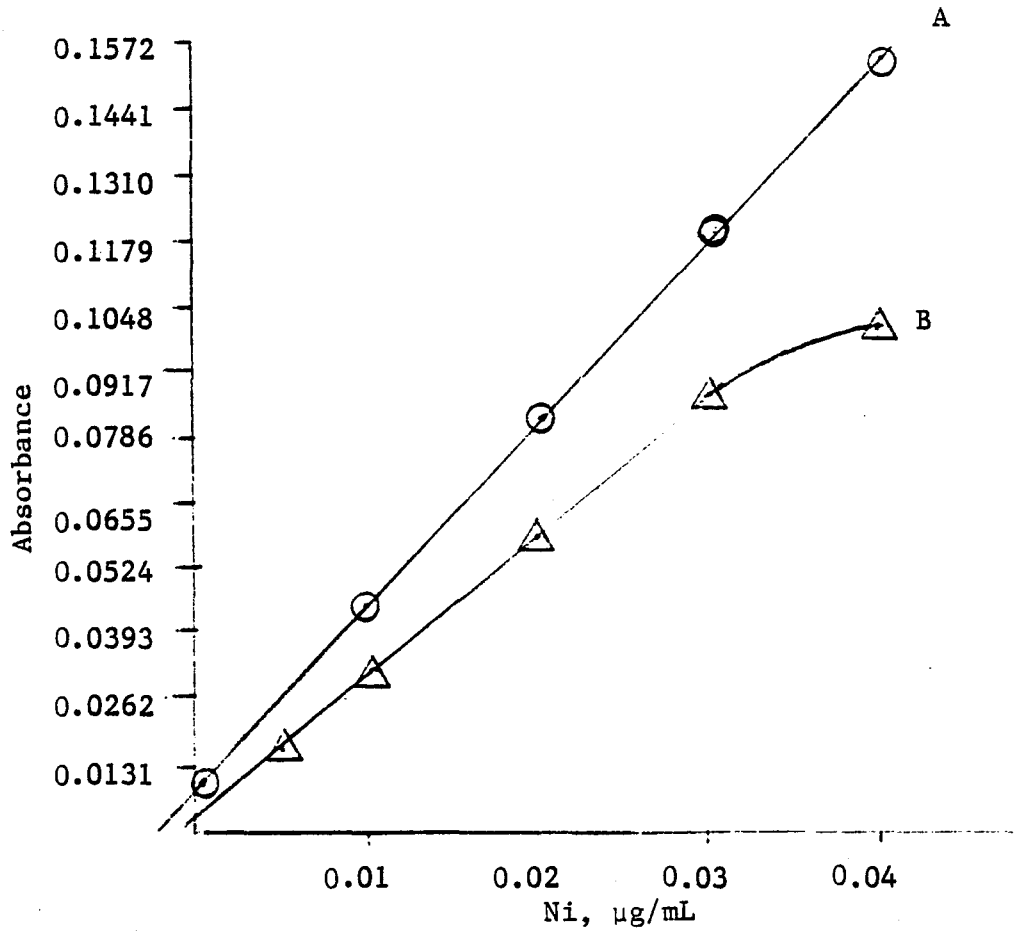

Figure 6. Instrumental response as a function of concentration of Nickel in two acid matrices.

drying = 150 °C (50 sec)
charring = 1300 °C (10 sec)
atomization = 2700 °C (10 sec)

A. Standard solutions in 1%HCl
B. Standard solutions in 1%HNO_3

Table 22. Instrumental precision for the analysis of nickel in 1% HCl.

Ni Taken (µg/mL)	Ni found (µg/mL)					Mean ± SD	% RSD
	1	2	3	4	5		
0.04	0.03669	0.0377	0.0387	0.0394	0.0400	0.0385 ± 0.0013	3.4
0.03	0.02923	0.0297	0.0304	0.0311	0.0317	0.0304 ± 0.0010	3.3
0.02	0.02045	0.0205	0.0215	0.0219	0.0221	0.0213 ± 0.0008	3.8
0.01	0.01120	0.0113	0.0112	0.0118	0.0119	0.0115 ± 0.0003	2.6
0.005	0.00668	0.0058	0.0060	0.0071	0.0061	0.0063 ± 0.0005	8.5
0.002	0.00295	0.0028	0.0035	0.0030	0.0028	0.0030 ± 0.0003	9.6

intercept: 0.0007053

slope: 0.002742

error: 0.003450

coefficient of correlation: 0.966

1% HCl final matrix

50 sec dry 150 °C

10 sec char 1300 °C

10 sec atomize 2700 °C

Table 23. Interferences in the analysis of nickel.

Species Studied	Conc. level in μg/mL	Concentrations of Ni in μg/mL		% Recovery ± SD
		Taken	Found ± SD	
NO_3^-	0.020	0.02038	0.02190 ±0.0005	107.5 ± 2.3
	0.20	0.02038	0.02066 ±0.0009	101.4 ± 4.4
	1.00	0.02038	0.01948 ±0.0004	95.6 ± 2.0
	4.00	0.02038	0.02018 ±0.0009	99.0 ± 4.5
SO_4^{-2}	0.020	0.02038	0.01966 ±0.0011	96.5 ± 5.6
	0.200	0.02038	0.01853 ±0.0017	90.9 ± 9.2
	1.00	0.02038	0.01800 ±0.0022	88.3 ±12.2
	4.00	0.02038	0.02042 ±0.0002	100.2 ± 1.0
Cu^{+2}	0.020	0.01653	0.01661 ±0.0003	99.8 ± 1.8
	0.200	0.01653	0.01635 ±0.0005	98.2 ± 3.1
	1.00	0.01653	0.01637 ±0.0001	98.3 ± 0.6
	4.00	0.01653	0.01606 ±0.0000	96.5 ± 0.0
Fe	0.020	0.01780	0.01843 ±0.0001	103.5 ± 0.5
	0.200	0.01780	0.01832 ±0.0002	102.9 ± 1.1
	1.00	0.01780	0.01886 ±0.0007	105.0 ± 3.7
	2.00	0.01780	0.02028 ±0.0003	113.9 ± 1.5
	4.00	0.01780	0.02084 ±0.0002	117.1 ± 1.0
Mo	0.020	0.01950	0.01868 ±0.0001	95.8 ± 0.5
	0.200	0.01950	0.01860 ±0.0002	95.4 ± 1.0
	1.00	0.01950	0.01973 ±0.0008	101.2 ± 4.1
	4.00	0.01950	0.02021 ±0.0005	103.6 ± 2.3
Ca	0.020	0.01778	0.01746 ±0.0003	98.2 ± 1.7
	0.200	0.01778	0.01738 ±0.0001	97.8 ± 0.6
	1.00	0.01778	0.01738 ±0.0003	100.0 ± 1.7
	4.00	0.01778	0.01738 ±0.0001	97.8 ± 0.6

Table 24. Interference of 4.0 μg/mL iron in the analysis of nickel as a function of char time and concentration of nickel.

Time of Char	Concentration of Ni in μg/mL		% Recovery ± SD
	Taken	Found ± SD	
120 sec	0.0200	0.0228 ± 0.0003	114.0 ± 1.3
60 sec	0.0200	0.0228 ± 0.0002	114.0 ± 0.7
10 sec	0.0178	0.0208 ± 0.0002	117.1 ± 1.0

Solutions of NBS Urban Particulate and Coal Fly Ash samples were prepared and analyzed for nickel. Both showed significant positive interferences, which were attributed to the large concentrations of iron present in both. The NBS Certificate of Analysis for NBS SRM 1633a (coal fly ash) gives values of 9.40% for iron and 127 ± 4 µg/gm for nickel, while the Certificate for SRM 1648 gives values of 3.91% for iron and 82 ± 3 µg/gm for nickel. In both cases, the iron to nickel ratio is high, well within the demonstrated range of interference by iron in nickel analysis. To match the standard matrix to the sample matrix, standard solutions containing 250 µg/mL iron for SRM 1633A and 400 µg/mL iron for SRM 1648 were prepared (12,13). Samples were analyzed against the modified standard curves and the results are presented in Table 25. The data indicate that it is possible to decrease the positive interference from iron by matrix matching. In these cases the recoveries are low when an iron-containing calibration curve is used. The low readings observed reflect negative interference, and its cause is not known. When iron is known or suspected to exist at large excess concentration in a sample being analyzed for nickel, the recommended procedure is to measure the iron concentration first. Then standard solutions for nickel are prepared which contain the same iron concentrations as the samples, and the samples are analyzed against the matched calibration standards.

One important observation is that the ratio of iron to nickel when both are present at the NIOSH recommended standard is approximately 60:1. At this ratio, there is only slight positive interference by iron in nickel analysis, as was demonstrated by the data in Table 23.

Optimization of Digestion Variables

Three acid combinations for the digestion of nickel compounds were examined (13-18); in each case NBS SRMs 1326 (tool steel) and 339 (stainless steel) were examined along with other nickel compounds. The procedures examined were as follows:

1. HNO_3-$HClO_4$-HF. To each Teflon beaker containing sample and filter, 5 mL of 70% HNO_3 was added. The beaker was covered with a Teflon watchglass and placed on a hotplate (110-140 °C) for 4 hours. The volume was reduced to about 1 mL, and 2 mL 70% HNO_3, 1 mL 60% $HClO_4$, and 5 drops 50% HF were added. The beaker was covered with a watchglass and heated on a 400 °C hotplate until dense fumes of $HClO_4$ persisted. The watchglass and the sides of the beaker were washed with distilled water and the solution taken to dryness. When cool, the residue was taken up with 25 mL of 1% HCl. Finally, the beaker was covered with Parafilm and the solution extracted ultrasonically for 30 minutes.

2. HNO_3-HCl. To each Teflon beaker containing sample and filter, 6 mL concentrated HNO_3 and 2 mL concentrated HCl were added; the beaker was covered with a watchglass and placed on a hotplate at 140 °C. The volume was reduced to approximately 1 mL. The watchglass was rinsed with deionized water and removed. The beaker was placed on a steam bath and allowed to go to dryness. Twenty-five mL of 1% HCl was pipetted into the beaker; it was covered with Parafilm and

Table 25. Determination of nickel in NBS SRMs.

Material	Amount of Iron Added to Standards	Weight of Material (gm) Dissolved in 25 ml	Amount (μg) of Nickel in the Material		% Recovery ± SD
			Taken	Found	
NBS SRM 1633A (coal fly ash)	0	0.2515	31.9405	43.70	134.4% ± 2.1%
		0.2505	31.7754	42.39	
		0.2541	32.2707	42.94	
NBS SRM 1648 (urban particulate)	0	0.1041	8.5362	9.64	111.7% ± 1.4%
		0.1022	9.3804	9.24	
		0.1031	8.4542	9.48	
NBS SRM 1633A (coal fly ash)	250 μg/mL	0.2515	31.9405	28.53±0.658	89.66% ± 0.47%
		*			
		0.2541	32.2707	29.04±0.795	
NBS SRM 1648 (urban particulate)	400 μg/mL	0.1041	8.5362	6.270±0.066	78.03% ± 5.25%
		0.1022	8.3804	6.444±0.286	
		0.1031	8.4542	7.081±0.329	

After digestion, all extracts were diluted to 10.0 mL with 1% HCl. The resulting solutions were analyzed against a series of standards ranging from 0.1 to 0.8 μg/mL.

* Solution spilled.

ultrasonically agitated for 30 minutes.

3. HNO_3-HF. To each Teflon beaker containing sample and filter, 10 mL of concentrated HNO_3 was added and the volume reduced on a hotplate to 1 mL. Eight mL of a 3:1 mixture of concentrated HF and HNO_3 was added. The beaker was placed on a 140 °C hotplate and allowed to go barely to dryness. Into the dry beaker was pipetted 10 mL of 1% HCl; the solution was covered with Parafilm and ultrasonically agitated for 30 minutes.

All of the solutions were analyzed under the optimized analytical conditions and the results are presented in Table 26. With the HNO_3-$HClO_4$-HF digestion, poor recoveries are observed for both tool steel and stainless steel, and with the HNO_3-HCl digestion, poor recovery is observed for tool steel and poor precision for stainless steel. With the HNO_3-HF digestion, percentage recoveries are good except for tool steel, which is high. Interference studies have shown that iron is a positive interference in nickel analysis, which exceeds 10% if the ratio of Fe:Ni exceeds 100:1. The NBS SRM Certificate of Analysis for 1326 gives a certified value for Ni of 0.230% by weight. Although no value is given for Fe, it is assumed to be at least 90%, well above the 100:1 ratio where major interference can be expected. Based upon this study, the HNO_3-HF digestion procedure is best for the analysis of nickel, and matrix matching techniques should be employed when large concentrations of iron are present.

The final digestion procedure is as follows:

The exposed filter is placed in a Teflon beaker and 10 mL 70% HNO_3 is added. The beaker is covered with a watchglass and allowed to sit on a hotplate at 150 °C for four hours or until the volume has been reduced to 1 mL. The watchglass is rinsed with deionized water into the beaker, and 4 mL 1:3 70% HNO_3-50% HF is added. The solution is taken to dryness on a steam bath, then allowed to cool, and the residue is taken up with 10.0 mL 1% HCl. After sonification for 30 minutes, the solution is ready for analysis.

Determination of Collection Efficiency

Four plastic cassettes, each containing one 0.8-µm pore size cellulose ester filter with backup pad, and four cassettes each containing two filters with backup pads, were placed in the aerosol generation system and loaded with nickel aerosol. After generation, filters and backup pads were removed and analyzed for nickel. The results are presented in Table 27.

No breakthrough occurred to the first backup pad or to the second filter. Flowrate did not decrease significantly during the loading.

Determination of the LAQL

Six filters were spiked at each of four concentration levels, approximately 2X, 7X, 20X, and 200X, where X is the level at which ten percent instrumental precision is attained. The filters were digested and analyzed for nickel.

Table 26. Determination of nickel using different digestion procedures.

Material	Weight of Material (gm) Dissolved in 25 mL	Amoung (gm) of Nickel in the Material		% Recovery ± SD
		Taken	Found	
HNO_3-$HClO_4$-HF Digestion				
NBS, SRM	0.1761	0.0004050	0.0001262	31.9 ± 0.7
1326	0.0879	0.0002022	0.0000659	
(Tool Steel)	0.0654	0.0001504	0.0000480	
NBS, SRM	0.1472	0.013086	0.0015815	32.0 ± 45.0
339	0.1097	0.009752	0.0008168	
(Stainless	0.0872	0.007752	0.0000160	
Steel)				
HNO_3-HCl Digestion				
NBS, SRM	0.1377	0.0003167	0.0001217	40.3 ± 6.7
1326	0.0903	0.0002077	0.0000992	
(Tool Steel)	0.1102	0.0002535	0.0000883	
NBS, SRM	0.2146	0.019078	0.016438	96.5 ± 10.7
339	0.0905	0.008046	0.007698	
(Stainless	0.0661	0.005876	0.006320	
Steel)				
HNO_3-HF Digestion				
Ni Metal	0.1002	0.1002	0.0966	98.6 ± 2.7
	0.1091	0.1091	0.1067	
	0.1066	0.1066	0.1083	
NBS, SRM	0.1016	0.0002337	0.0002972	123.6 ± 3.2
1326	0.0995	0.0002209	0.0002708	
(Tool Steel)	0.1021	0.0002348	0.0002842	
NBS, SRM	0.0983	0.008739	0.009250	104.5 ± 2.3
339	0.1154	0.010259	0.010858	
(Stainless	0.1091	0.009699	0.009878	
Steel)				
NBS, SRM	0.1054	0.08126	0.07972	97.3 ± 1.2
672	0.1021	0.07872	0.07706	
(Nickel	0.1232	0.09506	0.09125	
Oxide #2)				

Table 27. Collection efficiency for nickel.

	Ni, $\mu g/m^3$ found		
Cassette	Top Filter	Top Backup Pad	Second Filter
A	7.465	0	
B	7.435	0	
C	6.839	0	
D	7.805	0	
E	7.808	0	0
F	7.161	0	0
G	7.765	0	0
H	7.627	0	0

The results are presented in Table 28.

The LAQL for nickel is approximately 0.15 µg Ni per filter, less than one tenth of the NIOSH recommended standard.

Evaluation of the Stabilty of Loaded Filters

Sixteen filters were loaded with nickel by spiking with 25 µL of 6.0 µg/mL $Ni(NO_3)_2$ stock. Eight filters were analyzed the next day and eight were analyzed fourteen days later. The results of the study are presented in Table 29. The filters were stable over a fourteen day period at the 95% confidence level.

Eighteen filters were loaded with nickel in the aerosol generation system. During generation the humidity in the system was maintained at 85%. On days one, seven and fourteen, six filters at a time were digested and analyzed for nickel. The results are presented in Table 30. At the 95% confidence level, the filters were stable over a fourteen-day period.

Validation of the Method

The analytical method was validated with filters spiked with nickel at three concentration levels, 0.16 µg/filter, 0.80 µg/filter, and 3.20 µg/filter. Each filter was analyzed for nickel and the recoveries and their standard deviations calculated. The results are presented in Table 31. Validation of the analytical method was successful; all recoveries and their standard deviations are satisfactory.

The sampling and analytical method was validated with filters loaded with nickel in the aerosol generation system. Humidity was maintained at 85% during the course of the experiments. The data are presented in Table 32. All of the measured relative standard deviations are satisfactory for validation.

Filters loaded with nickel were analyzed by neutron activation analysis for comparison. The results of these analyses are presented in Table 33. At the 95% confidence level, the results are the same as those obtained by atomic absorption analysis, completing the validation successfully.

SUMMARY AND CONCLUSIONS

A method has been developed, evaluated and validated for the determination of inorganic nickel in the air of the workplace environment. Samples are collected on a 0.8-µm cellulose ester filter, digested with nitric-hydrofluoric acid, and analyzed by graphite furnace atomic absorption spectrophotometry. This method will appear in the NIOSH Manual of Analytical Methods as P&CAM 298 (revised).

Table 28. LAQL for nickel.

Ni taken µg/filter	Ni found* ± SD µg/filter	% Recovery ± SD
0.0375 (2x)	0.00542 ± 0.0029	144.5 ± 53.5
0.125 (7x)	0.139 ± 0.002	111.0 ± 11.6
0.375 (20x)	0.390 ± 0.002	104.1 ± 5.1
3.75 (200x)	3.918 ± 0.012	104.5 ± 3.1

*Six filters were prepared and analyzed at each level.

Table 29. The stability of filters spiked with nickel.

	DAY 1 Ni, μg/filter			DAY 14 Ni, μg/filter			
Filter #	Taken	Found	% Recovery	Filter #	Taken	Found	% Recovery
1	0.150	0.1624	108.3	9	0.150	0.1262	84.1
2	0.150	0.1340	89.3	10	0.150	0.1372	91.5
3	0.150	0.1422	94.8	11	0.150	0.1615	107.7
4	0.150	0.1655	110.3	12	0.150	0.1478	98.5
5	0.150	0.1477	98.5	13	0.150	0.1645	109.7
6	0.150	0.1568	104.5	14	0.150	0.1501	100.1
7	0.150	0.1584	105.6	15	0.150	0.1364	90.9
8	0.150	0.1289	85.9	16	0.150	0.1376	91.7
Mean ± SD		99.7 ± 009.0				96.8 ± 8.9	
%RSD		9.0				9.2	

Table 30. The stability of generated filters containing nickel.

DAY 1		DAY 7		DAY 14	
Filter #	Ni, $\mu g/m^3$	Filter #	Ni, $\mu g/m^3$	Filter #	Ni, $\mu g/m^3$
1	0.5199	7	0.6815	13	0.5972
2	0.6001	8	0.5609	14	0.5671
3	0.6020	9	0.5472	15	0.5632
4	0.6202	10	0.5943	16	0.5463
5	0.5096	11	0.5618	17	0.5317
6	0.5938	12	0.6789	18	0.5793
Mean ± SD	0.5743 ± 0.0470		0.6041 ± 0.0610		0.5641 ± 0.0233

Table 31. Validation of the nickel method: spiked filters.

	Ni, µg/filter		
Filter	Taken	Found	% Recovery
1	3.20	3.39	105.9
2	3.20	3.31	103.4
3	3.20	3.28	102.5
4	3.20	3.36	105.0
5	3.20	3.23	100.9
6	3.20	2.99	93.4
mean ± SD			101.9 ± 4.5
% RSD			4.4
7	0.795	0.820	103.1
8	0.795	0.786	98.9
9	0.795	0.792	99.6
10	0.795	0.783	98.5
11	0.795	0.792	99.6
12	0.795	0.778	97.9
mean ± SD			99.6 ± 1.8
% RSD			1.8
13	0.1627	0.1547	95.1
14	0.1627	0.1518	93.3
15	0.1627	0.1796	110.4
16	0.1627	0.1576	96.9
17	0.1627	0.1663	102.2
18	0.1627	0.1374	84.4
mean ± SD			9.70 ± 8.7
% RSD			9.0

Table 32. Generated filters for the validation of the nickel method.

	Filter #	Ni $\mu g/m^3$		Filter #	Ni $\mu g/m^3$		Filter #	Ni $\mu g/m^3$
	1	0.5199		7	1.940		13	30.34
0.04 x NIOSH	2	0.6001	0.125 x	8	1.923	2 x NIOSH	14	30.24
Std.	3	0.6020	NIOSH Std.	9	1.795	Std.	15	30.55
	4	0.6202		10	1.874		16	31.94
	5	0.5096		11	1.826		17	30.38
	6	0.5938		12	1.893		18	30.81
mean ± SD		0.5743 ± 0.0470			1.875 ± 0.056			30.71 ± 0.063
% RSD		8.19			2.98			2.07

Table 33. Comparison of AAS and NAA for the analysis of nickel.

Filter #	AAS $\mu g/m^3$	NAA $\mu g/m^3$
1	1.940	
2	1.923	
3	1.795	
4	1.874	
5	1.826	
6	1.893	
mean ± SD	1.875 ± 0.056	
20		1.802
21		1.951
22		1.843
mean ± SD		1.865 ± 0.077

TUNGSTEN

Two NIOSH recommended standards exist for tungsten in the workplace environment; the first, for soluble tungsten compounds, is 1 mg/m^3 measured as a time-weighted average for up to a ten-hour work shift in a forty-hour work week, and the second, for insoluble compounds, is 5 mg/m^3 for the same kind of sample. The method developed, evaluated, and validated for tungsten involves the separation of soluble and insoluble tungsten and their independent determination by flame atomic absorption spectrophotometry (19-21). NIOSH Method P&CAM 271, Particulate Tungsten and Compounds (22), was examined carefully and used as a starting point in the development of the new and more general method. The development, evaluation, and validation of a method for determination of soluble and insoluble tungsten in the workplace environment are described in the following sections. Experimental procedures and results are also described in the Sampling and Analytical Method, Backup Data, and Sampling Data Sheet for this substance.

EXPERIMENTAL

Reagents, laboratory glassware, equipment, and instrumentation which were used throughout this effort were as follows:

Reagents:

1. Tungsten Metal, Cerac, 99.9% pure
2. Tungsten Carbide, Cerac, 99% pure
3. Tungsten Trioxide, Cerac, 99.9% pure
4. Sodium Tungstate, Banco 1000 ppm standard
5. Copper Tungstate, Cerac, 99.9% pure
6. Cadmium Tungstate, Cerac, 99.9% pure
7. Tungsten Carbide-Cobalt, Cerac, 99% pure, containing 6% Cobalt
8. Tungsten Stock, 10000 ppm, prepared gravimetrically from reagent grade Na_2WO_4 and diluted with 1% NaOH
9. Iron Stock, prepared gravimetrically from purified grade Fe
10. Chromium Stock, Titrisol Dilut-it

11. Manganese Stock, Baker Dilut-it

12. Cobalt Stock, prepared gravimetrically from purified grade Co

13. Molybdenum Stock, prepared gravimetrically from $(NH_4)_6 Mo_7O_{24}$

14. Vanadium Stock, prepared gravimetrically from VCl_2

15. Graphite, Sargent technical grade

16. Concentrated HNO_3, Baker Analytical Reagent Grade

17. Concentrated HF, Baker Analytical Reagent Grade

18. Concentrated HCl, Baker Analytical Reagent Grade

19. Sodium Hydroxide, Baker Reagent Grade

20. Sodium Sulfate, Baker Reagent Grade

Glassware and Equipment:

1. Repipet, 10-mL

2. Pipettes, volumetric class A, 1, 2, 3, 4, 5, 6, 8, 10, 15, 20, 25-mL

3. Flasks, volumetric class A, 10, 25, 50, 100, 250, 1000-mL

4. Beakers, borosilicate glass, 50-mL

5. Beakers, Teflon, 100-mL

6. Filters, Millipore, 0.8- m cellulose ester, 37-mm diameter, 0.45-μm cellulose ester, 47-mm diameter

7. Backup pads, Millipore, cellulose, 37-mm diameter

8. Filter cassettes, Millipore, plastic 37-mm

9. Filtering apparatus, Millipore, funnel, clamp, frit and holder, bell jar and baseplate.

Instruments:

1. Atomic absorption spectrophotometer, Perkin-Elmer Model 372 with tungsten hollow cathode lamp and these settings:

wavelength	255.1 nm
slit	0.7 nm
flame	nitrous oxide - acetylene

2. Recorder, Datamark SR 6253 Servocorder, 10-mV scale

3. Aerosol generating system, described in Appendix A to this report.

Optimization of Instrumental Conditions

Instrumental variables including flame position, fuel flow, and wavelength were examined carefully and optimized to obtain the maximum signal for a working solution containing 1000 ppm W in 2% Na_2SO_4 and 1% NaOH (23). Figure 7 illustrates the instrumental response to the working standard at various wavelengths; based upon these results it was decided to examine 294.4 nm and 255.1 nm further. A series of standard solutions was prepared from a stock standard and determined by flame AAS at each of these wavelengths; the data are presented in Tables 34 and 35. Based upon these experiments, 255.1 nm shows better precision characteristics and for this reason it was the wavelength chosen for analysis.

Evaluation of Interferences

Solutions containing 50 µg/mL tungsten and interference concentrations of 50 µg/mL (1x), 500 µg/mL (10x), and 2500 µg/mL (50x) were prepared in 2% Na_2SO_4 and 1% NaOH and analyzed. Interferences examined were nickel, molybdenum, manganese, chromium, cobalt, and iron. The results are presented in Table 36. Of the species investigated, only iron interfered with the analysis of tungsten at the concentrations examined.

Development of Extraction and Digestion Procedures

The P&CAM 271 procedure was examined first, and consisted of a water extraction for soluble tungsten species, a dilute HCl extraction for interfering metals, and a HNO_3-HF digestion for insoluble tungsten species. The obtained recoveries from the analysis of spiked samples were acceptable for soluble species both in the presence or absence of insoluble tungsten, but not satisfactory for insoluble tungsten species (Table 37).

The following modified procedure was developed to improve analytical recoveries. (24-25). The exposed filter sample is placed on a 47-mm, 0.45-µm pore size cellulose ester filter in a Millipore filtering apparatus; 3.0 mL water is added and allowed to stand on the filter for three minutes, before suction filtration. Another 3 mL water is added and the filtration step is repeated. The filtrate is then transferred to a 10-mL volumetric flask; 1.0 mL 20% Na_2SO_4 is added and the solution is diluted to volume with distilled water. The resulting solution is analyzed for soluble tungsten. The residue and filters are digested in a Teflon beaker with 10 mL 1:1 HF-HNO_3. The volume is reduced to about 2 mL on a hotplate at 150 °C and then reduced to dryness on a steam bath. The residue is then extracted with only manual agitation with 10 mL cold 1% HCl; the solution is filtered through a 47-mm cellulose ester filter in a Millipore apparatus and the filtrate set aside for cobalt analysis. The filter and residue are ashed in a Teflon beaker with 10 mL 1:1 HNO_3-HF and the solution is taken to 1 mL on a

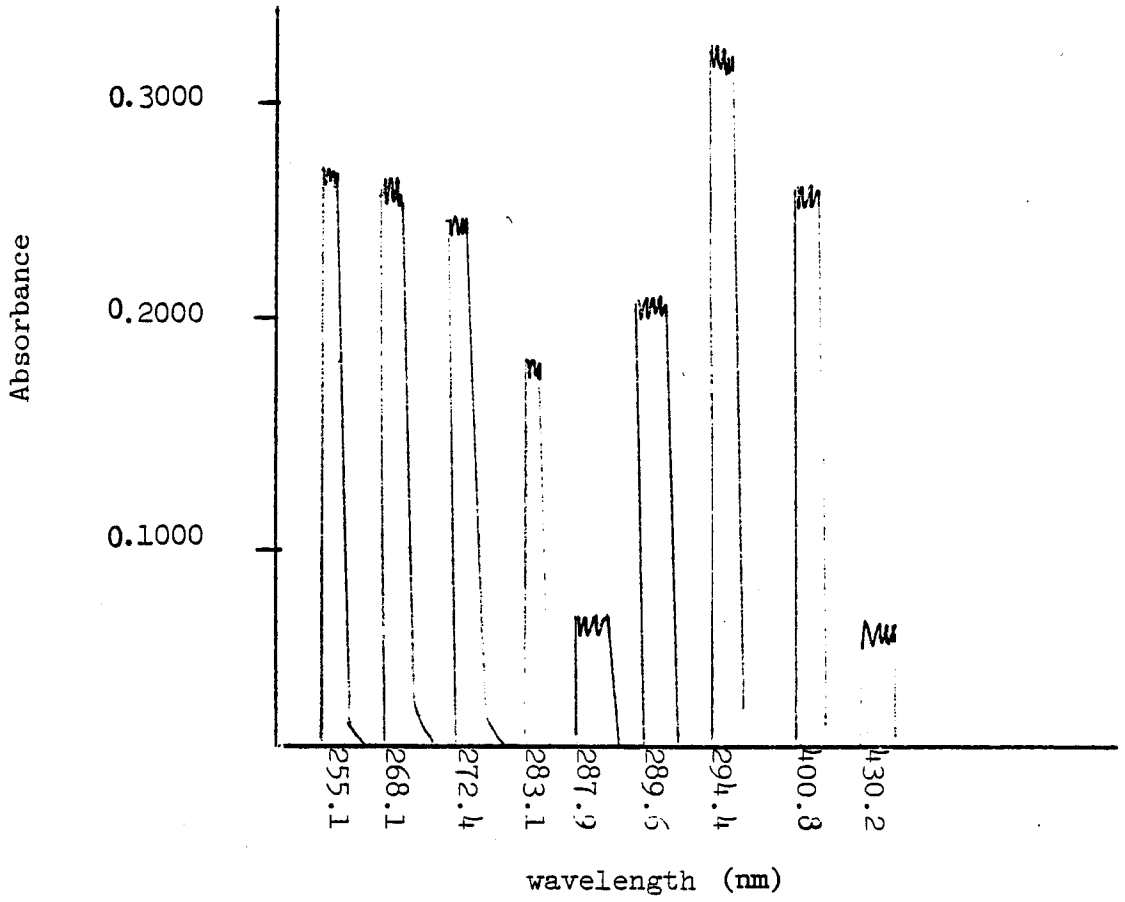

Figure 7. AA Response at different wavelengths for a 1000 ppm W + 2% Na_2SO_4 standard solution. Slit = 0.7 nm.

Table 34. **Instrumental precision for the analysis of tungsten at 255.1 nm.**

	Found (µg/mL)						
Taken (µg/mL)	1	2	3	4	5	**Mean ± SD**	% RSD
100	100.07	100.47	98.04	100.07	100.47	99.82 ± 1.017	1.02
50	49.75	51.78	50.56	48.53	50.56	50.24 ± 1.198	2.38
10	9.99	9.99	11.20	11.20	9.99	10.47 ± 0.663	6.33
5	5.12	5.93	3.49	4.31	3.49	4.47 ± 1.061	23.75
1*	---	---	---	---	---		

* Unable to distinguish from background noise.

Intercept -4.622

Slope 8.115

Coefficient of correlation 0.999

Table 35. **Instrumental precision for the analysis of tungsten at 294.4 nm.**

	Found (µg/mL)						
Taken (µg/mL)	1	2	3	4	5	Mean ± SD	%RSD
200	195.29	199.99	195.29	202.82	205.64	199.81 ± 4.58	2.29
100	99.32	99.32	98.38	101.21	102.15	100.08 ± 1.55	1.55
50	49.46	49.93	48.52	49.46	53.22	50.12 ± 1.81	3.61
10	12.30	9.47	8.06	10.89	9.95	10.13 ± 1.58	15.60
5	2.89	6.18	4.77	5.24	5.24	4.87 ± 1.22	25.06
1*	---	---	---	---	---		

* Unable to distinguish from background noise.

Intercept -2.285

Slope 9.408

Coefficient of correlation 0.999

Table 36. Interferences in the analysis of tungsten.

Species Studied	Conc. level in µg/mL	Concentration of W in µg/mL		
		Taken	Found*	% Recovery ± SD
Ni	50	50.0	49.317 ± 0.704	98.63 ± 1.4
	500	50.0	49.079 ± 1.505	98.16 ± 3.1
	2500	50.0	48.160 ± 1.109	96.32 ± 2.3
Mo	50	50.0	49.545 ± 1.100	99.09 ± 2.2
	500	50.0	49.317 ± 0.993	98.63 ± 2.0
	2500	50.0	50.010 ± 1.050	100.02 ± 2.1
V	50	50.0	50.80 ± 0.757	101.60 ± 1.49
	500	50.0	50.24 ± 0.895	100.48 ± 1.78
	2500	50.0	51.27 ± 0.668	102.54 ± 1.30
Mn	50	50.0	49.61 ± 1.589	99.22 ± 3.20
	500	50.0	50.80 ± 0.516	101.60 ± 1.02
	2500	50.0	50.80 ± 0.428	101.16 ± 0.85
Cr	50	50.0	48.11 ± 1.164	96.22 ± 2.42
	500	50.0	50.49 ± 0.983	100.98 ± 1.95
	2500	50.0	49.83 ± 0.497	99.66 ± 1.00
Co	50	50.0	50.31 ± 0.808	100.62 ± 1.61
	500	50.0	49.27 ± 1.880	98.54 ± 3.82
	2500	50.0	51.18 ± 0.937	102.36 ± 1.83

(Continued)

Table 36. Interferences in the analysis of tungsten.

Species Studied	Conc. level in µg/mL	Concentration of W in µg/mL		
		Taken	Found	% Recovery ± SD
Fe	50**	50.0	-	-
	500	50.0	48.91 ± 0.808	97.82 ± 1.65
	2500	50.0	47.80 ± 0.874	95.60 ± 1.83

* All solutions were measured in triplicate.

** Precipitate was visible in solution. In the case of iron, pH is critical. At pH = 2.5, $Fe(OH)_3$ precipitates, at pH = 1.4, H_2WO_4 precipitates.

Table 37. Recoveries of tungsten using P&CAM 271 Method.

Soluble, Na_2WO_4

Filter	W, µg taken	W, µg found	% Recovery
A	250	251.3	100.5
B	250	260.6	104.2
C	250	260.6	104.2
D	250	232.7	93.1
E	250	242.0	96.8
F	250	260.0	104.0
mean ± SD			100.5 ± 4.6

Insoluble, WC-Co

Filter	W, µg taken	W, µg found in HCl	W, µg found in HNO_3-HF	W, µg found total	% Recovery
A	6260	0	4460	4460	71.2
B	14560	36	12100	12140	83.4
C	11290	179	9610	9790	86.7
D	20910	143	17010	17150	82.0
E	16590	214	13290	13510	81.4
F	9180	214	6510	6720	73.3
mean ± SD					79.7 ± 6.1

hotplate at 150 °C and to dryness on a steam bath. The residue is taken up with 2.5 mL 0.5 M NaOH and 2.5 mL 20% Na_2SO_4; this solution is placed on a steam bath for 15 minutes, then transferred to a 25-mL volumetric flask, diluted to volume with water, and analyzed for insoluble tungsten. The results of a series of experiments are presented in Table 38. These results demonstrate the successful recovery of both soluble and insoluble species with the new procedure.

Determination of Collection Efficiency

Five plastic cassettes, each containing two 0.8-µm pore size cellulose ester filters with cellulose backup pads, each pair separated by a spacer, were placed in the aerosol generation system. A 20,000 ppm W solution was used to generate the aerosol within the sampling chamber. Filters were loaded for seven hours and then the cassettes were removed and all filters were analyzed for soluble tungsten.

Six plastic cassettes, each containing two 0.8-µm pore size cellulose ester filters with cellulose backup pads, were placed in the dust generation system and were loaded with WC (less than one µm particle size) at ten times the NIOSH recommended standard. After eight hours, the filters were removed and analyzed for insoluble tungsten. The results are presented in Table 39.

At the high concentrations of tungsten examined, no breakthrough occurred to the first backup pad or to the second filter. In no case had flow rate decreased more than ten percent.

Determination of the LAQL

For soluble tungsten (Na_2WO_4), six filters were spiked at each of three concentration levels, X, 2.5X and 20X, where X is the level at which ten percent instrumental precision is attained (~9 µg/mL). The filters were extracted and analyzed for soluble tungsten.

Because it was not possible to weigh insoluble spikes directly and because suspensions of insoluble tungsten compounds did not result in reproducible spikes, a spiking mixture was prepared by mixing 49.9765 grams of graphite with 0.005920 grams of WC-Co in a tumbler for 48 hours. Spikes were then prepared by weighing out the quantity of spiking mixture containing the required weight of tungsten. The highest weight spikes were prepared by weighing the WC-Co directly. Spiked filters were digested and analyzed for insoluble tungsten. The results are presented in Table 40.

For both soluble and insoluble tungsten, LAQL, the level at which ten percent analytical precision is attained, is lower than one tenth of the NIOSH recommended standard.

Evaluation of the Stability of Loaded Filters

Twelve filters were loaded with soluble tungsten by spiking with a measured quantity of Na_2WO_4 and approximately 500 µg of insoluble tungsten. Six filters were analyzed the next day and six were analyzed fourteen days later.

Table 38. Recoveries of soluble and insoluble tungsten compounds H_2O extraction, HNO_3-HF digestion, 1% HCL extraction.

Species	gm W Taken	gm W Found	%Recovery Soluble	%Recovery Insoluble
W	0.1043	0.1030		98.7
	0.1011	0.0952		94.2
	0.1012	0.1006		99.4
Mean ± SD				97.4 ± 2.8
WC	0.0959	0.0899		93.7
	0.0965	0.0911		94.4
	0.0953	0.0958		100.6
Mean ± SD				96.2 ± 0.38
WO_3	0.0802	0.0819		102.1
	0.0807	0.0798		98.8
	0.0814	0.0815		100.2
Mean ± SD				100.4 ± 1.6
Na_2WO_4	0.0628	0.0631	100.6	
	0.0628	0.0645	102.8	
	0.0630	0.0638	101.3	
Mean ± SD			101.6 ± 1.2	
WC-Co *	0.0879	0.0840		95.6
	0.0873	0.0849		97.2
	0.0886	0.0873		98.6
Mean ± SD				097.2 ± 0.15

*WC-Co contained 6% Co.

Table 39. Collection efficiency for tungsten.

Cassette	W, mg/m^3 found		
	Top Filter	Top Backup Pad	Second Filter
Soluble:			
1	2.019	0	0
2	2.044	0	0
3	1.961	0	0
4	1.973	0	0
5	2.034	0	0
Mean ± SD	2.006 ± 0.037		
%RSD	1.85		
Insoluble:			
1'	50.91	0	0
2'	48.75	0	0
3'	56.06	0	0
4'	52.88	0	0
5'	54.71	0	0
6'	52.12	0	0
Mean ± SD	52.57 ± 2.62		
%RSD	4.99		

Table 40. LAQL for tungsten.

Soluble:

W, taken µg/filter	W, found, ± SD µg/filter	% recovery ± SD
100 (X, 0.25S)*	108.4 ± 8.9	108.4 ± 8.2
250 (2.5X)	251.3 ± 1.2	100.5 ± 4.7
2000 (20X)	1965 ± 9.5	98.2 ± 4.8

Insoluble:

W, taken, µg/filter	W, found µg/filter	% recovery ± SD
481 (2X, 0.25S)	454 ± 41	94.4 ± 8.6
1580 (8X)	1430 ± 34	90.4 ± 2.2
84300 (400X)	83150 ± 1830	98.8 ± 2.2

* X = 10% instrumental precision level.

S = NIOSH-recommended standard.

Twelve filters were loaded with insoluble tungsten by spiking with a measured quantity of WC-Co- graphite. Six filters were analyzed the following day and six were analyzed fourteen days later. The results of the study of the stability of spiked filters are presented in Table 41. In each case the filters were stable over the fourteen-day period at the 95% confidence level.

Eighteen filters were loaded with soluble tungsten (Na_2WO_4) and insoluble tungsten (WC) in the aerosol generation system. During generation, the humidity in the system was maintained at 85%. On days one, seven, and fourteen, six filters were extracted and digested for soluble and insoluble tungsten. The results are presented in Table 42. At the 95% confidence level, the filters were stable over a fourteen-day period.

Validation of the Method

The analytical method was validated with filters spiked with soluble and insoluble tungsten at three concentration levels. The filters containing the highest level of soluble tungsten contained the lowest level of insoluble tungsten; this procedure was chosen to maximize potential cross-interference and to demonstrate effective separation of the soluble from the insoluble fractions. Each filter was analyzed for soluble and insoluble tungsten and the recoveries and their standard deviations calculated. The results are presented in Table 43. Validation of the analytical method was successful; all recoveries and relative standard deviations are satisfactory.

The sampling and analytical method was validated with filters loaded with soluble and insoluble tungsten in the aerosol generation system. Relative humidity was maintained at 85% during the course of the experiments. The data are presented in Table 44. All of the measured relative standard deviations are satisfactory for validation.

Filters loaded with soluble tungsten (13-15) and with both soluble and insoluble tungsten (34-36) were analyzed by neutron activation analysis for comparison. The results of these analyses are presented in Table 45. At the 95% confidence level, the results are the same as those obtained by atomic absorption analysis, completing the validation successfully.

Summary and Conclusions

A method has been developed, evaluated, and validated for the determination of soluble and insoluble tungsten in the air of the workplace environment. Samples are collected on a 0.8-μm cellulose ester filter, extracted with water from soluble tungsten species, and digested with nitric-hydrofluoric acid for insoluble tungsten species. Both fractions are analyzed by flame atomic absorption spectrophotometry. This method will appear in the NIOSH Manual of Analytical Methods as P&CAM 271 (revised).

Table 41. **The stability of filters spiked with tungsten.**

Soluble:		Day 1				Day 14	
		W, µg/filter				W, µg/filter	
Filter #	Taken	Found	%Recovery	Filter #	Taken	Found	%Recovery
1	100.0	93.4	**93.4**	7	100.0	110.2	**110.2**
2	100.0	108.7	**108.7**	8	100.0	90.9	**90.9**
3	100.0	98.5	**98.5**	9	100.0	107.9	**107.9**
4	100.0	103.6	**103.6**	10	100.0	106.9	**106.9**
5	100.0	88.4	**88.4**	11	100.0	93.1	**93.1**
6	100.0	98.5	**98.4**	12	100.0	110.2	**110.2**
Mean ± SD			**98.5 ± 7.2**				**103.2 ± 8.8**

Insoluble:		Day 1				Day 14	
		W, µg/filter				W, µg/filter	
Filter #	Taken	Found	%Recovery	Filter #	Taken	Found	%Recovery
1'	667.2	676.4	**101.4**	7'	308.0	299.3	**97.2**
2'	363.6	353.2	**97.1**	8'	354.0	378.0	**106.8**
3'	428.8	378.0	**88.2**	9'	440.6	535.5	**121.5**
4'	539.8	527.2	**97.7**	10'	428.8	456.8	**106.5**
5'	294.0	278.6	**94.8**	11'	553.1	535.5	**96.8**
6'	517.6	552.1	**106.7**	12'	302.8	338.6	**111.8**
Mean ± SD			**97.6 ± 6.2**				**106.8 ± 9.3**

Table 42. The stability of generated filters containing tungsten.

Soluble:

Day 1		Day 7		Day 14	
Filter #	W, $\mu g/m^3$	Filter #	W, $\mu g/m^3$	Filter #	W, $\mu g/m^3$
1	0.361	7	0.426	13	0.410
2	0.446	8	0.402	14	0.412
3	0.435	9	0.386	15	0.422
4	0.422	10	0.464	16	0.417
5	0.393	11	0.457	17	0.397
6	0.448	12	0.425	18	0.382
Mean ± SD	0.418 ± 0.034		0.427 ± 0.030		0.407 ± 0.015

Insoluble:

Day 1		Day 7		Day 14	
Filter #	W, mg/m^3	Filter #	W, mg/m^3	Filter #	W, mg/m^3
1	12.637	7	11.063	13	10.899
2	9.997	8	11.247	14	11.819
3	11.687	9	10.178	15	11.667
4	12.742	10	10.031	16	9.997
5	11.466	11	10.367	17	9.368
6	12.366	12	11.684	18	10.989
Mean ± SD	11.82 ± 1.03		10.76 ± 0.66		10.79 ± 0.95

Table 43. Validation of the tungsten method: spiked filters.

	Soluble W, mg			Insoluble W, mg		
Filter	Taken	Found	% Recovery	Taken	Found	% Recovery
1	0.2000	0.2024	101.20	6.568	6.414	97.7
2	0.2000	0.1610	80.50	6.703	6.911	103.1
3	0.2000	0.2024	101.20	7.589	7.366	97.1
4	0.2000	0.2024	101.20	6.818	7.009	102.8
5	0.2000	0.2024	101.20	6.921	6.332	91.5
6	0.2000	0.1885	94.25	6.901	6.622	96.0
Mean ± SD			96.59 ± 8.36			98.0 ± 4.4
% RSD			8.65			4.5
7	0.5000	0.4668	93.36	3.400	3.329	97.9
8	0.5000	0.4806	96.12	4.002	4.139	102.2
9	0.5000	0.4806	96.12	3.160	3.264	103.7
10	0.5000	0.4781	95.62	3.459	3.270	94.5
11	0.5000	0.4919	98.38	4.153	3.996	96.2
12	0.5000	0.4919	98.38	3.801	3.725	102.3
Mean ± SD			96.33 ± 1.89			99.5 ± 3.8
% RSD			1.96			3.8
13	1.000	0.9803	98.03	0.570	0.552	96.8
14	1.000	0.9525	95.25	2.006	1.905	95.0
15	1.000	0.8692	86.92	2.001	2.029	101.4
16	1.000	0.9386	93.86	1.706	1.758	103.0
17	1.000	0.8692	86.92	2.211	2.274	102.8
18	1.000	0.9525	95.25	1.509	1.491	98.8
Mean ± SD			92.60 ± 4.17			99.6 ± 3.3
% RSD			4.85			3.3

Table 44. Generated filters for the validation of the tungsten method.

Soluble Tungsten

	Filter #	W mg/m^3		Filter #	W mg/m^3		Filter #	W mg/m^3
0.4 x NIOSH std.	1	0.361	1 x NIOSH std.	7	1.164	2 x NIOSH std.	16	2.019
	2	0.446		8	1.066		17	2.044
	3	0.435		9	1.140		18	2.000
	4	0.422		10	1.069		19	1.961
	5	0.393		11	1.042		20	1.973
	6	0.448		12	1.143		21	2.034
Mean ± SD		0.418 ± 0.034			1.104 ± 0.051			2.005 ± 0.033
% RSD		8.13			4.61			1.66

Insoluble Tungsten

	Filter #	W mg/m^3		Filter #	W mg/m^3		Filter #	W mg/m^3
0.2 x NIOSH std.	22	0.8417	2 x NIOSH std.	28	12.637	4 x NIOSH std.	37	18.963
	23	0.8243		29	9.997		38	19.365
	24	0.8458		30	11.687		39	20.587
	25	0.8875		31	12.742		40	19.652
	26	0.8032		32	11.465		41	20.309
	27	0.8388		33	12.366		42	19.544
Mean ± SD		0.8402 ± 0.027			11.816 ± 1.03			19.737 ± 0.605
% RSD		3.21			8.72			3.07

Table 45. Comparison of AAS and NAA for the analysis of tungsten.

Filter	AAS mg/m^3 Soluble W	AAS mg/m^3 Total W	NAA mg/m^3 Total W
7	1.164		
8	1.066		
9	1.140		
10	1.069		
11	1.042		
12	1.143		
13			1.180
14			0.963
15			0.954
Mean ± SD	1.104 ± 0.051		1.032 ± 0.127
28		20.06	
29		20.46	
30		21.69	
31		20.75	
32		21.41	
33		20.64	
34			20.99
35			21.75
36			22.45
Mean ± SD		20.84 ± 0.60	21.73 ± 0.73

VANADIUM

Two NIOSH recommended standards exist for vanadium in the workplace environment. The first standard, for soluble compounds, is 0.05 mg V/m^3 as a ceiling concentration measured over a 15 minute time period. The second standard, for insoluble vanadium compounds, is 1.0 mg V/m^3 measured as a time-weighted average. Both standards apply for up to a ten hour work shift in a forty hour work week (26). The OSHA standards are stated differently: vanadium fume, 0.1 mg/m^3 (ceiling) and vanadium dust, 0.5 mg/m^3 (ceiling). The method which was developed, evaluated, and validated for vanadium involves the separation of soluble and insoluble vanadium and their independent determination by graphite furnace atomic absorption spectrophotometry.

NIOSH Methods P&CAM 290, Vanadium Oxides, S388, Vanadium Oxides-Fume, and S391, Vanadium Oxides-Dust, were examined carefully and used for the development of the new and more general method (27-29). In the following sections, the experiments performed and the results obtained in the development, evaluation, and validation of a method for determination of soluble and insoluble vanadium in the workplace environment are described. Experimental procedures and results are also described in the Sampling and Analytical Method, Backup Data, and Sampling Data Sheet for this method.

EXPERIMENTAL

Reagents:

1. Vanadium Stock Solution, (1000 µg/mL) Titrisol Dilut-It, $VOSO_4$ in 1 liter of 10% (v/v) HNO_3
2. Sulfate Stock Solution (1000 µg/mL). Prepared by dissolving 1.376 gm of $(NH_4)_2SO_4$ in 1 liter in deionized water
3. Nitrate Stock Solution (1000 µg/mL). Prepared by dissolving 1.291 gm of NH_4NO_3 in 1 liter deionized water
4. Iron Stock Solution (1000 µg/mL). Titrisol Dilut-It in 10% (v/v) HNO_3
5. Lead Stock Solution (1000 µg/mL), prepared gravimetrically from Fisher A.A. Standard Lead metal in dilute nitric acid
6. Molybdenum Stock Solution (1000 µg/mL) Fisher A.A. Standard molybdenum metal in dilute aqua regia

7. Titanium Stock Solution (1000 μg/mL)Fisher A.A. Standard titanium metal in dilute hydrochloric acid

8. Concentrated HNO_3, Baker Analytical Reagent Grade

9. Vanadium Pentoxide, V_2O_5 (954 μg/mL) Cerac/Pure certified chemicals in 0.03 M KOH

10. Potassium Hydroxide, pellets, Baker Analyzed Reagent

11. Vanadium Trioxide, V_2O_3, -200 mesh, Cerac/Pure certified chemicals, 99% pure

12. Vanadium Trichloride, VCl_3, -4 mesh, Cerac/Pure certified chemicals, 99% pure

13. EDTA, Baker Analyzed Reagent

14. Vanadium Metal, -200 mesh, Cerac/Pure certified chemicals, 99.5% pure

15. Vanadium Carbide, VC, -325 mesh, Cerac/Pure certified chemicals, 99% pure

16. Deionized Water

17. Argon Gas

Glassware and Equipment:

1. Pipets, volumetric class A, 1, 2, 3, 5, 7, 10, 15, and 50-mL

2. Flasks, volumetric class A, 10, 25, 100, and 1000-mL

3. Beakers, 50-mL, borosilicate glass

4. Steam bath

5. Hot Plate, 140-150 °C

6. Eppendorf Pipet, 100-μL

7. Filtration Apparatus, Millipore XX1004700

8. Filter unit, (37-mm diameter/0.8-μm pore size cellulose ester filter and cellulose backup pad in a 3-piece cassette), Millipore 037AD

9. Filter, cellulose ester, 47-mm diameter, 0.1-μm pore size

10. Bell Jar

11. Vacuum Line

12. Micropipetor, SMI

13. Parafilm, 4" wide

14. Watchglasses, nonribbed

15. Psychrometer

16. Atomic Absorption Instrument, A Perkin-Elmer 306 with D_2 background correction, HGA 2100 graphite furnace, AS-1 autosampler, Vanadium Hollow cathode lamp and pyrolytically coated graphite tubes.

Injection volume	= 10 or 50- μL
Wavelength	= 318.4 nm
Slit setting	= 3 (0.2 nm)
Scale expansion	= 5x
Argon flow	= 25
Drying time	= 35 sec
Drying temp	= 150 °C
Charring time	= 10 sec
Charring temp	= 1900 °C
Atomization time	= 10 sec
Atomization temp	= 2800 °C (or higher if attainable)
Lamp current	= 40 mamp

17. Recorder, Linear, 10 mv full scale

18. Fluid Atomization Aerosol Generator, Environmental Research Corporation, Model #7330

19. Electric Tube Furnace, Lindburg Hevi-Duty, Sola Basic Industries, Type #59344

20. Laminar Flow Box, containing 25 orifices calibrated with flows of 1.7 - 2.0 SLPM

21. Electrical Aerosol Size Analyzer, Thermo Systems, Inc. Model 3030

22. Fluidized Bed Aerosol Generator, Thermo Systems, Inc. Model 3400

Optimization of Instrumental Conditions

For the purpose of optimizing the instrumental conditions, a vanadium solution containing 0.1 μg/mL was prepared from the Standard Vanadium Stock Solution in 1% HNO_3 (30-31). The initial instrumental conditions were those recommended by the manufacturer. The parameters which were examined were the atomization temperature, char temperature, drying temperature, drying time, char time, atomization time, argon flow, lamp current, and injection volume, and these were optimized in that order. This was achieved by varying a given parameter while holding all other parameters constant. This parameter would

then be held constant at the optimal setting while each other parameter was optimized individually. Figure 8 presents the effect of atomization temperature on the AA response of 0.1 μg/mL vanadium. This indicates that the highest temperature attainable should be used for the atomization of vanadium, which in this case was 2800 °C. Figure 9 presents the effect of the charring temperature on the AA response of 0.1 μg/mL vanadium. The optimal charring temperature is 1900 °C. Figure 10 presents the effect of drying temperature on the response of 0.1 μg/mL vanadium. This shows an optimal drying temperature of less than 200 °C. All analyses have been done at 150 °C drying temperature to avoid the possibility of spattering.

Figure 11 presents the effect of drying time on the vanadium response. The graph indicates an optimal drying time of about 30 seconds. Figure 12 presents the effect of charring time on the vanadium response. This figure indicates that charring times of greater than 10 seconds result in losses of vanadium. The time required to atomize the sample completely was 10 seconds. The argon flow was set at 25, and changing the lamp current had no effect, so the suggested value of 40 watts was used.

These optimal conditions were used to determine the 10% precision level for vanadium in a 50-μL and a 10-μL injection. These data are presented in Tables 46 and 47, respectively. From these data it is apparent that the lowest level at which it is possible to determine vanadium at better than 10% relative standard deviation is slightly less than 0.006 μg/mL vanadium.

Evaluation of Interferences

Interferences were originally evaluated in a background matrix of 0.1% HNO_3. Because of problems encountered subsequently and because of information in the literature describing the interference of nitric acid in the determination of vanadium (12), all analyses have been done in a matrix of 0.01 N KOH.

Solutions containing 0.04 μg/mL vanadium and interference concentrations of 0.040 μg/mL (1x), 0.400 μg/mL (10x), 2.000 μg/mL (50x), and 8.000 μg/mL (200x) where the interferences were NO_3^-, $SO_4^=$, Al, Fe, Mo, and Ti were prepared in 0.01 N KOH. All solutions were analyzed in triplicate. The average of the three values was used to calculate the recovery data. The results of the experiment are given in Table 48. Sulfate, nitrate, and aluminum did not interfere in the analysis of vanadium under the conditions of this experiment. Iron did not interfere up to 50x the vanadium concentration. At the 200x level, iron gives a negative interference. Molybdenum does not interfere up to 10x the vanadium concentration. Above this, molybdenum gives a positive interference. Titanium does not interfere until it is greater than 10x the vanadium concentration. At the very high titanium concentration, titanium hydroxide precipitates and the interference effect is lost.

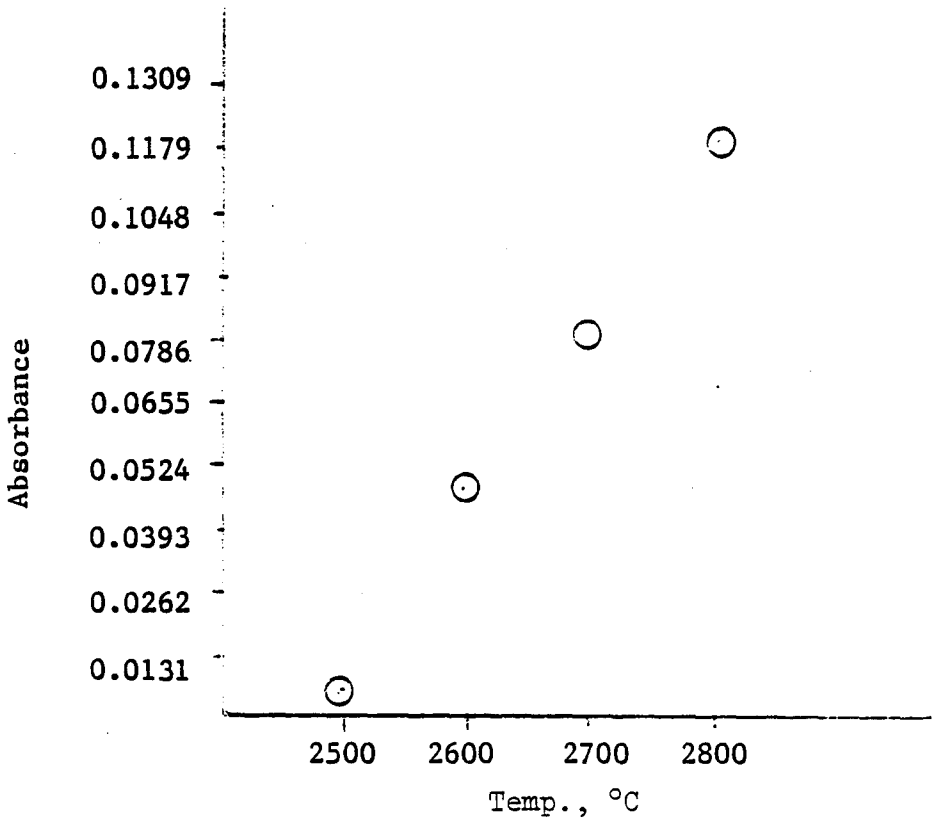

Figure 8. The instrumental response of 0.10 μg/mL vanadium in 1%HNO_3 as a function of atomization temperatures; each point represents the average of three measurements.

dry = 175 °C for 50 sec

char = 1700 °C for 10 sec

atomize = for 10 sec

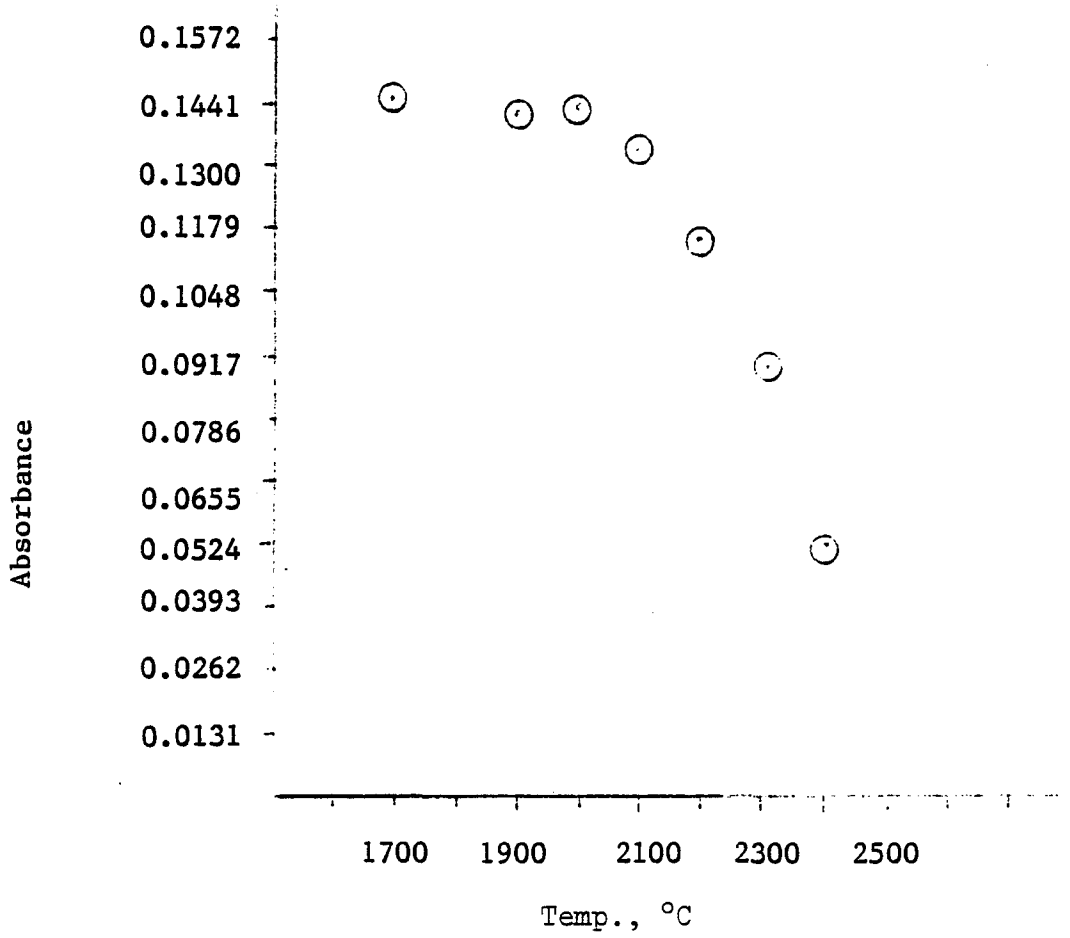

Figure 9. The instrumental response of 0.1 μg/mL Vanadium in 1%HNO_3 as a function of the charring temperature; each point represents the average of three measurements.

dry = 175 °C for 50 sec

char = for 10 sec

atomize = 2800 °C for 10 sec

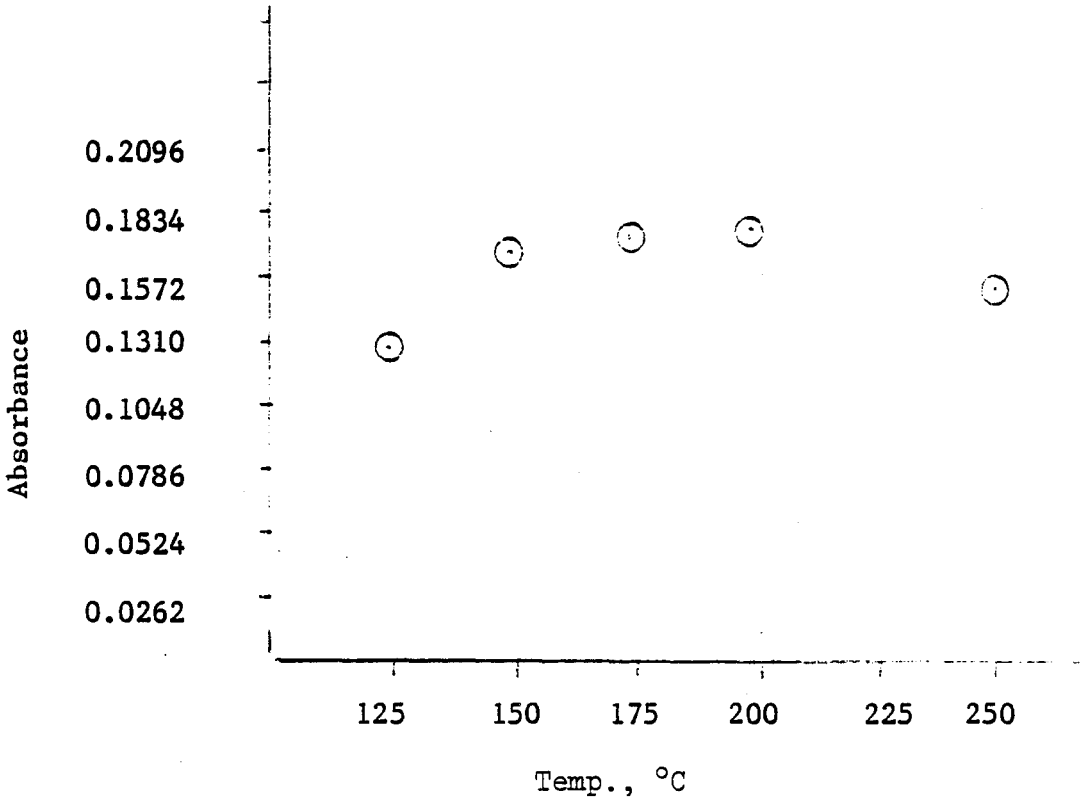

Figure 10. The instrumental response of 0.1 μg/mL Vanadium in 1%HNO_3 as a function of the drying temperature; each point represents the average of three measurements.

dry = 50 sec

char = 1900 °C for 10 sec

atomize = 2800 °C for 10 sec.

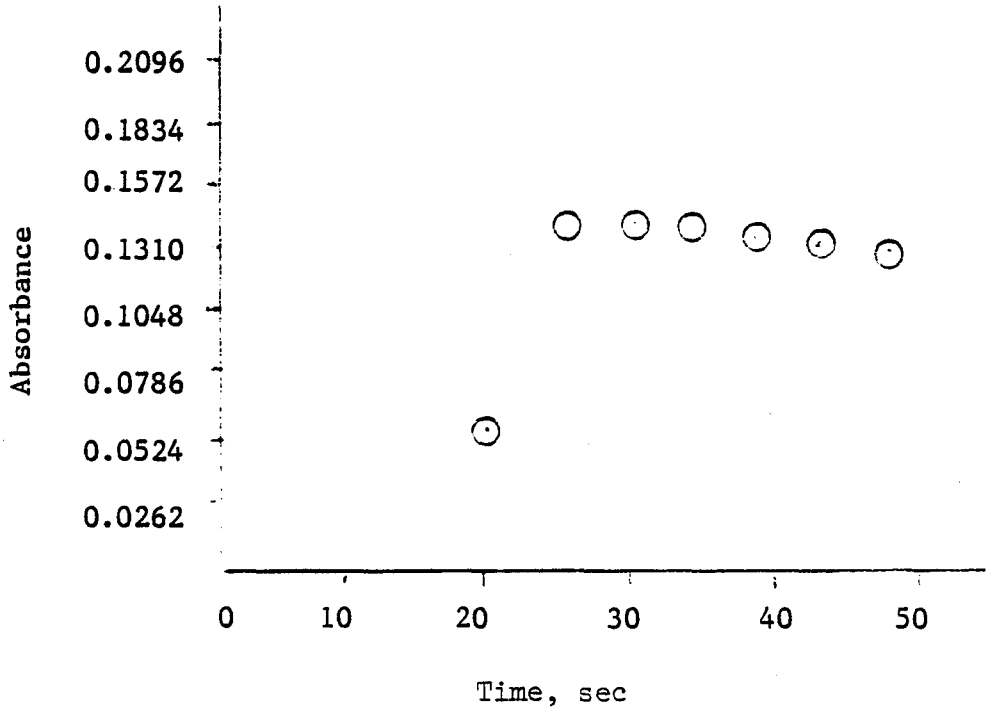

Figure 11. The instrumental response of 0.1 μg/mL Vanadium in 1%HNO_3 as a function of drying time; each point represents the average of three measurements.

dry = 200°C

char = 1900 °C for 10 sec

atomize = 2800 °C for 10 sec.

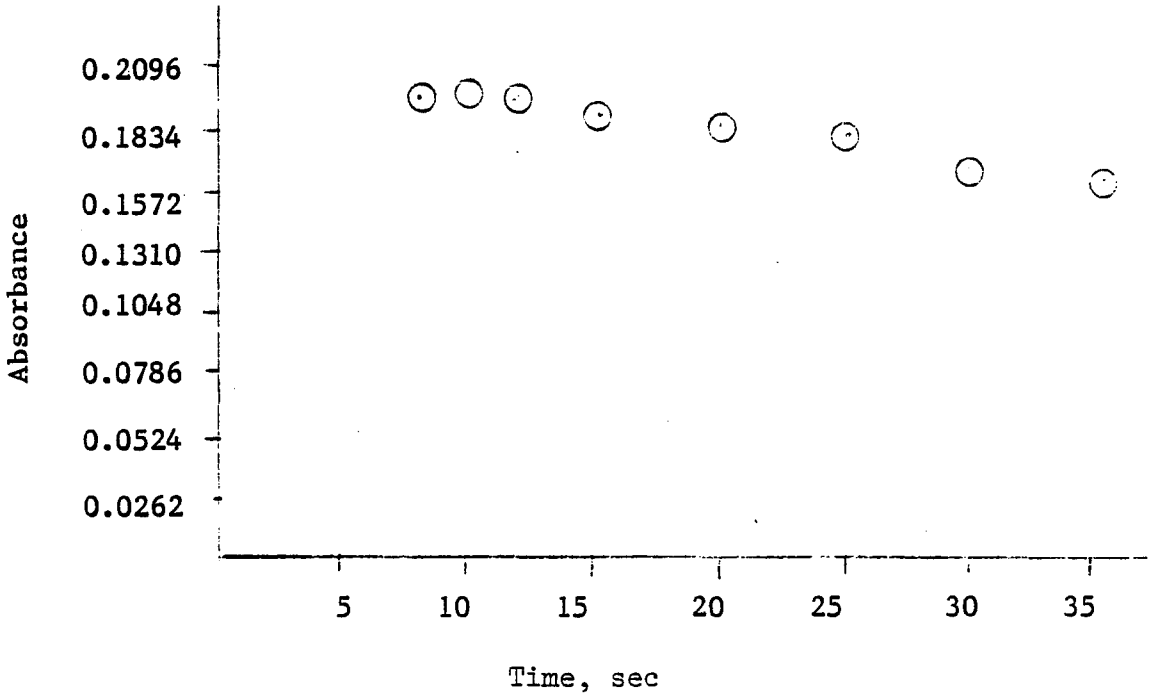

Figure 12. The instrumental response of 0.1 μg/mL Vanadium in 1%HNO_3 as a function of the charring time; each point represents the average of three measurements.

dry = 200 °C for 30 sec

char = 1900 °C

atomize = 2800 °C for 10 sec.

Table 46. Instrumental precision for the analysis of vanadium (50 µl injection).

Taken (µg/mL)	Found (µg/mL) 1	2	3	4	5	Mean ± SD	% RSD
0.090	0.0941	0.0886	0.0883	0.0872	0.0899	0.0896 ± 0.0027	3.0
0.060	0.0622	0.0596	0.0596	0.0591	0.0596	0.0600 ± 0.0012	2.1
0.042	0.0429	0.0426	0.0430	0.0419	0.0426	0.0426 ± 0.0004	1.0
0.030	0.0309	0.0302	0.0299	0.0303	0.0298	0.0302 ± 0.0004	1.5
0.018	0.0186	0.0173	0.0163	0.0174	0.0176	0.0174 ± 0.0008	4.6
0.006	0.0054	0.0068	0.0065	0.0059	0.0058	0.0061 ± 0.0006	9.5

intercept: 0.0001674

slope: 0.0008557

error: 0.001265

coefficient of correlation: 0.998

1%HNO_3 final matrix

30 sec dry 150 °C

10 sec char 1900 °C

10 sec atomize 2800 °C.

Table 47. Instrumental precision for the analysis of vanadium (10 µl injection).

Taken (µg/ml)	Found (µg/mL) 1	2	3	4	5	Mean ± SD	%RSD
0.75	0.743	0.759	0.760	0.748	0.734	0.749 ±0.011	1.4
0.50	0.506	0.511	0.506	0.500	0.498	0.504 ±0.005	1.1
0.35	0.336	0.334	0.356	0.351	0.356	0.347 ±0.010	2.8
0.25	0.240	0.248	0.242	0.254	0.252	0.247 ±0.006	2.5
0.15	0.150	0.156	0.154	0.151	0.151	0.152 ±0.003	1.7
0.05	0.046	0.050	0.052	0.053	0.053	0.051 ±0.003	5.9

intercept:	.006097	1%HNO_3 final matrix	
slope:	.1020	15 sec	dry 150 °C
error:	.00699	10 sec	char 1900 °C
coefficient of correlation:	.999	10 sec	atomize 2800 °C.

Table 48. Interferences in the analysis of vanadium.

Species Studied	Conc. Level in μg/mL		Concentration of V in μg/mL		
			Taken	Found ± SD	% Recovery ± SD
$SO_4^=$	1x	0.040	0.040	0.0402 ± 0.0019	100.5 ± 4.7
	10x	0.400	0.040	0.0386 ± 0.0002	96.6 ± 0.5
	50x	2.000	0.040	0.0411 ± 0.0007	102.9 ± 1.6
	200x	8.000	0.040	0.0389 ± 0.0008	97.1 ± 2.0
NO_3^-	1x	0.040	0.040	0.0392 ± 0.0004	98.0 ± 1.1
	10x	0.400	0.040	0.0389 ± 0.0004	97.3 ± 1.1
	50x	2.000	0.040	0.0403 ± 0.0005	100.8 ± 1.4
	200x	8.000	0.040	0.0404 ± 0.0002	101.0 ± 0.5
Al	1x	0.040	0.040	0.0388 ± 0.0004	97.1 ± 1.0
	10x	0.400	0.040	0.0380 ± 0.0004	95.1 ± 1.1
	50x	2.000	0.040	0.0374 ± 0.0004	93.5 ± 1.1
	200x	8.000	0.040	0.0396 ± 0.0008	99.1 ± 2.0
Fe	1x	0.040	0.040	0.0407 ± 0.0010	101.7 ± 2.5
	10x	0.400	0.040	0.0422 ± 0.0005	105.5 ± 1.2
	50x	2.000	0.040	0.0409 ± 0.0002	102.4 ± 0.6
	200x	8.000	0.040	0.0354 ± 0.0005	88.4 ± 1.3
Mo	1x	0.040	0.040	0.0397 ± 0.0005	99.2 ± 1.4
	10x	0.400	0.040	0.0397 ± 0.0008	99.2 ± 2.0
	50x	2.000	0.040	0.0436 ± 0.0011	109.0 ± 2.5
	200x	8.000	0.040	0.0450 ± 0.0015	112.5 ± 3.4
Ti	1x	0.040	0.040	0.0384 ± 0.0002	96.0 ± 0.6
	10x	0.400	0.040	0.0393 ± 0.0004	98.3 ± 1.0
	50x	2.000	0.040	0.0487 ± 0.0007	121.7 ± 1.4
	200x	8.000	0.040	0.0404 ± 0.0002	101.0 ± 0.5

Development of Extraction and Digestion Procedures

To address the NIOSH recommended standards, it is desirable to separate vanadium species into two categories, soluble and insoluble. Soluble was originally defined as that which dissolved in 0.01N KOH as described in P&CAM 290, in which an ultrasonic extraction in 3 mL of 0.01 N KOH was used.

Vanadium trioxide, V_2O_3, was originally assigned to the soluble vanadium category. An attempt was made to prepare a solution of V_2O_3 in KOH at a concentration of 1000 µg/mL vanadium as a soluble spike stock. The solid V_2O_3 did not dissolve completely.

The first possibility examined was that the solubility limit of V_2O_3 had been exceeded since the solution was intensely colored. However, an attempt to dissolve a lesser quantity of V_2O_3 produced a less intensely colored solution which still contained large amounts of undissolved solid.

At this point, a quantitative study was undertaken. Varying weights of V_2O_3 were weighed onto filters in 50-mL beakers. These samples were ultrasonically extracted in 3 mL 0.01 N KOH and then filtered through a 0.8-µm pore size filter. During the filtration, some of the undissolved particulates passed through the filters. These were allowed to settle and the extracts were analyzed by nitrous oxide flame AA. The results are presented in Table 49.

Table 49. Solubility of V_2O_3 in 0.01 N KOH.

mg V Taken	mg V Found	% V Dissolved
2.923	0.543	18.6
9.993	1.550	15.5
16.043	4.869	30.3
17.606	5.635	32.0
22.365	7.678	34.3

The results indicated that 0.01 N KOH did not dissolve large quantities of V_2O_3, yet it did not appear to be a simple solubility limit problem, but perhaps a kinetic problem. When the initial quantity of V_2O_3 contained 22.4 mg of vanadium, 7.7 mg went into solution, yet when the initial quantity contained only 2.9 mg of vanadium, it would not all dissolve.

The next experiment was to determine whether V_2O_3 is soluble at 10 times the NIOSH recommended standard for soluble vanadium, which is 2.2 mg of V_2O_3 in 1000 mL solvent. Both water and 0.01 N KOH were examined. The solutions

were ultrasonically extracted for 15 minutes and allowed to settle; the water solution dissolved 22.5% and the KOH dissolved 27.7% of the V_2O_3.

About a week later, upon examining the two solutions just described, it was observed that the solid in the KOH solution had dissolved. This suggests that there are slow kinetics involved in the dissolution of vanadium trioxide.

Vanadium trioxide was not extracted effectively using 0.01 N KOH. A study was conducted to determine if another inorganic extraction medium would prove more effective without dissolving any of the other insoluble vanadium compounds. Approximately 0.1 gm of vanadium, vanadium carbide, and vanadium trioxide were weighed into 5 different 50-mL beakers for a total of 15 samples. To one sample of each compound was added 25 mL of a different solvent. They were extracted ultrasonically for 10 minutes. The samples were then centrifuged for approximately 45 minutes to remove any suspended particulates. The results of this experiment are presented in Table 50. This study showed no real advantage to switching from 0.01 N KOH as the extraction solvent.

One last possibility was to preoxidize the V_2O_3 to V_2O_5 before the extraction. Unfortunately, even hydrogen peroxide oxidizes not only the V_2O_3, but also the vanadium carbide and vanadium metal.

The experiments previously described show that vanadium trioxide does not fall entirely into the soluble or the insoluble category. For this reason, V_2O_3 was not used for any of the soluble or insoluble studies.

The four remaining compounds that were studied were vanadium pentoxide and vanadium trichloride for the soluble species and vanadium metal and vanadium carbide for the insoluble species. During the study on V_2O_3, a problem with the dissolution of insoluble vanadium species during extraction of soluble species was noted. This phenomenon was quantified and an attempt was made to eliminate or reduce this cross interference.

The method for soluble vanadium was to be validated at the levels of 0.3, 1.5, and 3.0 μg soluble vanadium in the presence of 30 μg of insoluble vanadium. The worst case for cross contamination problems would be 0.3 μg soluble vanadium with 30 μg insoluble vanadium present. Vanadium metal is the most easily dissolved of the insolubles so it is the most important insoluble species to examine.

The method must not be biased by more than 10%. For the case in question, 0.3 μg soluble vanadium must not show up as any greater than 0.33 μg vanadium, therefore, not more than 0.03 μg of the 30 μg insoluble vanadium can be extracted into the soluble fraction. This corresponds to dissolution of the insoluble vanadium of 0.1% or less. A soluble extraction using 3 mL of 0.01 N KOH in an ultrasonic bath was performed on four filters spiked with vanadium metal. The two fractions were separated by filtering through a 0.1-μm pore size filter. The soluble fraction was analyzed to determine the percent dissolved. The results are shown in Table 51.

Table 50. Solubility of "insoluble" vanadium species during extraction for "soluble" species.

	Extraction solvent									
	DI Water		0.01 N KOH		0.01 N KOH		1.0% HNO_3		10% HNO_3	
Analyte	Anal. Conc. in µg/mL	% Dis-solved	Anal. Conc. in µg/mL	% Dis-solved	Anal. Conc. in µg/mL	% Dis-solved	Anal. Conc. in µg/mL	% Dis-solved	Anal. Conc. in µg/mL	% Dis-solved
V	1.86	0.05	19.10	0.48	24.79	0.61	2.80	0.07	2180	52.7
VC	1.86	0.05	4.96	0.15	4.86	0.15	2.80	0.08	600	18.5
V_2O_3	121	4.41	103	3.69	325	11.8	538	19.2	1550	56.9

Table 51. Dissolution of vanadium metal during ultrasonic extraction for soluble vanadium using 0.01 N KOH.

Sample	µg V Taken	µg V Found	% Dissolved
1	1053	2.204	0.209
2	606	1.291	0.213
3	1458	3.439	0.236
4	423	0.929	0.220
Mean = 0.220 ± 0.012% dissolved, 5.4% RSD.			

A loss of 0.22% is acceptable from the standpoint of the insoluble vanadium analysis but is unacceptably high for the soluble vanadium analysis. An attempt was made to make the extraction less drastic by using deionized water as the extraction solvent. To keep the analytical matrix unchanged (0.01 N KOH), 100 µl of 1.0 N KOH was added to each 10-mL volumetric flask before filling. The results of this experiment are shown in Table 52.

Table 52. Dissolution of vanadium metal during ultrasonic extraction for soluble vanadium using deionized water.

Sample	µg V Taken	µg V Found	% Dissolved
1	1232	1.300	0.105
2	970	0.962	0.099
3	510	0.518	0.102
Mean = 0.102 ± 0.003% dissolved, 3.1% RSD.			

Changing to water as an extraction solvent resulted in definite improvement, but still too great a quantity of vanadium metal dissolved into the soluble fraction. Since it was not possible to go to a less severe extraction solvent, the method of extraction had to be less drastic. To do this, the ultrasonic portion of the extraction was removed. The new method of extraction is as follows: a 47-mm, 0.1-µm pore size cellulose ester filter is placed on the glass frit bottom portion of a Millipore filtration apparatus #XX1004700. The top is clamped in place and the funnel is placed onto the top of a bell jar containing a small beaker to catch liquids. The system is placed under vacuum and water is added to seat the filter. While

the vacuum is still running, the upper portion of the filtration apparatus is unclamped and removed. This assures that the 47-mm filter does not stick to this upper portion. At this point the vacuum is turned off and the beaker in the bell jar is replaced with a clean 50-mL beaker. The sample on a 37-mm, 0.8-μm pore size cellulose ester filter is placed on top of the center of the 47-mm filter. The top of the filtration apparatus is then clamped back into place.

Three mL of deionized water is then pipetted onto the filter and allowed to sit for four minutes. Vacuum is then applied. The vacuum is turned off and an additional three mL of deionized water is placed into the funnel and allowed to sit for two minutes. Vacuum is again applied. When the solution has drained, the vacuum is turned off and approximately 2 mL of deionized water is placed onto the filter as a final rinse and is then immediately pulled through by applying vacuum for a third time.

While the vacuum is still on, the clamp is removed and the upper portion of the filtration assembly is removed. This will leave the filter pair attached to the glass frit and the vacuum is turned off.

The beaker inside the bell jar containing the soluble vanadium fraction is then transferred and rinsed into a 10-mL volumetric flask which contains 100 μL of 1.0 N KOH. The volumetric flask is then filled to the mark with deionized water. The soluble vanadium fraction is now ready for analysis.

Three filters were weighed out with varying amounts of vanadium metal and then taken through the soluble extraction just described. The results of the experiment are given in Table 53.

Table 53. Dissolution of vanadium metal during static extraction for soluble vanadium using deionized water.

Sample	μg V Taken	μg V Found	% Dissolved
1	1018	0.3995	0.039
2	829	0.2543	0.031
3	1210	0.4030	0.033

Mean = 0.034 $\pm$ 0.004% dissolved, 12.7% RSD.

This is now an acceptably low percent dissolution for the vanadium metal. The next step is to be sure that the soluble extraction is still vigorous enough to extract the soluble vanadium species effectively.

To test the extraction efficiency, six filters were spiked with V_2O_5 and six with VCl_3. The filters were allowed to dry and then were taken through the soluble extraction just described. The results of the experiments are given

in Tables 54 and 55.

Table 54. Extraction efficiency for V_2O_5 of static soluble extraction.

Sample	µg V Taken	µg V Found	% Recovery
1	0.4770	0.4572	95.8
2	0.4770	0.4897	102.7
3	0.4770	0.4745	99.5
4	0.4770	0.4785	100.3
5	0.4770	0.4501	94.4
6	0.4770	0.4542	95.2

Mean = 98.0 ± 3.3% recovery.

Table 55. Extraction efficiency for VCl_3 of static soluble extraction.

Sample	µg V Taken	µg V Found	% Recovery
1	11.12	12.47	112.1
2	11.12	11.98	107.8
3	11.12	11.42	102.7
4	11.12	11.22	100.9
5	11.12	10.40	93.5
6	11.12	10.80	97.1

Mean = 102.4 ± 6.8% recovery.

After completion of the soluble extraction procedures, the upper portion of the filtration set-up that came into contact with the filters should be rinsed into a fresh 50-mL beaker with 10% (v/v) HNO_3 to wash off any clinging insoluble vanadium particles. The 37/47-mm filter pair should now be placed into this same beaker and the solution taken to dryness on a 100 °C steam bath.

When the residue is dry, 15 mL of concentrated HNO_3 is placed into the beaker containing the insoluble vanadium. The beaker is then covered with a non-ribbed watchglass and placed on a 140-150 °C hotplate until the volume is reduced to ∿2 mL. The beaker is transferred to a 100 °C steam bath and the watchglass is rinsed into the beaker with a small portion of 10% HNO_3 and then removed. The beaker is then taken to dryness.

The beaker is allowed to cool and 50 mL of 0.01 N KOH is pipetted into the beaker. It is then carefully covered with parafilm to avoid spillage and ultrasonically shaken for 15 minutes. The insoluble vanadium fraction is now

ready for analysis.

This digestion method has been tested on vanadium metal and on vanadium carbide. Six filters were weighed out with varying amounts of each of the two insoluble vanadium species. Using larger, weighable amounts eliminates any possibility of a spiking method error at this point. The results of these two experiments are given in Tables 56 and 57.

Table 56. Digestion of vanadium metal with HNO_3.

Sample	µg V Taken	µg V Found	% Recovery
1	2067	2033	98.3
2	1683	1598	95.0
3	2149	2107	98.0
4	1736	1782	102.7
5	1848	1825	98.8
6	3360	3271	97.4

Mean = 98.4 $\pm$ 2.5% recovery.

Table 57. Digestion of vanadium carbide with HNO_3.

Sample	µg V Taken	µg V Found	% Recovery
1	1667	1606	96.4
2	1521	1511	99.4
3	1546	1516	98.0
4	1421	1432	100.8
5	1394	1412	101.3
6	1488	1470	98.8

Mean = 99.1 $\pm$ 1.8% recovery.

These data show good recoveries with this digestion for both vanadium metal and vanadium carbide. The final test is to see if both soluble and insoluble vanadium species can be spiked onto a filter with good results in the analysis of the soluble fraction. Each of 6 filters was spiked with 30 µg of vanadium as vanadium carbide as well as 15 µl of 17.20 µg/mL V as vanadium trichloride. These filters were allowed to dry and were then taken through the extraction for soluble just described. The results are given in Table 58.

Table 58. Recovery of VCl_3 in the presence of vanadium metal.

Sample	µg V Taken	µg V Found	% Recovery
1	0.2670	0.2305	86.3
2	0.2670	0.2645	99.1
3	0.2670	0.2798	104.8
4	0.2670	0.2600	97.4
5	0.2670	0.2498	93.6
6	0.2670	0.2412	90.4
Mean recovery = 95.3 ± 6.6% recovery.			

Six additional filters were spiked with 20 µg of vanadium as VC and 15 µL of 19.08 µg/mL vanadium as vanadium pentoxide. The results are given in Table 59.

Table 59. Recovery of V_2O_5 in the presence of vanadium carbide.

Sample	µg V Taken	µg V Found	% Recovery
1	0.2862	0.2641	92.3
2	0.2862	0.2787	97.7
3	0.2862	0.2884	100.8
4	0.2862	0.2906	101.5
5	0.2862	0.2641	92.3
6	0.2862	0.2451	85.6
Mean = 95.0 ± 6.1% recovery.			

These experiments show that soluble vanadium compounds are successfully recovered using a static extraction with deionized water without introducing cross contamination from the insoluble vanadium species and that insoluble vanadium compounds are completely digested using concentrated nitric acid.

Particle Size Measurements

Validation of the method requires the generation of representative test atmospheres. For the soluble vanadium species, the generated test atmospheres were required to consist of vanadium fume; the fume generation system is described in Appendix A to this report. To ensure that actual vanadium fume and not just vanadium aerosol was being generated, a particle size measurement was performed. This was achieved with a Thermo Systems, Inc. Model 3030 electrical aerosol size analyzer which is designed to

measure particles in the 0.0032 to 1.0 μm diameter range.

The vanadium fumes were produced originally from a 1000 ppm solution of V_2O_5 in dilute KOH with an atomization pressure of 35 psig. This gave an average particle diameter of 0.033 μm. When the atomization pressure was dropped to 10 psig to reduce the flow through the 1000 °C furnace, the average particle size was reduced to 0.024 μm.

In order to achieve even smaller particles, the fumes were generated by using the EDTA complex of VCl_3 in KOH (pH = 10 - 11). The size distribution obtained was as follows:

Average Particle Diameter, μm	# of Particles
0.0042	7.6×10^5
0.0075	2.5×10^6
0.0133	6.0×10^5
0.0237	2.3×10^4
0.0422	1.9×10^4
0.0750	3.0×10^3
0.133	6.4×10^2

These data are shown graphically in Figure 13. This shows that vanadium fume is being generated.

Determination of Collection Efficiency

Six aerosol monitors, each containing two 0.8-μm pore size cellulose ester filters and cellulose ester backup pads were placed over six orifices in the fume generation system. Fume was generated with a solution of 500 μg/mL (as V) VCl_3-EDTA complex for six hours. These cassettes were removed and the filters analyzed using the extraction described previously.

A second set of six double stage cassettes was placed into the dust generation system and was loaded with vanadium carbide. These samples were analyzed using the digestion described previously.

Longer than a 4-hour sampling time was required in both cases because high enough vanadium concentrations could not be obtained. All results have been normalized to a 4-hour sample for the insoluble dust generations and to a 15-minute sample for the soluble fume generations. In both cases the top filter, top backup pad, and bottom filter were analyzed.

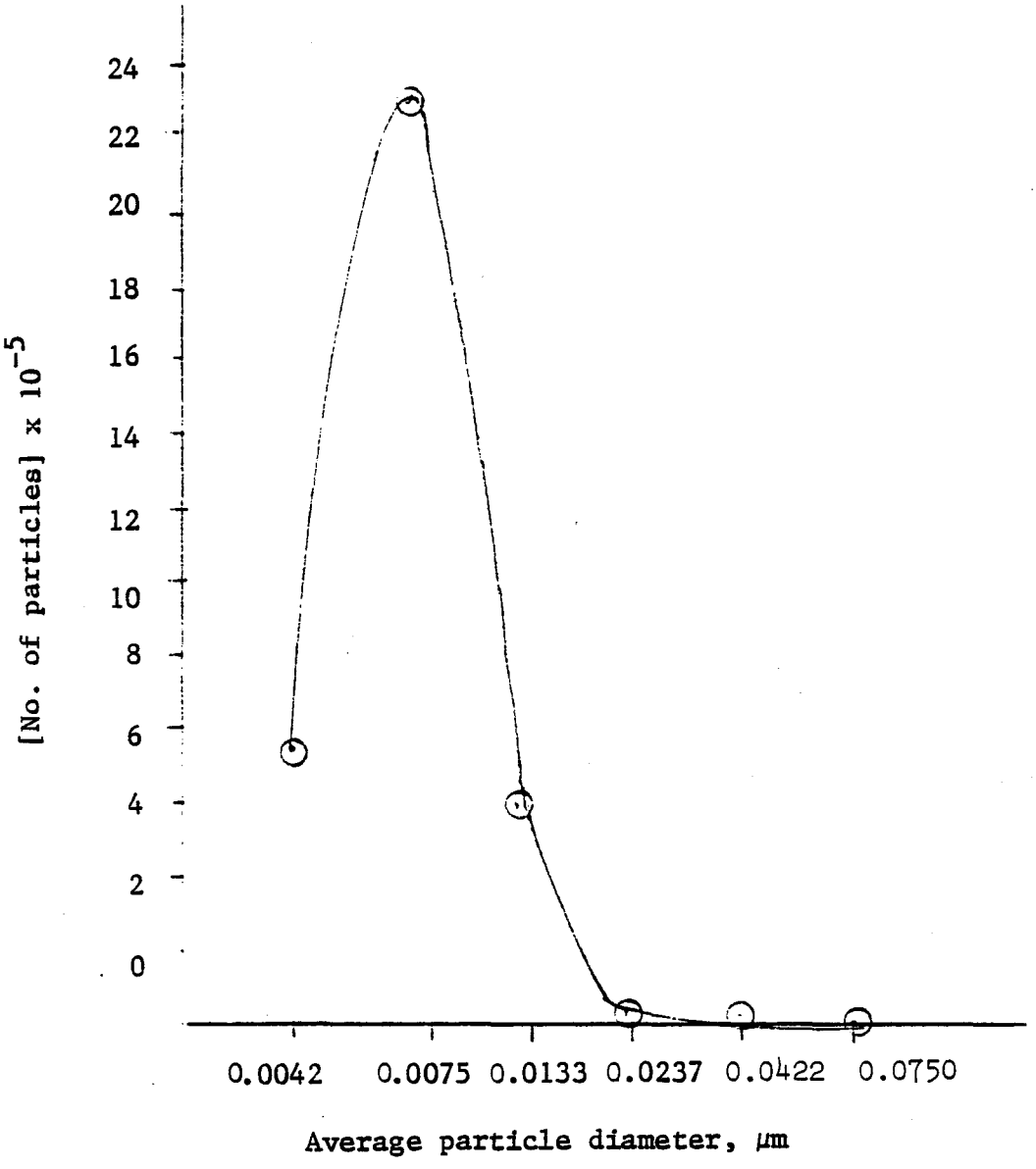

Figure 13. Vanadium fume particle size.

The data from the soluble collection efficiency experiment are given in Table 60. This shows a collection efficiency of greater than 0.986 in all cases.

The data from the insoluble collection efficiency experiment are given in Table 61. This shows a collection efficiency of 1.00 in all cases.

Determination of the Lowest Analytically Quantifiable Level (LAQL)

To determine the LAQL for soluble vanadium, six filters were spiked at each of 3 levels as follows. The 2X level (where X is the 10% precision level) was spiked by micropipetting 10 µL of 12 µg/mL V as V_2O_5 onto a 37-mm 0.8- µm cellulose ester filter. The 20X and 200X levels were prepared by micropipetting 20 µL of 60 µg/mL V and 20 µL of 600 µg/mL V, respectively, onto cellulose ester filters. These filters were allowed to dry and then extracted as described previously. All samples were analyzed in the graphite furnace.

The spiking solution of V_2O_5 was calibrated against standard vanadium solution. Its concentration was determined to be 954 µg/mL V.

Table 62 gives the percent recovery and standard deviation results for the experiments described above. Figure 14 displays the log of the vanadium concentration vs the log of the percent relative standard deviation. According to this graph, 10% RSD corresponds to a vanadium concentration of 0.0135 ppm or 0.135 µg/filter which is less than 1/10 the NIOSH recommended standard of 0.15 µg V/filter.

The LAQL for insoluble vanadium is required to be 50 µg of V per filter or less. All attempts to spike physically that small quantity of vanadium onto a filter failed. As an alternative, the entire experiment was scaled up by a factor of five, allowing spiking by direct weighings.

The experiment was performed by weighing 125 or 250 µg of Vanadium Carbide onto each of a set of twelve 37-mm filters. These filters were each taken through the extraction for soluble vanadium described previously. The KOH used for extraction was increased from 3 to 15 mL. The 37 - 47-mm filter pair was then placed into a 100-mL beaker. In order to scale up the experiment, four more pairs of filters were added to the beaker. Fifty mL of concentrated HNO_3 was added for the insoluble digestion instead of the usual 10 mL and the final solution was diluted to 250 mL with 0.01 N KOH instead of the normal 50 mL.

The two levels described above correspond to 20 µg and 40 µg of vanadium per filter. The third level of 400 µg V per filter was not done by scaling up, but by weighing 500 µg of VC directly onto each of a set of six filters and then taking them through the soluble extraction and insoluble digestion procedure for vanadium.

The percent recoveries and relative standard deviations for all three levels are listed in Table 63. All three levels gave relative standard deviations of 5% or less. The LAQL for insoluble vanadium is, therefore, less than

Table 60. Collection efficiency for soluble vanadium fume.

Cassette	V, $\mu g/m^3$ found			Total % Breakthrough
	Top Filter	Top Backup Pad	Bottom Filter	
1	850.1	1.118	11.007	1.42
2	850.2	4.070	1.977	0.71
3	912.5	1.806	1.297	0.34
4	884.5	3.100	2.961	0.68
5	869.0	2.755	2.984	0.66
6	863.5	4.346	1.632	0.69
Mean	872.0	2.87	3.64	0.75
SD	24.0	1.26	3.67	0.35

Table 61. Collection efficiency for insoluble vanadium dust.

Cassette	V, mg/m^3 found		
	Top Filter	Top Backup Pad	Bottom Filter
1	9.708	ND*	ND
2	9.641	ND	ND
3	10.186	ND	ND
4	9.953	ND	ND
5	9.705	ND	ND
6	9.753	ND	ND
Mean	9.82		
SD	0.21		

* 2σ detection limit = 0.21 mg/m^3.

Table 62. Analytical recovery of soluble vanadium.

200 X				20 X				2 X			
Filter #	V µg		% Recovery	Filter #	V µg		% Recovery	Filter #	V µg		% Recovery
	Taken	Found			Taken	Found			Taken	Found	
1	11.45	10.94	95.57	1	1.145	1.058	92.4	1	0.1145	.0993	86.7
2	11.45	10.88	94.98	2	1.145	1.029	89.9	2	0.1145	.1231	111.9
3	11.45	10.66	93.10	3	1.145	1.029	89.9	3	0.1145	.1092	95.4
4	11.45	10.72	93.65	4	1.145	1.142	99.8	4	0.1145	.0923	80.6
5	11.45	10.82	94.50	5	1.145	1.065	93.0	5	0.1145	.1071	93.5
6	11.45	11.77	102.8	6*	1.145			6	0.1145	.1235	107.9
Mean		10.96				1.065				0.1099	
SD		± 0.41				± 0.046				± 0.014	
Recovery		95.8				93.0				96.0	
% RSD		3.7				4.3				12.5	

* Solution spilled.

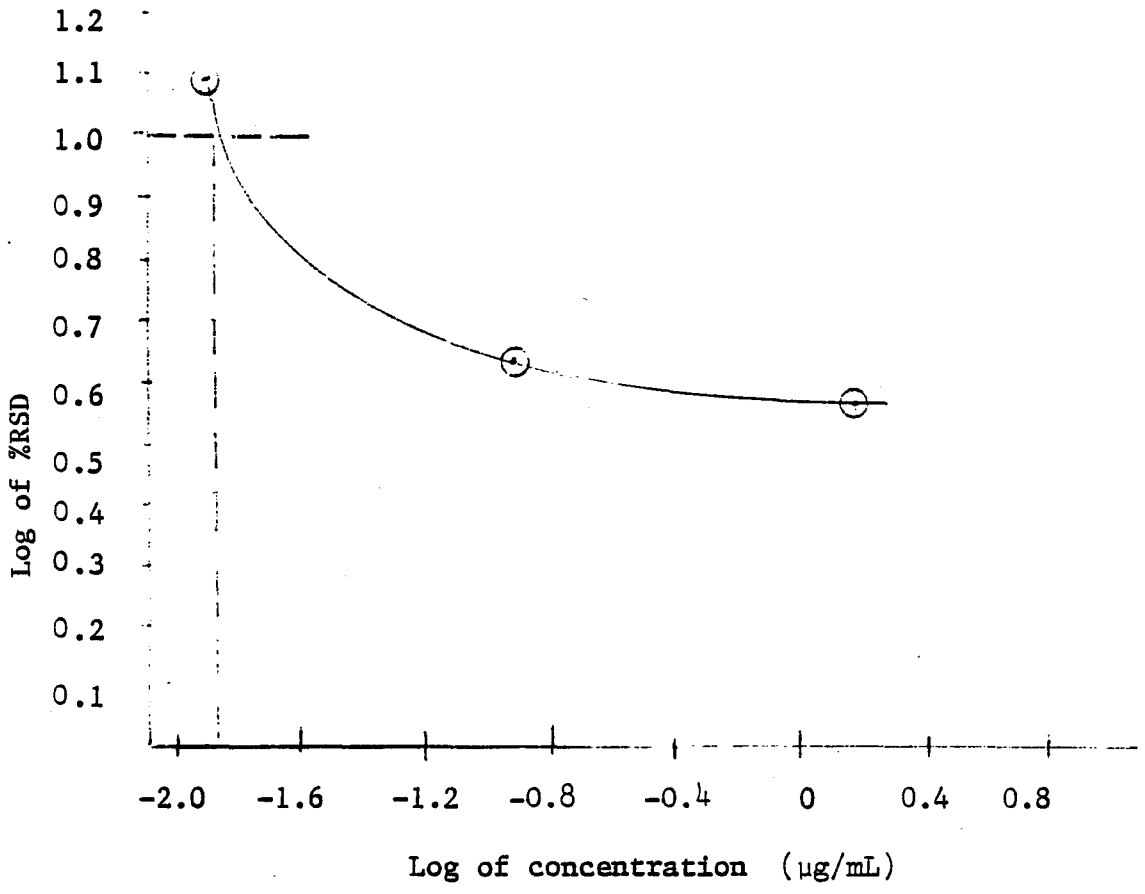

Figure 14. Evaluation of LAQL for soluble vanadium species.

Table 63. LAQL for insoluble vanadium.

Sample	µg V/filter Taken	µg V/filter Found	Percent Recovery
1	18.95	18.16	95.8
2	20.03	19.70	98.4
3	20.09	18.16	90.4
4	21.36	22.40	104.9
5	19.00	18.25	96.2
6	20.22	19.19	94.9
7	38.46	35.45	92.2
8	41.82	40.76	97.5
9	39.76	38.24	96.2
10	40.56	42.21	104.1
11	42.14	43.20	102.5
12	39.56	36.82	93.0
13	419.0	420.2	100.3
14	382.7	371.5	97.1
15	402.6	386.1	95.9
16	399.1	384.5	96.3
17	414.0	398.3	96.2
18	418.3	421.8	100.8

Summary of Insoluble Vanadium LAQL

Filters	µgV/filter	% Recovery ± RSD
1-6	20	96.8 ± 4.8
7-12	40	97.6 ± 4.9
13-18	400	97.8 ± 2.2

20 μg/filter.

Evaluation of the Stability of Loaded Filters

Studies were conducted to determine whether filters loaded with vanadium by spiking and by generation are stable when stored for 14 days. Twelve filters were spiked at the NIOSH recommended standard for soluble vanadium; six were analyzed after one day, and the remaining six were analyzed after fourteen days. The results are presented in Table 64.

Twelve filters were spiked at the NIOSH recommended standard for insoluble vanadium. Six were analyzed after one day and the remaining six were analyzed after fourteen days. The results are presented in Table 65.

The difference between the means of the samples analyzed on days one and fourteen is not significant at the 95% probability level for both the soluble and the insoluble study, indicating that spiked filters are stable in storage.

Eighteen filters were loaded sequentially with 0.8 times the NIOSH recommended standard for soluble vanadium and 0.5 times the NIOSH recommended standard for insoluble vanadium in the generation system. The relative humidity was kept at about 80% during the sample generation. Six were analyzed on day one, six on day seven, and six on day fourteen. The results are presented in Tables 66 and 67.

The differences between the means from days one, seven, and fourteen are not statistically significant at the 95% probability level for either soluble or insoluble vanadium, indicating that filters generated under high humidity are stable over a fourteen-day period.

Validation of the Method

The method was originally validated using mixed spikes. To validate the soluble portion of the analysis, three sets of six 37-mm filters were spiked with 0.3, 1.5, and 3.0 μg of soluble vanadium as V_2O_5 using a micropipet. Each filter had previously been spiked with approximately 30 μg of insoluble vanadium by direct weighing of vanadium carbide. These 18 filters were then taken through the soluble extraction and insoluble digestion for vanadium. Because it was not possible to weigh out only 30 μg accurately, the results of the insoluble portion are only semi-quantitative. The results are given in Table 68.

To validate the insoluble portion of the analysis, three sets of six 37-mm filters were spiked with 100, 500, and 1000 μg of insoluble vanadium, respectively, by direct weighing of vanadium carbide. Each filter was also spiked with 25 μg of soluble vanadium as V_2O_5. These 18 filters were taken through the soluble extraction and insoluble digestion for vanadium. The results of these experiments are given in Table 69.

These experiments show that the method is valid using spiked filters.

Table 64. The stability of filters spiked with soluble vanadium.

Samples Stored One Day After Spiking			Samples Stored Fourteen Days After Spiking		
Taken	µg V found	% Recovery	taken	µg V found	% Recovery
0.4770	0.4713	98.8	0.4770	0.5161	108.2
0.4770	0.4836	101.4	0.4770	0.4283	89.8
0.4770	0.4967	104.1	0.4770	0.4787	100.3
0.4770	0.4811	100.9	0.4770	0.5058	106.0
0.4770	0.4271	89.5	0.4770	0.4116	86.3
0.4770	0.4730	99.2	0.4770	0.4322	90.6
mean		99.0			96.9
SD		5.1			9.2

Table 65. The stability of filters spiked with insoluble vanadium.

Samples Stored One Day After Spiking			Samples Stored Fourteen Days After Spiking		
Taken	µg V found	% Recovery	taken	µg V found	% Recovery
419.0	420.2	100.3	396.9	376.2	94.8
382.7	371.5	97.1	415.1	397.8	95.8
402.6	386.1	95.9	413.1	405.9	98.2
399.1	384.5	96.3	415.0	396.9	95.6
414.0	398.3	96.2	400.7	391.4	97.7
418.3	421.8	100.8	418.2	390.5	93.4
mean		97.8			95.9
SD		2.2			1.79

Table 66. The stability of generated filters containing soluble vanadium.

Samples Stored One Day After Generation (mg/m^3)	Samples Stored Seven Days After Generation (mg/m^3)	Samples Stored Fourteen Days After Generation (mg/m^3)
0.03704	0.03829	0.04048
0.04428	0.04126	0.03476
0.03677	0.03635	0.03336
0.04090	0.04534	0.03532
0.04314	0.04430	0.04004
0.04042	0.03915	0.03901
mean 0.04043	0.04078	0.03716
SD 0.00308	0.00352	0.00340
% RSD 7.61	8.63	8.18

Table 67. The stability of generated filters containing insoluble vanadium.

Samples Stored One Day After Generation (mg/m^3)	Samples Stored Seven Days After Generation (mg/m^3)	Samples Stored Fourteen Days After Generation (mg/m^3)
0.4958	0.3271	0.5473
0.5211	0.4315	0.5358
0.4921	0.3855	0.4425
0.4926	0.4833	0.4909
0.4603	0.4924	0.5057
*	0.4724	0.4859
mean 0.4924	0.4318	0.5013
SD 0.0216	0.0647	0.0378
% RSD 4.39	14.98	7.54

* Sample Spilled

Table 68. Validation of the vanadium method: spiked soluble vanadium.

Filter	SOLUBLE			INSOLUBLE		
	µg V taken	µg V found	Percent recovery	µg V taken	µg V found	Percent recovery
1	.2862	.3072	107.3	28.8	28.3	98.1
2	.2862	.2971	103.8	29.2	28.1	96.1
3	.2862	.3044	106.4	29.6	33.3	112.6
4	.2862	.2967	103.7	29.6	33.6	113.5
5	.2862	.2994	104.6	25.6	27.1	105.9
6	.2862	.2892	101.0	31.6	33.5	106.0
Mean ± SD			104.5 ± 2.2			105.4 ± 7.2
% RSD			2.1			6.8
7	1.431	1.370	97.0	30.0	23.9	79.5
8	1.431	1.355	94.7	27.8	28.0	100.7
9	1.431	1.399	97.8	30.4	28.7	94.3
10	1.431	1.390	97.2	23.2	25.4	109.4
11	1.431	1.388	97.0	28.4	27.2	95.8
12	1.431	1.432	100.0	26.8	27.4	102.1
Mean ± SD			97.3 ± 1.7			97.0 ± 10.1
% RSD			1.7			10.4
13	3.085	3.115	101.0	31.24	27.09	86.7
14	3.085	3.114	100.9	27.40	26.21	95.7
15	3.085	3.169	102.7	28.04	32.08	114.4
16	3.085	3.125	101.3	27.24	29.76	109.3
17	3.085	3.207	103.9	32.84	31.05	94.6
18	3.085	3.222	104.4	32.04	26.27	82.0
Mean ± SD			102.4 ± 1.5			97.1 ± 12.6
% RSD			1.5			12.9

Table 69. Evaluation of the vanadium method: spiked insoluble filters.

	SOLUBLE			INSOLUBLE		
Filter	µg V taken	µg V found	Percent recovery	µg V taken	µg V found	Percent recovery
1	101.7	105.8	104.1	23.85	23.92	100.3
2	96.7	101.2	104.7	23.85	25.31	106.4
3	27.1	26.3	97.0	23.85	25.10	105.2
4	93.3	100.0	107.2	23.85	23.65	99.2
5	105.2	105.0	99.8	23.85	23.71	99.4
6	105.9	106.4	100.5	23.85	25.51	106.9
Mean ± SD			102.2 ± 3.8			102.9 ± 3.6
% RSD			3.7			3.5
7	517.9	517.9	100.0	23.85	23.95	100.4
8	517.1	535.5	103.6	23.85	24.68	103.5
9	511.6	484.7	94.8	23.85	24.45	102.5
10	519.8	496.2	95.5	23.85	25.06	105.1
11	515.5	491.0	95.2	23.85	24.99	104.8
12	519.9	522.0	100.4	23.85	25.32	106.2
Mean ± SD			98.2 ± 3.6			103.8 ± 2.1
% RSD			3.7			2.0
13	1010	1038	102.8	23.85	24.95	104.6
14	1001	949	94.8	23.85	24.88	104.3
15	1017	1011	99.4	23.85	25.89	108.6
16	1007	940	93.3	23.85	25.32	106.2
17	1037	987	95.2	23.85	26.01	109.1
18	1016	985	96.9	23.85	26.37	110.6
Mean ± SD			97.1 ± 3.5			107.2 ± 2.6
% RSD			3.6			2.4

To validate the method using generated test atmospheres, 18 filters were loaded with soluble vanadium fume with 6 each at 0.25, 1.2, and 2.3 times the NIOSH recommended standard for a ceiling concentration. Eighteen additional filters were loaded with insoluble vanadium dust with 6 each at 0.21, 1.0, and 2.5 times the NIOSH recommended standard for a 4 hour time-weighted average. The results of these experiments are given in Tables 70 and 71. The data show that the method for soluble vanadium fume is valid. The validation of the insoluble vanadium dust method is inconclusive due to problems in obtaining a homogeneous test atmosphere because of the particle size of the vanadium dust. The dust generator can generate efficiently with particles up to 20 μm. The smallest insoluble vanadium particle size available was -325 mesh, which corresponds to a cutoff diameter of 44 μm.

The final stage in the validation of the method for soluble vanadium fume is comparison to an independent method. During the generation of the middle test level for the validation of the soluble method, an additional three samples were collected. These three generated samples plus a spiked sample and a blank filter were sent for analysis by instrumental neutron activation analysis by General Activation Analysis, Inc. The results of the analysis by NAA indicated a bias between the two methods, but also produced a spiked recovery of 137%. An additional three spikes were sent to General Activation Analysis and were analyzed along with the original spike and two of the generated samples, which were re-analyzed. The third sample had accidently been destroyed following the initial determination. The average spike recovery for the second analysis by NAA was 97.7%. The sample values obtained from the second NAA analysis were closer to those obtained by AAS, but still did not match, indicating an inconsistency in the results. Both methods were re-examined to locate the problem.

Because NAA is a nondestructive method, the two samples and 4 spikes were returned and re-analyzed by Atomic Absorption Spectrometry. These six filters were extracted and were analyzed and the six generated samples originally analyzed by AAS were re-analyzed. The results of the second analysis by AAS correlate very well with the results of the second determination by NAA, as is shown in Table 72. The average recovery of the 4 spikes by AAS and by NAA was 97.7%. The percent difference between the average mg/m^3 for the two samples analyzed by both methods was 0.67%. The percent difference between the average mg/m^3 for the two samples analyzed by NAA versus the six samples analyzed by AAS was 3.7%, indicating that the two methods yield the same results for soluble vanadium fume.

SUMMARY AND CONCLUSIONS

The method for the analysis of soluble vanadium fume has been successfully validated over a much lower range than was previously possible. The new LAQL is 0.005 mg V/m^3. This new method also makes it possible to do a quantitative separation of the soluble and insoluble species of vanadium. A method was also developed for the analysis of the insoluble fraction but the validation was unsuccessful due to an inability to generate a homogeneous test atmosphere.

Table 70. Generated filters for the evaluation of the soluble vanadium method.

0.25 times standard		1.2 times standard		2.3 times standard	
Filter #	µg V per filter	Filter #	µg V per filter	Filter #	µg V per filter
1	0.3102	1	1.363	1	2.761
2	0.3279	2	1.487	2	3.046
3	0.3234	3	1.326	3	2.910
4	0.2916	4	1.520	4	2.859
5	0.3162	5	1.578	5	2.780
6	0.3225	6	1.374	6	2.804
Mean	0.3153		1.441		2.861
SD	± 0.0132		± .101		± 0.105
% RSD	4.2		7.0		3.6

NOTE: All values for µg of vanadium per filter have been normalized to a sample volume of 25 L.

Table 71. Generated filters for the evaluation of the insoluble vanadium method.

0.21 times standard		1.0 times standard		2.5 times standard	
Filter #	µg V per filter	Filter #	µg V per filter	Filter #	µg V per filter
1	70.76	1	432.0	1	982.0
2	75.76	2	388.8	2	987.6
3	89.44	3	373.8	3	1021.2
4	82.24	4	388.2	4	1009.2
5	91.48	5	430.0	5	1025.6
6	102.96	6	383.3	6	852.8
Mean	85.44		399.4		979.7
SD	11.65		25.1		64.6
% RSD	13.64		6.28		6.59

NOTE: All values for µg of vanadium per filter have been normalized to a sample volume of 400 L.

Table 72. Comparison of AAS and NAA for the analysis of soluble vanadium.

Filter #	AAS_3 mg/m^3	NAA_3 mg/m^3
2	0.05453	
6	0.05304	
7	0.05497	
9	0.06310	
13	0.05948	
14	0.06080	
Mean ± SD	0.05765 ± 0.040	
8		sample destroyed
12		0.06362
19		0.05602
Mean		0.05982

TALC

The NIOSH recommended standard for airborne talc in the workplace environment, twenty million particles per cubic foot, is based upon the number of particles per unit volume of air, while the method developed and evaluated for the determination of talc by X-ray diffraction is based upon the weight of talc per unit of volume of air. NIOSH Method P&CAM 259 (32), Free Silica in Airborne Dust, was examined carefully and used as a guide in the development of a method for talc. In the following sections, the experiments performed for the development and evaluation of a method for the determination of talc in the workplace environment are described (33-35). Experimental procedures and results are also described in the Sampling and Analytical Method, Backup Data, and Sampling Data Sheet on this substance.

EXPERIMENTAL

Reagents, laboratory glassware, equipment, and instrumentation which were used throughout the effort for talc were as follows:

Reagents:

1. Talc, TA-99; NYTAL 400
2. 2-propanol, Baker reagent grade
3. α-Al_2O_3, Linde A
4. LiF, Baker Reagent Grade
5. Concentrated HCl, Baker Analytical Reagent Grade
6. NH_4OH, Baker Reagent Grade.

Glassware and Equipment:

1. Pipettes, Eppendorf; 1-mL; Oxford, 1-5-mL
2. Flasks, volumetric class A, 100-mL
3. Flasks, Erlenmeyer, wide mouth, tapered stopper, 125-mL
4. Beakers, borosilicate glass, 30-mL

5. Filtering tower, Millipore XX10 02500 with tower modified to an 8-mm bore

6. Filters, Millipore, 0.45-μm Metricel, 37-mm diameter

7. Filters, silver membrane, 25-mm diameter, 0.45-μm

8. Filter cassettes, Millipore, plastic

9. Ultrasonic agitator

10. Low temperature asher, LFE Model 302

Instruments:

1. X-ray diffractometer, Philips Constant potential diffractometer with broad focus copper target X-ray tube, rotating sample holder, graphite crystal monochromator, and scintillation detector. These settings were used:

Divergence slit	0.5°
Receiving slit	1°
Anti-scatter slit	4°
Pulse height analyzer	differential mode
Take off angle	4°

Data collection under control of the angle mode programmer consisted of accumulating counts for 20 seconds at increments of 0.05° 2θ. This output was recorded by an ASR 33 teletypewriter.

Optimization of Instrumental Conditions-Determination of Precision

A suspension of 5.384 mg TA-99 talc in 100.0-mL 2-propanol was prepared using ultrasonic agitation and manual shaking. Silver membrane filters were suspended in concentrated ammonia for five-minutes, then washed twice with 2-propanol and air dried. Aliquots of the suspension were pipetted onto the cleaned filters through an 8-mm diameter filtering tower; filters were prepared containing from zero to sixty-five micrograms talc per filter. The filters were air dried and XRD analysis was performed on each filter. The peak areas of the 002 and 006 reflections were obtained by step scanning the peaks in a fixed-time mode and printing out the accumulated counts. Data from the experiments are given in Table 73.

Least squares regression analysis was applied to the data in Table 73 and the following calibration equations were generated:

$$\mu g \text{ talc} = 0.0250 \text{ (002 peak area)} + 2.96$$
$$\mu g \text{ Talc} = 0.0356 \text{ (006 peak area)} + 0.87$$

with coefficient of determination $r^2 = 0.951$ for the 002 data set and $r^2 = 0.979$ for the 006 data set. These relationships were used to generate

Table 73. Preliminary standardization data for talc.

Std.	Conc. (µg Talc)	Peak Areas		µg Talc Calculated From Regression	
		002	006	002	006
01A	0	-64	61		
01B	0	-61	46		
11A	5.4	115	126		
11B	5.4	117	119		
12A	10.8	270	196		
12B	10.8	449	285		
13A	21.5	641	559		
13B	21.5	753	533		
14A	43.1	1989	1181	52.7	42.9
14B	43.1	1616	1293	43.3	46.9
14CG	43.1	1877	1417	49.9	51.3
14DG	43.1	1799	1142	47.9	41.5
14E	43.1	1258	1105	34.4	40.2
14F	43.1	1284	1068	35.0	38.9
15A	64.6	2303	1679		
15B	64.6	2295	1813		

calculated talc concentrations for the six standards at the 43.1 µg level. The averages and standard deviations corresponding to the two reflections are 43.9 ± 7.7 µg for the 002 reflection and 43.6 ± 4.7 µg for the 006 reflection.

Calibration data are plotted in Figures 15 and 16. The calibration curves are linear in the range of weight of talc which was examined.

Because it was suspected that the orientation of the talc particles on the silver filter might affect the peak areas, co-deposition with a carrier was examined as a means to achieve random orientation. Talc and carrier, either α-Al_2O_3, or LiF were placed on the silver membrane filters according to the following procedure:

> A filtering tower was placed over the silver filter and the apparatus was placed on a vacuum flask. An aliquot of 2-propanol was placed in the filtering tower; this was followed by an aliquot of a suspension of the carrier in 2-propanol and finally by an aliquot of a suspension of talc in 2-propanol. The filters were air dried. All samples contained 40 µg talc, while the quantity of carrier varied from zero to 1800 µg. XRD analysis was performed on each filter.

Figure 17 presents data for the experiment using α-Al_2O_3 as carrier. From this graph, it may be concluded that while the peak area is decreased in the presence of carrier, substantial peaks are still detected. For the 002 reflection of talc, a 50% reduction in peak area occurs at a volume ratio of 7:1, while for the 006 reflection, a 50% reduction occurs at a volume ratio of 14:1. LiF was also successful as a carrier but was not pursued since it is not readily available in a controlled particle size as is the 0.3-µm α-Al_2O_3 polishing compound.

The 10% instrumental precision level, X, was determined for the analysis of talc by XRD both in the absence and in the presence of α-Al_2O_3 carrier.

Standard silver membrane filters containing 3.9 µg, 19.5 µg and 39.0 µg of talc were prepared and analyzed by X-ray diffraction at the 002 and 006 peak. Each filter was analyzed several times, and was removed from the instrument between analyses. The data are presented in Table 74. X is approximately 8 µg talc per filter for the 006 peak and 12 µg talc per filter for the 002 peak.

A similar experiment was performed with 600 µg α-Al_2O_3 co-deposited with the talc on each filter, and the data are presented in Table 75. X for talc co-deposited with α-Al_2O_3 is 25 µg per filter for the 006 peak and 35 µg per filter for the 002 peak.

Development of Procedures for Preparing Standards and Samples of Talc

Procedures for the preparation of talc for XRD were examined. The basic procedure to be evaluated comprised the following steps:

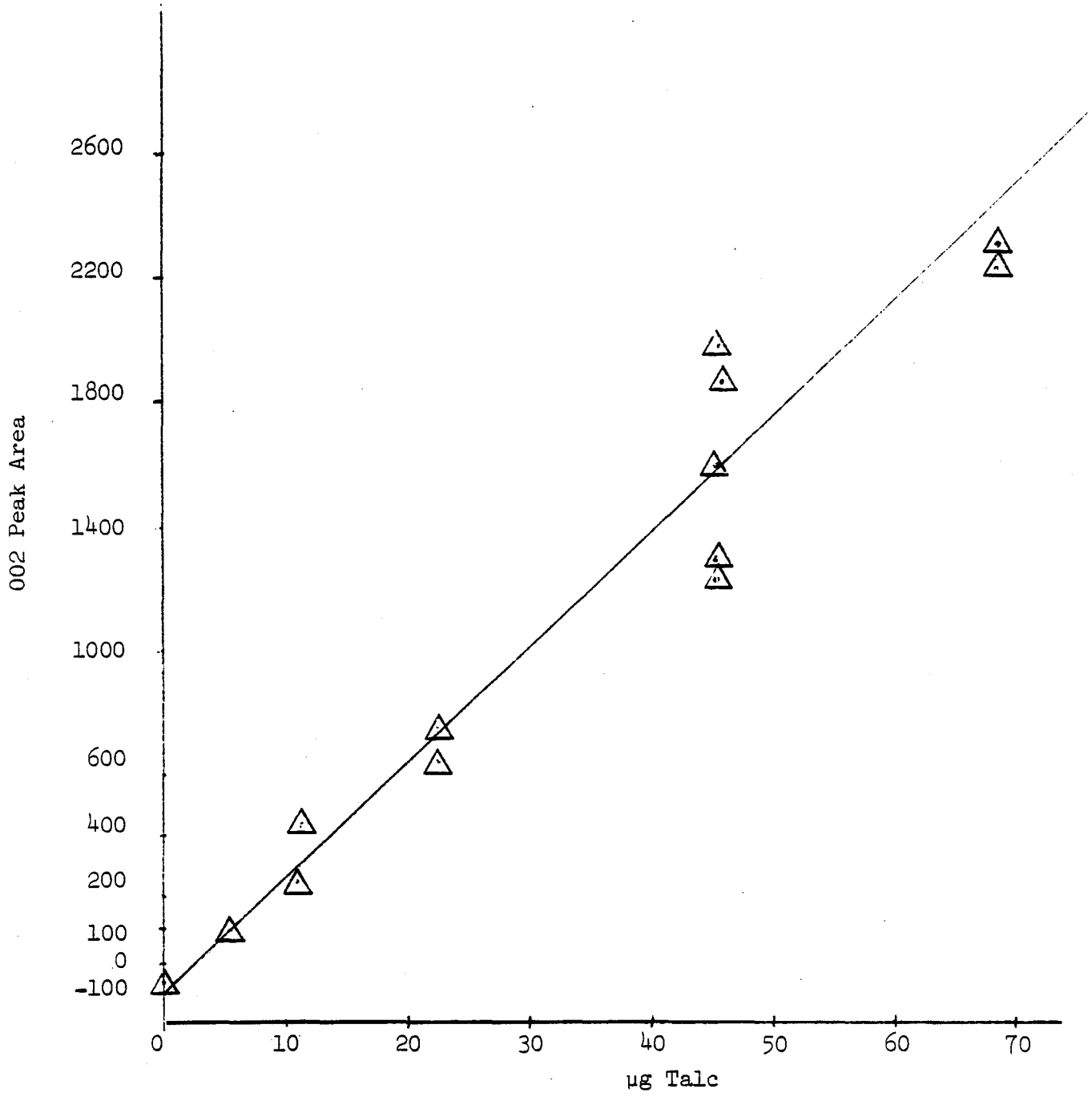

Figure 15. Calibration curve for talc analysis by XRD 002 peak area vs weight talc.

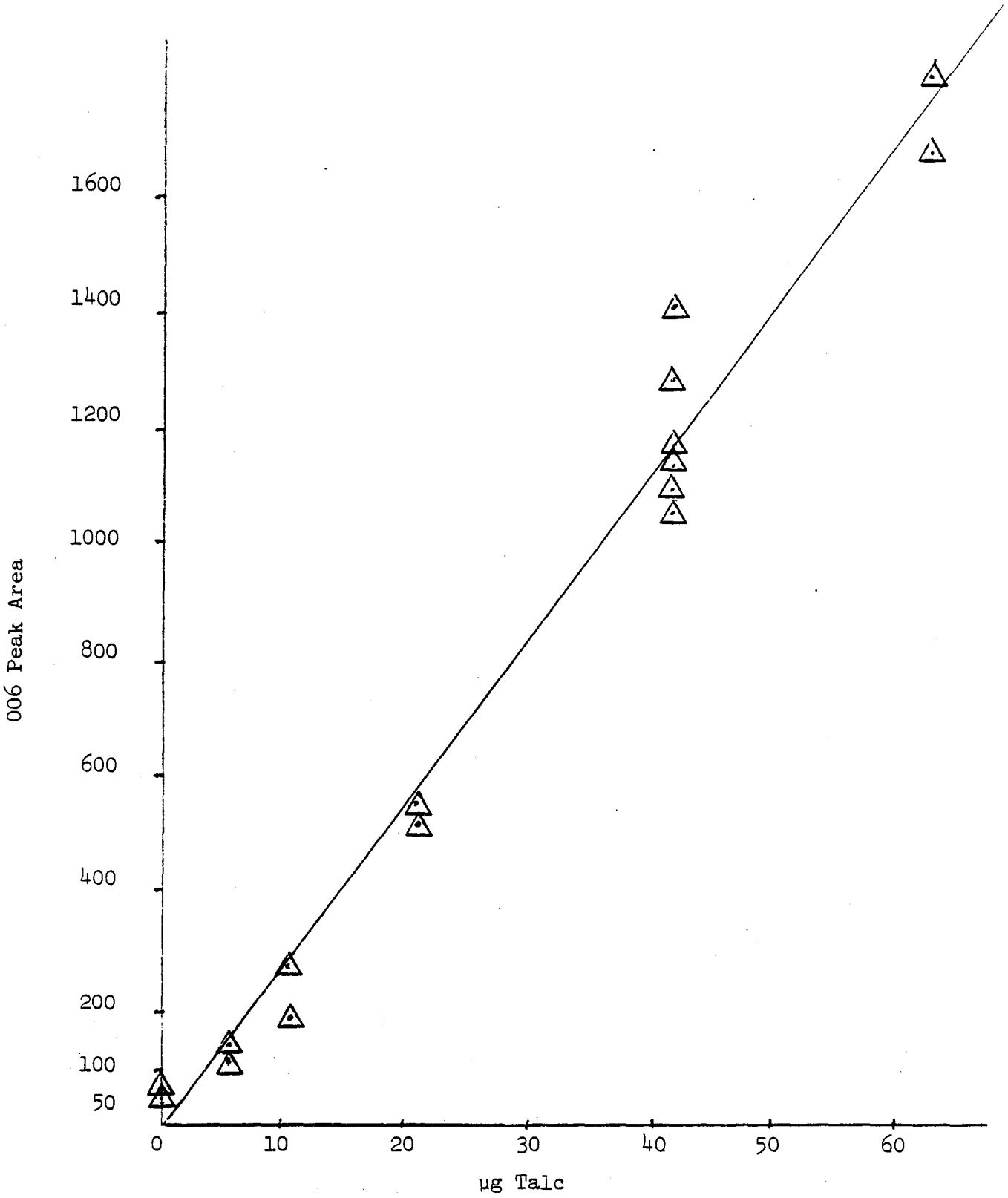

Figure 16. Calibration curve for talc analysis by XRD 006 peak areas vs weight talc.

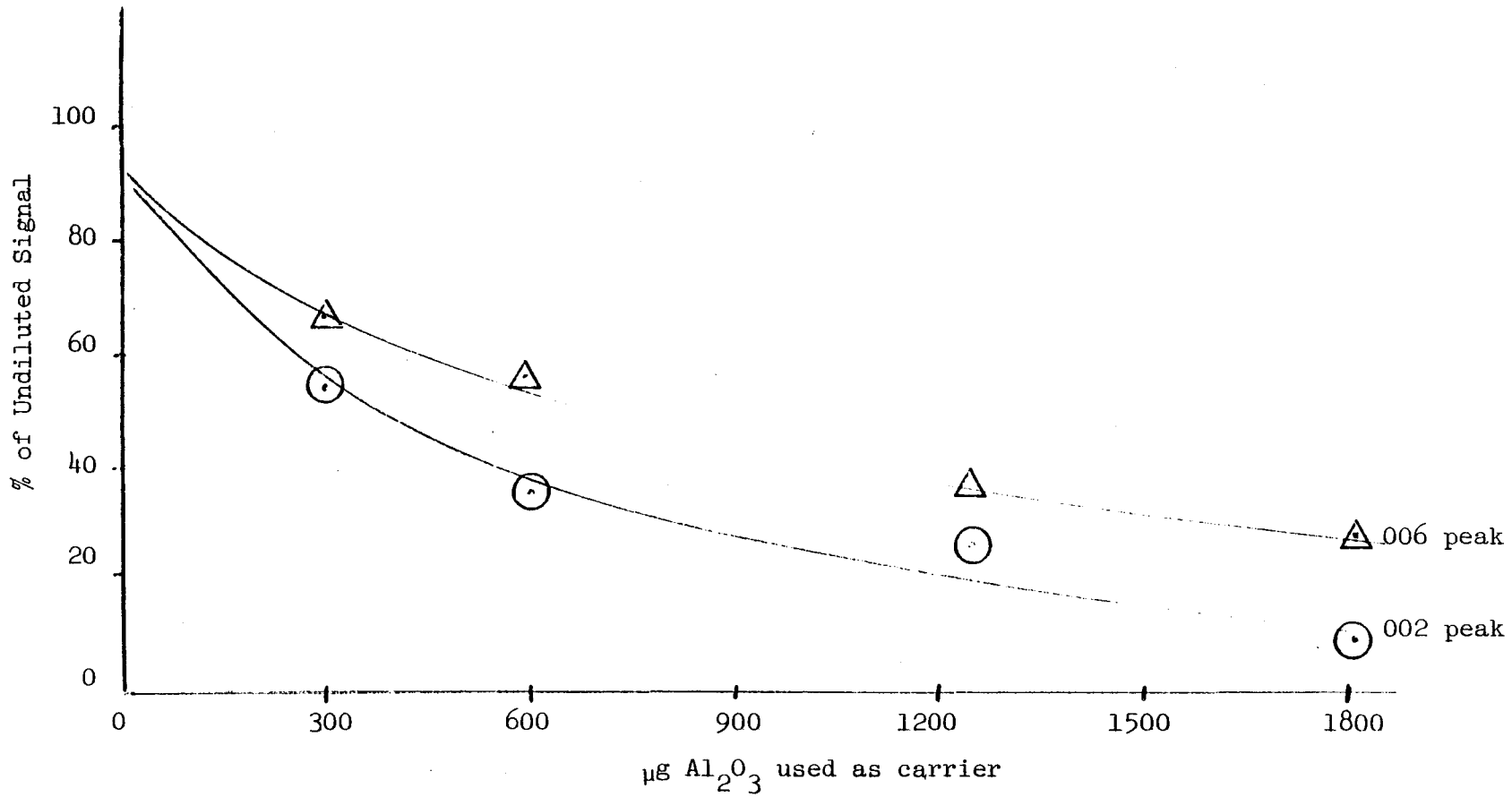

Figure 17. Peak areas of talc signals in the presence of carrier
% of undiluted signal vs μg α-Al_2O_3.

Table 74. Evaluation of X for talc.*

Sample	µg talc	002 net peak	002 % RSD	006 net peak	006 % RSD
51B	3.9	129	24	72	21
52B	9.76	376	15	178	6.7
53A	19.52	871	4.9	363	4.4
54E	39.04	1790	3.9	739	3.0

Table 75. Evaluation of X for talc co-deposited with α-Al_2O_3.*

Sample	µg talc	002 net peak	002 % RSD	006 net peak	006 % RSD
α 70H	9.93	158	37	90	33
α 71L	19.7	334	18	237	13
α 74A	49.2	735	8.0	569	5.3
α 74B	49.2	766	7.7	598	5.0
α 72J	98.4	1678	3.5	1146	2.6

* X is the quantity of talc for which 10% instrumental precision is attained.

1. Collection of talc on PVC filters

2. Plasma ashing of loaded filters

3. Transfer to Ag filters

4. XRD analysis.

Possible variables in these steps were examined experimentally; these included changes introduced by the plasma ashing and by transfer to the silver membrane filters with 6 N HCl. The experiments are presented in Table 76.

From these experiments, it is clear that results with good precision may be obtained when talc samples are handled in a consistent way. It is clear also that acidification during transfer results in a slight change in peak area; because acidification aids in the transfer, this procedure will be specified for both samples and standards. The following procedure will be used for preparation of all samples and standards.

1. Collect samples on 0.45-μm PVC filters.

2. Ash loaded filter in low temperature asher.

3. Add 2 mL 6 N HCl to ash; agitate ultrasonically and let stand 3 minutes.

4. Add 2 mL 2-propanol containing 600 μg α-Al_2O_3 and agitate ultrasonically for 2 minutes.

5. Mount Ag filters under 8-mm bore filtering tower and add approximately one-half inch 2-propanol with vacuum off.

6. Pour sample on top of liquid in tower; apply vacuum; do not allow all liquid to pass.

7. Wash beaker with 2-propanol; add washes to tower.

8. Draw all liquid through Ag filter; air dry filter.

9. Conduct XRD analyses.

Determination of Collection Efficiency

The performance of a 10-mm nylon cyclone in the collection of talc was evaluated by loading talc onto Metricel filters in the dust generation system for seven hours. Six cassettes had nylon cyclones attached and three had no cyclones. The data are presented in Table 77. About 78% of the talc, all of which was respirable, passed through the cyclone, which is functioning much like a human lung. The nylon cyclone will be part of the sampling apparatus

Table 76. Evaluation of sample handling procedures for talc.

Sample	Sample Weight µg	Peak Area/Sample Weight 002	006
A1A	321.1	46.07	19.87
A1B	304.3	39.41	17.73
A1C	320.0	43.59	18.48
mean ± SD		43.02 ± 3.37	18.69 ± 0.77
A2A	320.2	39.45	16.69
A2B	316.2	41.91	16.66
A2C	302.0	42.80	15.50
mean ± SD		41.39 ± 1.23	16.28 ± 0.48
B1A	297.4	45.04	18.93
B1B	312.6	44.55	18.27
B1C	301.8	39.59	17.64
mean ± SD		43.06 ± 3.01	18.28 ± 0.65
B2A	309.0	38.94	12.74
B2B	313.4	43.24	17.09
B2C	319.7	39.10	15.45
mean ± SD		40.43 ± 1.72	15.09 ± 1.55
C1A	317.8	40.48	17.86
C1B	305.6	44.54	18.44
C1C	338.9	38.01	17.96
mean ± SD		41.01 ± 3.30	18.09 ± 0.30
C2A	306.6	38.18	12.51
C2B	300.8	32.00	14.38
C2C	307.4	39.47	15.47
mean ± SD		36.55 ± 3.99	14.12 ± 1.49

First character: A = TA-99 talc, as received
B = TA-99 talc, plasma ashed
C = TA-99 talc, plasma ashed in the presence of PVC

Second character: 1 = Acidified before transfer to Ag filter
2 = Not acidified

Third character: A, B, C - triplicate analyses.

Table 77. Performance of a nylon cyclone in the collection of talc.

Sample *	$\mu g/m^3$ talc	Sample	$\mu g/m^3$	Sample †	$\mu g/m^3$
1C	646	7	813	10B	0
2C	602	8	796		
3C	624	9	802		
4C	639				
5C	576				
6C	654				
mean ± SD	624 ± 30		804 ± 9		
% RSD	4.8		1.1		

* Nylon cyclone attached

† Blank

Table 78. Collection efficiency for talc.

Cassette	filter 1	back-up pad 1	filter 2
1	111.5	0	0
2	134.4	0	0
3	108.3	0	0
4	103.9	0	0
5	112.0	0	0
6	106.1	0	0

for the proposed method.

Breakthrough of talc from the Metricel filter was determined by placing two filter-backup pad pairs in series in each cassette and quantifying talc on the first filter, its backup pad, and the second filter. The data are presented in Table 78. No breakthrough was observed in any of the cassettes.

Determination of the LAQL

The lowest analytically quantifiable level, LAQL, was determined for talc and for talc co-deposited with α-Al_2O_3. Samples of talc were prepared at 1 X, 2 X, 10 X, and 50 X, where X was as described previously, and were analyzed according to the procedure described previously. The data are presented in Table 79. LAQL is determined by interpolation of the data in Table 79, accomplished graphically with a logarithmic plot of % RSD versus µg talc per filter, Figure 18. LAQL for the 006 peak is about 30 µg per filter and for the 002 peak is about 50 µg per filter.

Calibration curves, log µg talc versus log peak area (accumulated counts), were prepared from the LAQL data in Table 79 and are presented in Figure 19. A series of samples was prepared and analyzed by gravimetry and by X-ray diffraction as a check on recoveries. These results are presented in Table 80. Recoveries were satisfactory for the 006 peak, but slightly biased for the 002 peak.

Samples of talc co-deposited with 600 µg α-Al_2O_3 were then prepared and LAQL determined. The data are presented in Table 81. LAQL was found to be about 25 µg for the 006 peak and 40 µg for the 002 peak.

An important observation may be made concerning the values of X and LAQL, presented in Table 82. When no carrier is present, there is a significant difference between X and LAQL, yet when α-Al_2O_3 is present, there is little difference. Also, while X is much higher in the presence of a carrier than in its absence, there is little difference in LAQL in the absence or presence of a carrier. This suggests that while co-deposition of α-Al_2O_3 with the talc sample results in a loss of signal intensity, it aids in reproducible deposition and makes instrumental reproducibility the limiting factor.

Evaluation of the Stability of Loaded Filters

Filters were spiked with 160 µg talc and analyzed either one day or fourteen days after preparation. Because stability in the cassette during transport was considered most important to evaluate, filters were left in the cassettes and ashed just prior to analysis. The results are presented in Table 83. At the ninety-five percent probability level, the results are the same on day one and day fourteen, so the spiked samples are stable over a fourteen-day period.

Filters were loaded with talc in the dust generation system; during loading the humidity was maintained at 80%. On days one, seven, and fourteen, six filters were ashed and prepared for X-ray diffraction analysis. Each was analyzed for talc, and the results are presented in Table 84.

Table 79. LAQL for talc.

Sample Series	µg Talc	002 Mean	002 SD	002 % RSD	006 Mean	006 SD	006 % RSD
70	9.9	433	208	48.0	225	85	38.0
71	19.7	963	170	17.7	446	56	12.7
72	98.4	4607	111	2.4	1852	108	5.8
73	495.0	18995	1031	5.4	7979	346	4.3

Table 80. Recoveries of talc.

Sample	µg talc gravimetric (taken)	µg talc XRD-002 (found)	Recovery	µg talc XRD-006 (found)	Recovery
J1	280.3	290	1.04	270	0.96
J2	247.6	300	1.21	275	1.11
J3	265.0	310	1.17	285	1.08
J4	272.4	300	1.10	295	1.08
J5	251.7	285	1.13	275	1.09
J6	294.4	340	1.15	275	0.93
J7	318.1	340	1.07	370	1.16
J8	321.6	340	1.06	320	1.00
J9	342.4	380	1.11	335	0.98
Mean			1.12		1.04
SD			0.06		0.08
% RSD			0.05		0.08

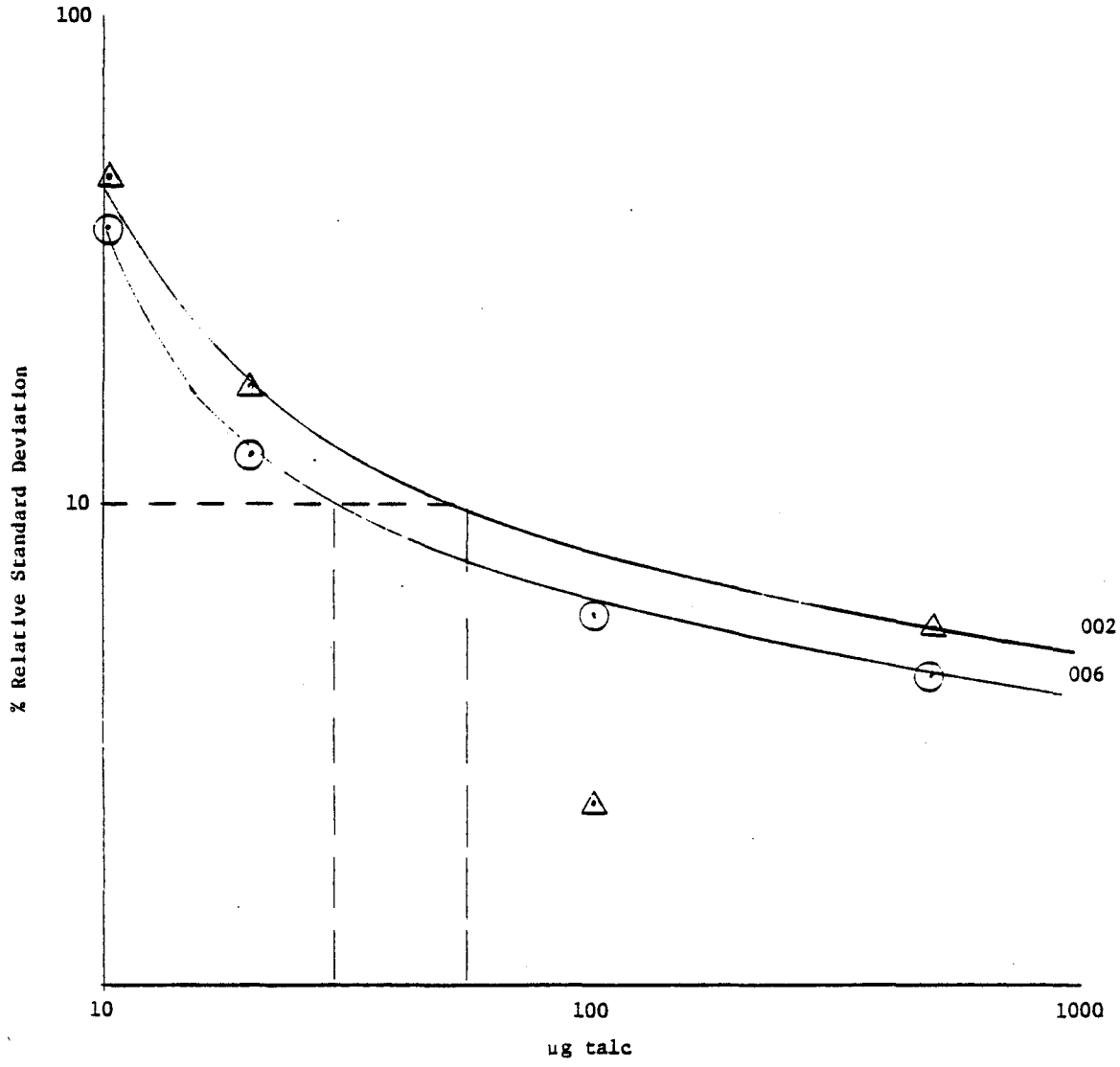

Figure 18. Evaluation of LAQL for talc.
(log-log plot)

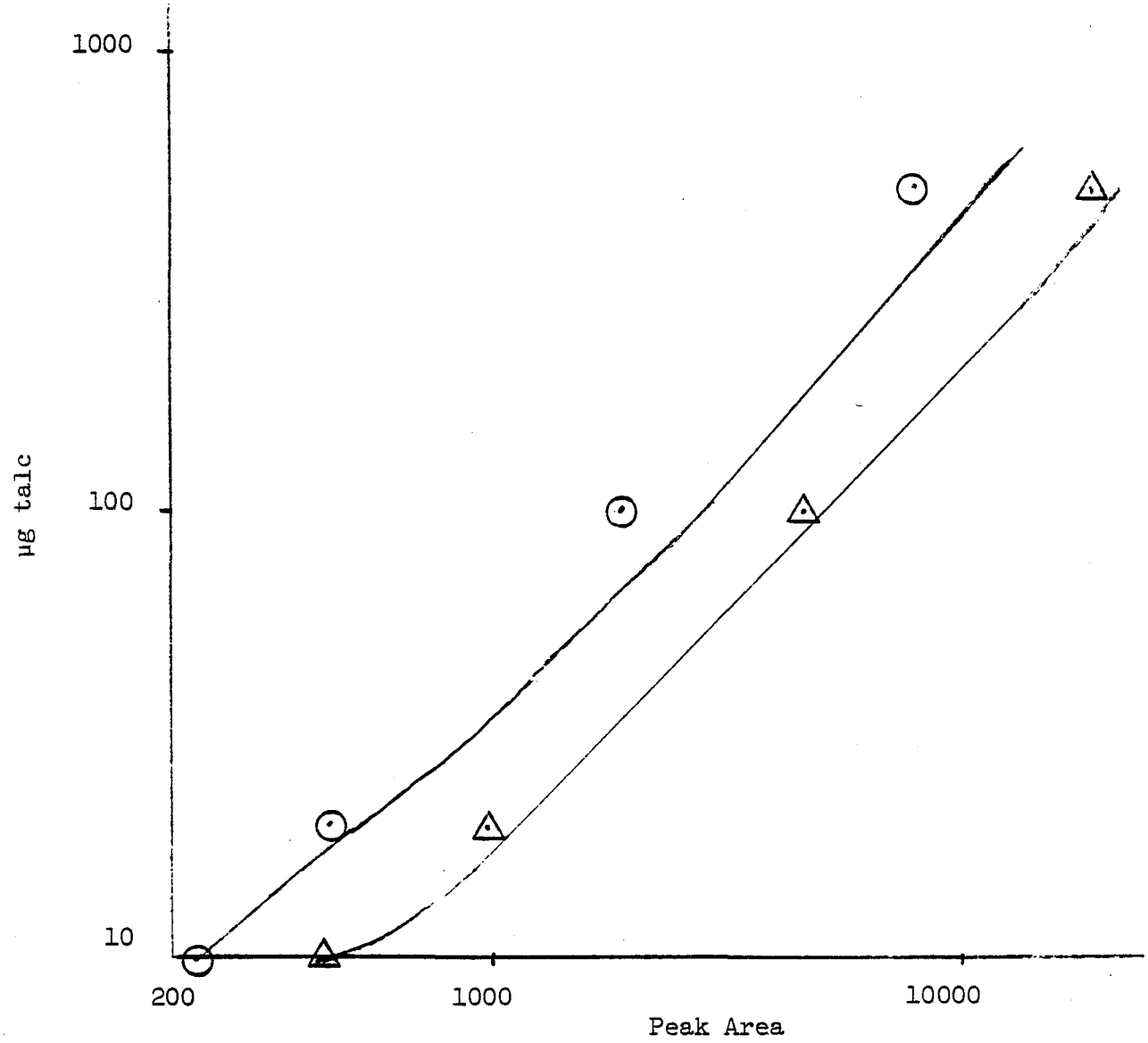

Figure 19. Calibration curves for talc determination by XRD.
(log-log plot)

Table 81. LAQL for talc co-deposited with α-Al_2O_3.

Sample Series	µg Talc	Peak area, 002			Peak area, 006		
		Mean	SD	% RSD	Mean	SD	% RSD
α 81	30.9	706	81	11.5	393	37	9.4
α 82	60.8	1217	108	8.9	765	53	6.9
α 83	125.0	2235	170	7.6	1485	80	5.4
α 84	247.0	4203	220	5.2	2772	128	4.6

Table 82. Comparison of X and LAQL levels.

	X, µg	LAQL, µg
No Carrier		
002	12	50
006	8	30
α-Al_2O_3 Carrier		
002	35	40
006	25	25

Table 83. Stability of filters spiked with talc.

Sample	µg talc taken	002 µg talc found, day 1	006 µg talc found, day 1
91A	160	159	153
91C	160	168	166
91D	160	168	158
91E	160	161	156
91F	160	155	158
91G	160	159	165
mean		162	159
SD		5	5
% RSD		3	3

Sample	µg talc taken	002 µg talc found, day 14	006 µg talc found, day 14
91H	160	155	157
91I	160	173	157
91J	160	166	175
91K	160	155	152
91L	160	152	151
91N	160	148	151
mean		158	157
SD		9	9
% RSD		6	6

Table 84. The stability of generated filters for talc.

Sample	µg/m^3 talc found, 002 day 1	006 day 1
9	302	249
10	274	298
11	267	285
12	278	306
13	302	325
15	289	262
mean	285	288
SD	15	28
% RSD	5	10

Sample	µg/m^3 talc found, 002 day 7	006 day 7
17	254	220
19	263	228
20	268	254
21	315	288
23	312	284
24	317	320
mean	288	266
SD	29	38
% RSD	10	14

Sample	µg/m^3 talc found, 002 day 14	006 day 14
2	255	221
4	293	228
5	275	226
6	235	235
7	270	225
8	274	241
mean	267	229
SD	20	8
% RSD	7	3

At the 95% probability level, the results are the same days one, seven, and fourteen for the 002 peaks. For the 006 peaks, the measured value is significantly smaller on day fourteen. Based on the data collected for the 002 peaks, the samples appear stable over the fourteen-day period.

Evaulation of the Method

Six filters were spiked at each of three levels of talc, 160 µg, 315 µg, and 608 µg. Each filter was analyzed and analytical recoveries and precision calculated. The results are presented in Table 85. Precision is satisfactory in all cases; analytical recovery is satisfactory in all cases except the 002 peak of the highest level, where results are high.

Six filters were loaded in the dust generation system at each of three levels of talc. The filters were ashed and analyzed and the precisions calculated. The results are presented in Table 86. The precisions for the generated samples are not acceptable according to the criteria for validation. Careful examination of the data suggests that the problem lies in the generation system, not in the analytical method; this is supported by the observation that the standard deviations for the gravimetric determination are of the same order of magnitude as those for the X-ray method. In fact, normalization of the X-ray data to the gravimetric data suggests that the analytical method is very reproducible. These data are presented in Table 87. Sample fourteen has been eliminated from this consideration because of incorrect calibration of the sampling port. The failure to meet the validation criteria occurred in the sampling phase, not the analytical phase.

Examination of a Different Talc

In conducting this study, application to a variety of talcs was limited by the availability of respirable materials. At the concentrations where this focussed (tens of micrograms), use of material with a particle size greater than 5-µm results in statistical difficulties due to the limited number of crystallites which contribute to the diffraction pattern (36). For this reason, development and evaluation of the method for talc was conducted with TA-99 talc which meets the respirable defintion. Another talc of fine but unknown particle size, NYTAL 400, was examined using this method. Samples containing 606 µg NYTAL 400 were prepared by spiking and analyzed by the developed method. Qualitative examination showed the presence of tremolite, chrysolite, and talc. The 006 peak of talc showed severe interference from the 310 peak of tremolite, and the 002 peak showed partial interference from the 020 peak of tremolite.

The 002 peak of each sample was scanned as in the TA-99 studies, and previously obtained TA-99 standard data were used in the quantification. The 002 talc peak was integrated over a 1° - 2θ range, terminating with a reading 0.2° - 2θ past the highest individual datum in the talc peak. Background was quantified by integrating the 0.5° - 2θ region immediately below the peak area and multiplying by two.

Table 85. Evaluation of the analytical method for talc.

Sample	Talc µg taken	Talc µg found 002	Recovery	006	Recovery
91A	160	159	0.99	153	0.96
91C	160	168	1.05	166	1.04
91D	160	168	1.05	158	0.99
91E	160	161	1.01	156	0.98
91F	160	155	0.97	158	0.99
91G	160	159	0.99	165	1.03
mean		162	1.01	159	1.00
SD		5	0.03	5	0.03
% RSD			3		3
94B	315	291	0.92	305	0.97
94C	315	308	0.98	322	1.02
94D	315	328	1.04	310	0.98
94E	315	318	1.01	320	1.02
94F	315	332	1.05	324	1.03
94G	315	310	0.98	308	0.98
mean		314	1.00	315	1.00
SD		15	0.05	8	0.03
% RSD			5		3
101A	608	728	1.20	628	1.03
101B	608	671	1.10	638	1.05
101D	608	738	1.21	634	1.04
101E	608	804	1.32	597	0.98
101F	608	747	1.23	640	1.05
101G	608	670	1.10	631	1.04
mean		726	1.19	628	1.03
SD		51	0.08	16	0.03
% RSD			8		3

Table 86. Evaluation of the sampling and analytical method for talc.

Sample	µg/m^3 talc found	
	002	006
7	245	245
8	109	112
12	135	130
14	109	103
17	111	140
19	77	99
mean	131	138
SD	59	55

Sample	µg/m^3 talc found		
	002	006	Gravimetric
8	726	851	666
9	765	869	722
12	583	679	536
14	1451	1264	724
18	882	1042	
19	849	895	
mean	876	933	660
SD	301	199	91

Sample	µg/m^3 talc found	
	002	006
8	2636	2726
9	2818	3020
12	2482	2929
13	3695	3919
17	4204	4545
18	3202	3371
mean	3173	3418
SD	668	693

Table 87. Normalization of analytical data for talc, $\mu g/m^3$.

Sample	002	Gravimetric	Ratio
8	726	666	1.09
9	765	722	1.06
12	583	530	1.10

Table 88. Analysis of Nytal- 400 for talc.

Sample	002 peak, net	µg talc
N400-A	1494	90.3
N400-B	1516	91.7
N400-C	1450	87.7
N400-D	1564	94.6
N400-E	1673	101.0
N400-F	1378	83.3
mean ± SD		91.4 ± 6.0

The data are presented in Table 88. The average value for talc, 91.4 μg, is 15.1 percent of the total sample, compared to the manufacturer's reported value of 20 to 40 percent talc.

Summary and Conclusions

A new method for the sampling and analysis of airborne talc has been developed and evaluated. Sampling consists of drawing air through a 10-mm nylon cyclone attached to a personal sampling device containing a 0.45-μm pore-size Metricel filter. The loaded filter is radio-frequency ashed, transferred to a silver membrane filter, and analyzed by X-ray diffraction. Samples are stable in storage for fourteen days. The analytical method satisfies the criteria for validation, but the overall sampling and analytical method does not. Additional work is needed in the sampling part of the method. Further work on the analytical method is needed to apply it to talcs other than the relatively high purity cosmetic and pharmaceutical grades. The possibilities of using one of the α-Al_2O_3 lines as an internal standard or adding another substance to the α-Al_2O_3 for that purpose should be explored. Correction for matrix absorption may be possible with the use of an internal standard or a substrate standard (32,37). The method of standard additions may be applicable to bulk respirable material to generate standards appropriate to the analysis of personal samples of the same composition.

WOOD DUST

Wood dust is a potentially hazardous substance found in some workplace environments. In recognition of the risks involved for workers, NIOSH has recommended a standard of 2 mg wood dust/m^3 as a maximum allowable concentration. The OSHA standard is 1.5 mg/m^3 (total dust) or 5 mg/m^3 (respirable dust). The method described here has been developed to provide a means of quantifying wood dust in the atmosphere. In the following sections, the experiments performed in the development, evaluation, and validation of the wood dust method are described (38). Experimental procedures and results are also described in the Sampling and Analytical Method, Backup Data and Sampling Data Sheet on this substance.

EXPERIMENTAL

The following is a list of the materials used in performing the experiments described in this section:

Reagents:

1. Glass fiber filters, 37-mm Gelman AE
2. Wood dust, fine, mixed woods, obtained from NIOSH - Morgantown, described in the next Section.
3. Concentrated H_2SO_4, Baker Reagent Grade.

Instruments:

1. Microbalance, Cahn model 26
2. Weighing room, capable of maintaining a controlled environment of 70 °F and 40-45% relative humidity
3. Class A volumetric pipettes, various sizes
4. Glass petri dishes, Kimax 60-mm x 15-mm
5. Crystallizing dishes, Pyrex 190-mm x 100-mm
6. Humidity chamber, a plexiglass container measuring 38 cm x 22 cm x 23 cm
7. Plastic filter holder cassettes, 37-mm Millipore

8. Oven capable of maintaining 105 °C ± 2 °C

9. Fluidized bed aerosol generator, Thermo Systems, Inc., Model 3400

10. Laminar flow box, containing 25 orifices calibrated to flows of approximately 1.7 SLPM.

11. Vacuum Oven

Definition of Analytical Conditions

Before the wood dust method could be developed, it was necessary to define the conditions and parameters under which the experiments would be performed (39). The potential for change in mass of the samples was of primary concern in the gravimetric method. The problem of interferences was another consideration.

The wood dust used in all experiments is a mixture of varieties of wood and was originally collected in a furniture factory. Likely major components of the dust were pine, walnut, and cherry. This dust was sized at NIOSH - Morgantown into coarse and fine fractions with a high capacity cyclone, with an effective cut diameter of 10 μm for 50% of the particles. The fine fraction which passed through this cyclone is the wood dust that was used for all experiments.

An experiment was performed to determine the size distribution of the wood dust. An Andersen impactor was used to separate the dust into size ranges, which were quantified with particle size cutoff values characteristic of the impactor (40). Slightly over one half of the wood dust comprised of particles greater than 21 μm diameter. Approximately 23% is in the 9-21 μm range, and the remaining 27% is below 9 μm. The data are presented in Table 89.

The feasibility of pyrolysis of the samples was examined to reduce the possibility of interferences from other dusts. The filters could be weighed, the samples collected and weighed, then the wood dust pyrolyzed and the filter weighed again. Particulates that are stable to pyrolysis would no longer interfere, the weight of wood dust would be the weight after collection minus the weight after pyrolysis.

Experiments on wood dust were undertaken to optimize the pyrolytic conditions. The wood dust was found to be almost completely pyrolized when heated to 450 °C for 30 minutes. The glass fiber filters, however, changed in mass in an inconsistent fashion, varying as much as 100 μg between their initial and final weights. Because of these problems in the stability of the filters, it was decided that the pyrolysis step should not be part of the analytical method.

Table 89. Wood dust particle sizing.

Stage	mass (mg)	% of total	size range
0	4.8	50.4	> 21.3
1	0.83	8.7	13.3 - 21.3
2	1.32	13.9	9.0 - 13.3
3	0.91	9.6	6.2 - 9.0
4	0.72	7.6	4.0 - 6.2
5	0.48	5.0	2.0 - 4.0
6	0.42	4.4	1.3 - 2.0
7	0.04	0.4	0.87 - 1.3
8	0.00	00.0	0.87

Other experiments were conducted to determine the effects of humidity on wood dust and on the glass fiber filters. Five sulfuric acid solutions were made with varying proportions of acid and deionized water; these solutions, when placed in a closed chamber resulted in controlled humidity atmospheres. The density of each solution was measured gravimetrically, and the humidity at equilibrium determined. Twelve glass fiber filters were equilibrated under a controlled climate (70 °F, 40% relative humidity) for 16 hours. Eight of these filters were spiked with approximately 800 μg of wood dust. The other four filters were used as blanks.

The following procedure was repeated for each of the five sulfuric acid solutions:

1. About 300 mL of the sulfuric acid solution was placed in a crystallizing dish. The dish was put in the humidity chamber, the chamber was closed, and the atmosphere in the chamber was allowed to equilibrate for at least 24 hours.

2. The 12 filters were equilibrated at 70 °F and approximately 40% relative humidity for at least 12 hours, followed by weighing on the microbalance. The filters, in petri dishes, were placed on a rack in the humidity chamber with the tops of the petri dishes removed. The filters were left in the chamber for at least 16 hours.

3. The filters were removed from the chamber and weighed immediately.

4. The filters were dried in an oven at 105 °C for two hours, equilibrated at 70 °F and approximately 40% relative humidity for two hours, and weighed again.

5. The filters were dried in an oven at 105 °C for 14 more hours, equilibrated at 70 °F and approximately 40% relative humidity for two hours, then weighed.

The measured densities of the sulfuric acid solutions, together with the humidity that each of the solutions will generate are listed in Table 90 (41). These solutions were used to produce the various humidities for the study.

Table 91 lists the changes in mass for each filter under the different humidities and drying conditions. Given for each filter are the spike amount, the mass change after 0 hours drying time (after immediate removal from the humidity chamber), after 2 hours drying time, and after 16 hours total drying time.

Table 92 gives the average and standard deviations of the changes in mass for both the spiked and blank filters listed in Table 91. Weighing after 16 hours of drying from 44% RH could not be accomplished due to a malfunction of the controlled temperature/humidity weighing room. Also, loss of some wood

Table 90. Sulfuric acid solutions used in humidity study for wood dust.

Measured Density	Relative Humidity
1.20	80%
1.25	70%
1.37	44%
1.40	38%
1.50	19%

Table 91. Wood dust humidity study (all masses in micrograms).

Change in Mass at Given Humidity																	
Humidity		19%			38%			44%			70%			80%			
Hours Drying Time		0	2	16	0	2	16	0	2	16	0	2	16	0	2	16	
Filter	Spike Amt.																
1	749	3	-52	-53	13	- 9	-12	25	7		49	15	29	61	16	- 8	
2	735	4	-53	-58	60	40	29	25	10		49	14	7	56	8	-34	
3	752	- 8	-70	-74	12	-11	-18	24	8		56	16	6	66	11	-13	
4	808	-25	-79	-74	12	- 7	-22	16	3		64	21	15	60	11	-18	
5	764	- 5	-57	-39	9	-14	-22	21	2		61	16	7	61	6	-16	
6	801	- 3	-56	-42	9	-14	-21	21	3								
7	844	- 2	-49	-55	10	- 5	- 5	16	6		62	49	18	69	17	2	
8	781	-16	-62	-69	9	-14	-14	17	10		62	22	12	61	8	-13	
9	-	- 1	-48	-55	10	- 1	9	15	9		45	16	10	52	16	- 2	
10	-	- 4	-47	-46	11	- 4	8	12	0		40	15	10	54	14	- 6	
11	-	3	-35	-42	10	- 6	- 3	13	1		40	19	10	47	14	- 6	
12	-	- 2	-48	-42	7	- 8	- 5	8	1		41	16	11	54	12	- 8	

Table 92. Wood dust humidity study summary.

Average Change In Mass (µg) At Given Humidity															
Humidity	19%			38%			44%			70%			80%		
Hours Drying Time	0	2	16	0	2	16	0	2	16	0	2	16	0	2	16
Mean for spiked filters	-10	-60	-58	17	-12	-14	21	6		58	22	13	62	11	-14
SD	12	10	13	18	31	8	4	3		6	12	8	4	4	11
Mean for blanks	- 4	-44	-54	9	- 6	- 2	12	3		41	17	10	52	14	- 5
SD	3	6	13	1	2	7	3	4		2	2	1	3	2	2

dust from filter #6 invalidated the data for that filter at the 70% and 80% humidities.

The results of this experiment indicate that changes in the mass of spiked filters on the order of 10% of the NIOSH recommended standard (800 µg wood dust for a 4-hour sample) can be expected due to varying humidity, if precautions are not taken. This study also indicates that varying humidities affect the mass of the filters to a much greater extent than the mass of the wood dust on the filter.

The variation in the mass of a filter due to humidity appears to be the limiting factor in obtaining accurate and precise quantification of wood dust concentrations.

With the proper precautions, these effects can be minimized. To achieve consistent and meaningful results, exposed filters should be dried at 105 °C for a minimum of 16 hours, followed by equilibration for a minimum of 12 hours in a controlled climate of 70 °F and a consistent humidity in the 40% - 45% range, and then weighed.

Determination of Instrumental Precision

Instrumental precision was determined by repetitive weighing of a single filter (Gelman A/E glass fiber) on a Cahn 26 automatic electrobalance. The mean weight of the filter and the standard deviation were 0.0816384 gm ± 0.0000018, or 0.0022 % RSD.

Determination of LAQL

Twenty-two glass fiber filters were heated to 450 °C for one hour. The filters were placed in a climate controlled weighing room (70 °F and 40% relative humidity), where they were alowed to equilibrate for 12 hours, then weighed on a Cahn 26 microbalance. Eighteen of the filters were spiked with wood dust which had been conditioned previously by heating to 105 °C for two hours, then equilibrated for 24 hours under controlled climate conditions. The wood dust was placed on the filters with small steel forceps. The 18 filters were spiked at three levels: six with 80 µg of wood dust; six with 160 µg; and six with 800 µg. The 22 filters were then weighed as samples.

The experimental data are summarized in Table 93. The spike level of 80 µg, if collected by a personal sampling device during a 4-hour period at 1.7 liters/minute, would correspond to 0.2 mg/m^3, which is one tenth the NIOSH recommended standard for wood dust. LAQL, the level at which 10% analytical precision is attained, is below this level.

COLLECTION EXPERIMENTS

A series of experiments were performed to determine the behavior of wood dust with several collection devices. In a preliminary experiment to simulate the wood dust fraction that would be ingested into a human lung, nylon cyclones were attached to filter cassettes. The data are given in Table 94. Little wood dust was collected with this arrangement. This is most likely due to

Table 93. LAQL for wood dust.

Wood Dust Level	Filter	Spike µg	Found µg
1 X NIOSH-recommended Standard	1	796	788
	2	826	826
	3	832	831
	4	806	806
	5	804	802
	6	831	830
0.2 X NIOSH-recommended Standard	7	159	158
	8	160	158
	9	162	157
	10	162	158
	11	158	151
	12	159	158
0.1 X NIOSH-recommended Standard	13	81	79
	14	79	74
	15	79	78
	16	80	79
	17	79	74
	18	78	76
Blank	19	0	0
	20	0	-4
	21	0	0
	22	0	4

Summary of Recoveries

Filters	Spike Level, µg	% Recovery	% RSD
1-6	800	99.7	0.36
7-12	160	98.0	1.4
13-18	80	96.9	2.7

Table 94. Wood dust collection with cyclones.

Sample*	Wood Dust $\mu g/m^3$	Sample	Wood Dust $\mu g/m^3$
1C	25.6	7 (no cyclone)	1000.0
2C	23.6		
3C	82.1		
4C	113.7		
5C	81.5		
6C	254.9		
Mean ± SD	96.9 ± 85.0		
% RSD	87.8		

* Samples 1C-6C were collected through a nylon cyclone.
Sample 7 was collected with no cyclone.

electrostatic charge, which may encourage the growth of large particles that are not collected.

As a substitute for the cyclones, multiple stage cassettes with a 5 μm-pore size polyvinyl chloride filter on top and a glass fiber filter below, forming a poor man's dichot, were examined (42).

The experimental results are given in Table 95. The masses of wood dust on the top filter range from 1700 to 2200 μg. The backup pads all lost weight. The bottom filter changed in mass randomly and by small amounts.

The very large losses in weight of the backup pads are probably due to their composition (cardboard) and their relatively high masses compared to the filters. The procedures of heating and equilibration may cause losses of moisture and/or volatile components. The effect of humidity changes on the mass of a backup pad has not been examined, and may be great. In view of this, the weight changes of the backup pads are not considered to be meaningful values for the purposes of this experiment. A visual examination of the backup pads was made, and no wood dust was visible.

The bottom filters changed slightly in mass, with an average weight loss for the six filters of -1.0 μg. This indicates no breakthrough of wood dust to the bottom filters.

From the results, it appears that essentially all of the wood dust was collected on the 5-μm filters. Few of the particles are smaller than 5 microns in size. Also, static charge may cause clumping of small particles into larger clusters which are collected on the filter. The multi-staged cassette does not result in effective separation of wood dust.

To determine collection efficiency of the glass fiber filters, twelve filters were preconditioned by placing them in cassettes and pulling approximately 1.7 liters/minute of air through them for one hour. The filters were equilibrated at 70 °F and 40% relative humidity for 12 hours, then weighed on the microbalance.

The 12 filters were assembled into 6 cassettes, 2 stages per cassette. Wood dust was loaded onto the filters at approximately 4.5 times the NIOSH recommended standard. The cassettes were open-faced during generation, and no backup pads were used. Relative humidity was maintained at about 85% during generation. The filters were dried, equilibrated and weighed by the procedure described previously.

Table 96 lists the results of the experiment. The average collection efficiency is greater than 98%, with no filter collecting less than 97.5% of the wood dust sample. The standard deviation for the six filters is less than 0.5%.

Evaluation of the Stability of Loaded Filters

Table 95. Collection of wood dust with a poor-man's dichot.

µg Wood Dust Found		
Top Filter	Backup Pad	Bottom Filter
1971.4	- 818	1.0
2225.0	- 982	-16.0
1737.8	- 620	9.3
2171.6	-1886	2.1
2027.7	- 735	- 7.8
1905.8	- 931	5.5

Table 96. Wood dust collection efficiency.

Wood Dust Found, µg		
Top Filter	Bottom Filter	Collection Efficiency
3763.5	69.7	0.9818
3636.3	85.8	0.9769
3710.4	54.9	0.9854
4000.6	73.3	0.9820
4292.3	59.3	0.9864
3652.5	75.1	0.9772
Mean		0.9816
SD		0.00398
% RSD		0.405

Stability studies were conducted on both spiked and generated filters. For the first stability study, six glass fiber filters were allowed to equilibrate overnight in a climate controlled room (70 °F and 40 - 45% RH). The filters were spiked with approximately 400 µg of wood dust, with the weighings done on a Cahn 26 microbalance.

The filters were stored in glass petri dishes except during weighings. The filters were re-weighed one day and 14 days after spiking.

The data from the experiment are presented in Table 97. Recoveries for the 1-day and 14-day weighings are within 3.1% of each other, which indicates that the spiked filters were stable for the length of the experiment.

In the generated stability study, six filters were preconditioned by placing them in cassettes and pulling approximately 1.7 liters/minute of air through them for one hour. The filters were dried at 105 °C for 16 hours and equilibrated at 70 °F and 40% relative humidity for 12 hours. The filters were weighed on the microbalance.

Wood dust was loaded onto the filters at approximately 0.5 times the NIOSH recommended standard. The cassettes were open-faced during generation, and no backup pad was used. The wood dust was generated at about 85% relative humidity.

The filters were dried, equilibrated, and weighed by the procedure described previously.

The loaded filters were weighed after 1 day, after 7 days, and after 14 days. Between weighings, the filters were stored in glass petri dishes under controlled climate conditions.

The results of the three sets of analyses are listed in Table 98. The criterion for acceptance is that the means of the six samples be within 10% of each other. The largest difference in the means is between days 1 and 14, where the difference is 5.9%, which is within the required 10% limit.

Validation of the Method

The validation was done in two parts--validation of the analytical method alone, and validation of the combined sampling and analytical method.

To evaluate the analytical method, eighteen glass fiber filters were allowed to equilibrate overnight in a climate controlled room (70 °F and 40 - 45% relative humidity). The filters were spiked at three levels with wood dust; six with approximately 400 µg, six with approximately 800 µg, and six with approximately 1600 µg. The filters were then weighed as unknown samples on a Cahn 26 microbalance.

The experimental data are summarized in Table 99. All three spike levels produced standard deviations of 0.5% or less, with recoveries within 0.4% of the expected values. These results satisfy the criteria for validation of

Table 97. Stability of spiked filters.

Filter	Taken µg	1 Day		14 Days	
		Found µg	% Recovery	Found µg	% Recovery
1	420	424	101.0	435	103.5
2	417	418	100.1	436	104.5
3	393	391	99.5	403	102.5
4	401	400	99.7	410	102.2
5	407	412	101.2	421	103.6
6	388	386	99.6	400	103.3
Mean			100.2		100.3
SD			0.7		0.8
% RSD			0.7		0.8

Table 98. Stability of generated filters.

Filter	Wood Dust Found, µg/m^3		
	Day 1	Day 7	Day 14
1	1.360	1.391	1.434
2	1.263	1.305	1.355
3	1.421	1.462	1.512
4	1.293	1.307	1.353
5	1.287	1.327	1.365
6	1.476	1.522	1.563
Mean	1.350	1.386	1.430
SD	0.0846	0.0901	0.08967
% RSD	6.3	6.5	6.27

Table 99. Validation of the analytical method for wood dust.

Filter	Taken	Found	% Recovery	Mean	SD	% RSD
1	796.4	798.5	100.3			
2	840.6	843.3	100.3			
3	814.4	812.3	99.7	100.1	0.3	0.3
4	829.3	832.6	100.4			
5	861.2	862.7	100.2			
6	839.5	838.4	99.9			
7	1546.7	1547.9	100.1			
8	1612.8	1613.2	100.0			
9	1567.9	1571.4	100.2	100.1	0.1	0.1
10	1625.6	1629.4	100.2			
11	1672.5	1676.0	100.2			
12	1597.5	1599.5	100.1			
13	421.1	419.2	99.5			
14	418.6	421.0	100.6			
15	418.0	418.8	100.2	100.4	0.5	0.5
16	414.5	417.7	100.8			
17	423.5	425.2	100.4			
18	389.6	392.2	100.7			

the analytical method.

For the validation of the sampling and analytical method, eighteen filters were preconditioned by placing them in cassettes and pulling approximately 1.7 liters/minute of air through them for one hour. The filters were dried at 105 °C for 16 hours and equilibrated at 70 °C and 40% relative humidity for 12 hours. The filters were weighed on the microbalance.

Wood dust was loaded onto the 18 filters in three sets of six; one set was loaded at the NIOSH recommended limit, one set at 0.5 times the limit, and one set at 2.0 times the limit. The cassettes were open-faced during generation, and no backup pad was used. The three generations of wood dust were done at a humidity of about 85%.

The filters were dried, equilibrated and weighed by the procedure described previously.

The data are presented in Table 100. At the three levels examined, the analytical method has a relative standard deviation of less than seven percent, which satisfies the criteria for validation.

As an independent check on the accuracy of the method, a small quantity of wood dust was spiked quantitatively with aqueous copper solution. Six samples were prepared in the dust generation system, were analyzed for wood dust by the gravimetric method, and were then digested and analyzed for copper by graphite furnace atomic absorption spectrophotometry. The results of this experiment are presented in Table 101. At the 99% probability level, there is no significant difference between the results found by the two methods.

SUMMARY AND CONCLUSIONS

The experiments decribed in this section were performed in order to develop and validate a method for sampling and analysis of airborne wood dust. The method chosen uses a gravimetric procedure, since wood dust is not a pure chemical compound and most other analytical methods are not applicable. As such, the method developed is subject to interference by other particulates which may be present in the sampling environment.

Experimental results show a pronounced effect on the mass of the filters when the humidity varies. This variation in humidity also affects the mass of the wood dust to a lesser extent. Because of these effects, filters are conditioned according to specific procedures before both the initial and final weighings. This involves drying of the filters to remove moisture and volatile components, followed by equilibration in a controlled atmosphere.

The loaded filters were shown to be stable over a 14 day period. This was true for both spiked and generated samples. The collection efficiency of the glass fiber filters used was greater than 97.5%. The method was successfully validated for both spiked and generated filters.

Table 100. Validation of the wood dust method - generated filters.

Wood Dust Level	Found µg	mg/m^3 (normalized for a 4 hour sample)
0.5 x NIOSH recommended standard	611.0	1.37
	552.3	1.26
	561.2	1.43
	559.6	1.27
	548.8	1.28
	598.4	1.47
	mean	1.35
	SD	0.090
	% RSD	6.7
1.0 x NIOSH recommended standard	935.5	2.10
	939.0	2.33
	1082.6	2.35
	971.7	2.39
	989.3	2.31
	970.0	2.22
	mean	2.28
	SD	0.106
	% RSD	4.6
2.0 NIOSH recommended standard	2033.0	4.82
	1866.4	4.47
	1646.2	4.30
	1703.1	4.16
	1994.6	4.52
	1962.1	4.60
	mean	4.48
	SD	0.232
	% RSD	5.2

Table 101. Analysis of wood dust by gravimetry and graphite furnace atomic absorption analysis.

Gravimetry µg wood dust found	µg copper expected	GFAAS µg copper found	% recovery
2286	1.273	1.409	110.7
1819	1.013	1.049	103.6
2142	1.193	1.092	91.5
2273	1.266	1.162	91.8
1923	1.071	1.025	95.7
2004	1.116	1.070	95.9
mean			98.2
SD			7.5
% RSD			7.7

CONCLUSIONS AND RECOMMENDATIONS

The methods for nickel, tungsten, soluble vanadium and wood dust have been fully validated during this study. Additional questions remain to be examined to accomplish validation of the method for arsenic, insoluble vanadium, and talc. Independent confirmation of the accuracy of the determination of arsenic should be undertaken. In addition, generation of reliable synthetic atmospheres of insoluble vanadium and talc should be pursued. When reliable atmospheres of these substances are available, the precision and accuracy of the sampling and analytical methods should be assessed.

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APPENDIXES

A - G

CONTENTS

APPENDIX A

AEROSOL GENERATION AND SAMPLING SYSTEM

The aerosol generation and sampling system used for the validation study has been designed specifically to simulate aerosol and vapor concentrations found in workplace environments. This system was used first for the collaborative testing of the NIOSH P&CAM 173 (1) and consisted of three components: an aerosol generator, a laminar flow chamber, and a filter sampling system. A diagram of the overall generation/sampling system is shown in Figure A-1. The aerosol generator produces dried particles which are diluted by filtered room air prior to their introduction into the flow chamber where turbulent flows are damped and laminar flows developed. At the bottom of the flow chamber generated particulates can be either collected by the filter sampling system or exhausted through a high-volume blower. Each component of the system is described in detail below:

Aerosol Generation

Several aerosol generation devices can be utilized in conjunction with this system. In the present study the following devices were used:

(1) Metal aerosols were produced by nebulizing aqueous solutions of their nitrate salts by means of the commercially available Environmental Research Corporation (ERC) Model 7330 Fluid Atomization Aerosol Generator. Figure A-2 outlines the ERC generator which utilizes a 3-jet Collison nebulizer. Regulated high pressure air (about 45 psi) from an external compressed air supply flows through a dryer, another pressure regulator, a filter and then is split into two parts, the atomizer air and the dilution air. The atomizer air nebulizes the metal-salt solution in the Collison nebulizer and carries the freshly-generated aerosol to the mixing chamber, mixes with dry dilution air, and passes into the charge neutralization chamber. In this chamber a Krypton 35 radioactive source produces bipolar ions to neutralize the static electric charges on the generated aerosol. After passage through the charge neutralization chamber the particulates are dried and have approximately an equilibrium Boltzmann charge distribution. The distribution of mass as a function of the particle size of aerosols generated with a three-jet Collison nebulizer, for dibutyl phthalate, a non-volatile liquid, is approximately log-normal with a particle size having a mean-mass diameter of 2.75 microns and a geometric standard deviation of 2.0. Approximately 95% of the particle mass is associated with particles with diameters less than 10.0 microns. When aqueous solutions of soluble compounds are atomized during this study, the particle size distribution shifts towards smaller particle diameters.

(2) When a test atmosphere of metal oxide fume was required, one of two fume generators was used in place of the fluid atomization generator. The devices used were all assembled in the laboratory from easily available parts. Two main designs were utilized. In the first, fumes are produced by thermal decomposition of aerosol particles generated from specific

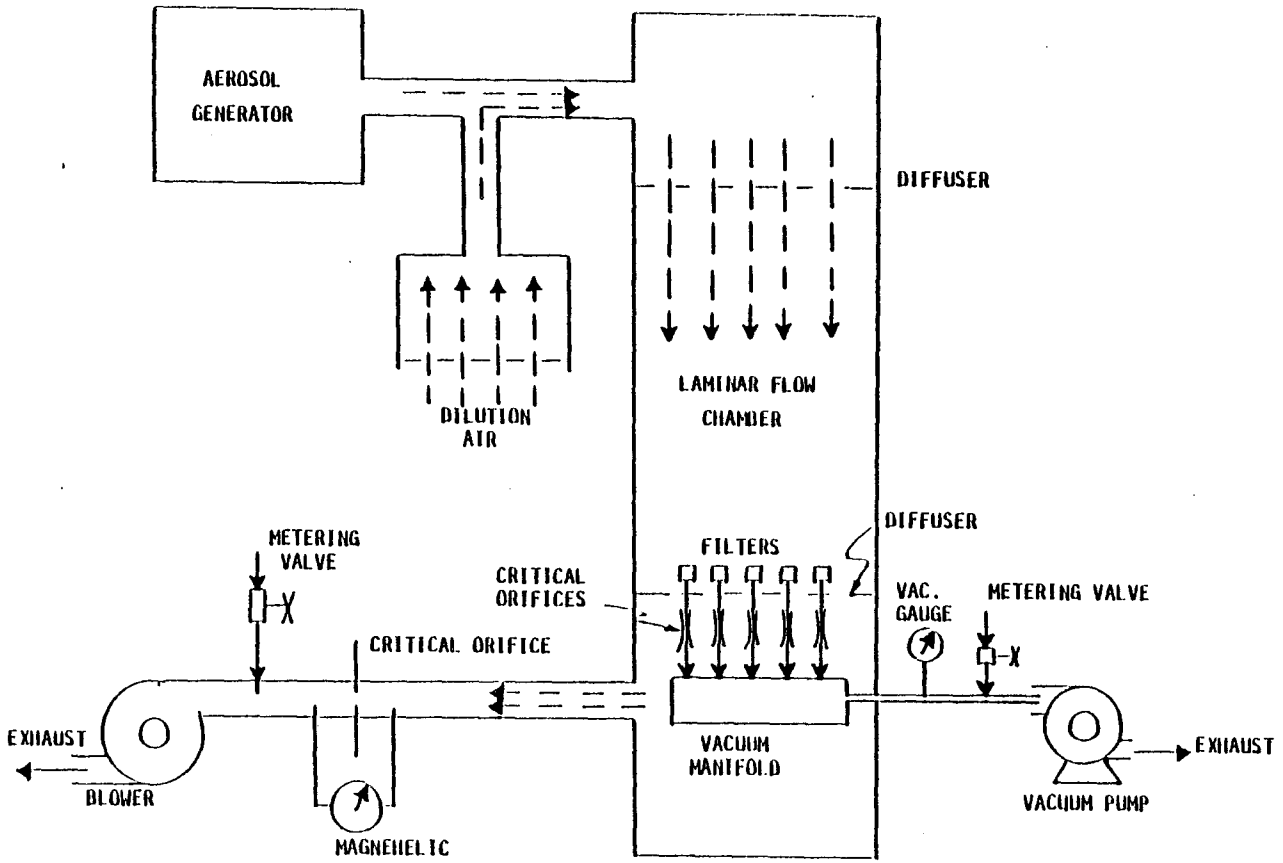

Figure A-1. Diagram of the aerosol generation and filter sampling system.

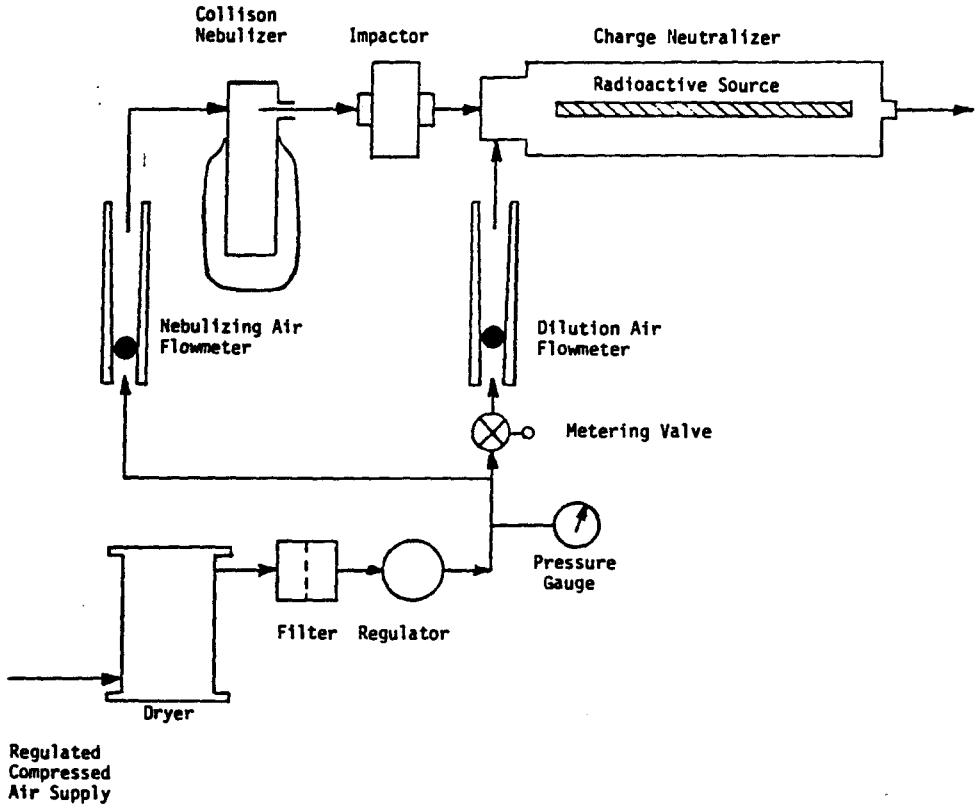

Figure A-2. Diagram of the ERC 7330 aerosol generator.

metal compounds (organic salts or chelates). Figure A-3 outlines the system used for the generation of V_2O_5 fumes. The Collison nebulizer is used to atomize an aqueous solution of the EDTA chelate of the metal. The atomization gas is compressed air. The stream first passes through a one inch i.d. quartz tube which is heated to 1100 °C. The flow must be sufficiently small to allow the particles to remain in the furnace long enough to achieve complete thermal decomposition. The metal oxide is then mixed with an appropriate amount of air to provide the final flow desired. Particles obtained by this method had diameter less than 0.025 μm.

The second type of fume generation system was based on direct sublimation of chemical compounds. Figure A-4 presents the system used for the generation of As_2O_3 fume. Because of the low fume production, this generator was not used with the regular laminar flow chamber but instead a special smaller chamber was constructed for the As_2O_3 fume sampling. The dimensions of this chamber were 1' x 1' x 2'. The temperature of the oven was 150 °C. This was the maximum temperature which could be used without excessive As_2O_3 concentration in the line. As shown in Figure A-4, the fumes were diluted with air immediately after generation. The median diameter of the As_2O_3 particles was not measurable with either the electric aerosol analyzer or the optical particle counter. This indicates that the size of the generated fume particles was below 0.007 μm in diameter.

(3) Aerosols of insoluble dust particles were generated by utilizing the TSI Model 3400 fluidized bed dust generator. Figure A-5 is a diagram of the fluidized bed generator.

The dust to be generated is stored in the powder reservoir. A bead chain passes through the powder and carries small quantities of the material into the fluidized bed. The powder chamber contains a rake assembly which passes through the powder, keeping the distribution even and in contact with the chain at all times. The bead chain is purged with clean air before it returns to the powder reservoir, preventing contamination from beads in the fluidized bed.

The fluidized bed chamber is filled with copper beads. Clean, dry air enters the bottom of the chamber and flows up through the beads, creating a 'boiling' effect. The powder that enters the fluidized bed on the bead chain is dispersed by the beads, breaking up agglomerates of the fine powder particles.

Laminar Flow Chamber

The dried and neutralized particles from the aerosol generation device are further diluted by filtered room air (filtered by an industrial grade HEPA filter with 99.97% efficiency) before injection into the top plenum of the laminar flow chamber. The chamber is a 61 x 61 x 183-cm rectangular box constructed of 1/16" thick 6061-T6 aluminum and includes a 30-cm plenum at the top and bottom. A perforated screen with 1/16" holes separates each plenum from the main chamber and damps out turbulent flows, thus aiding in the development of laminar flow. The bottom screen also supports twenty-five 37-mm diameter standard

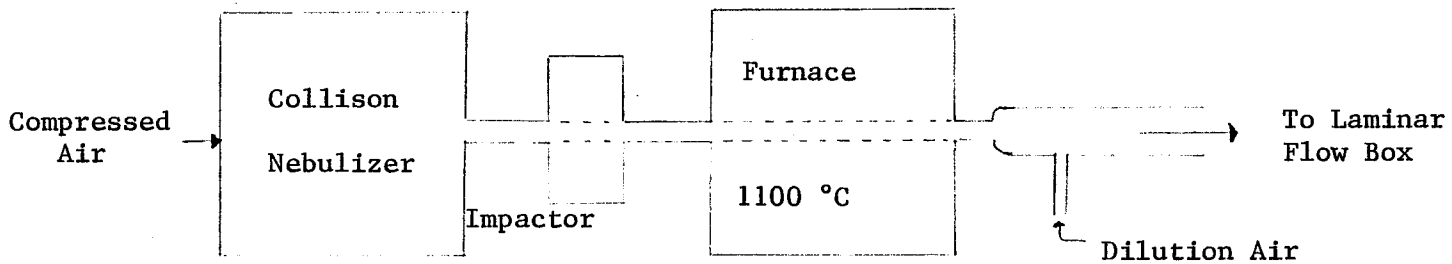

Figure A-3. Metal oxide fume generator.

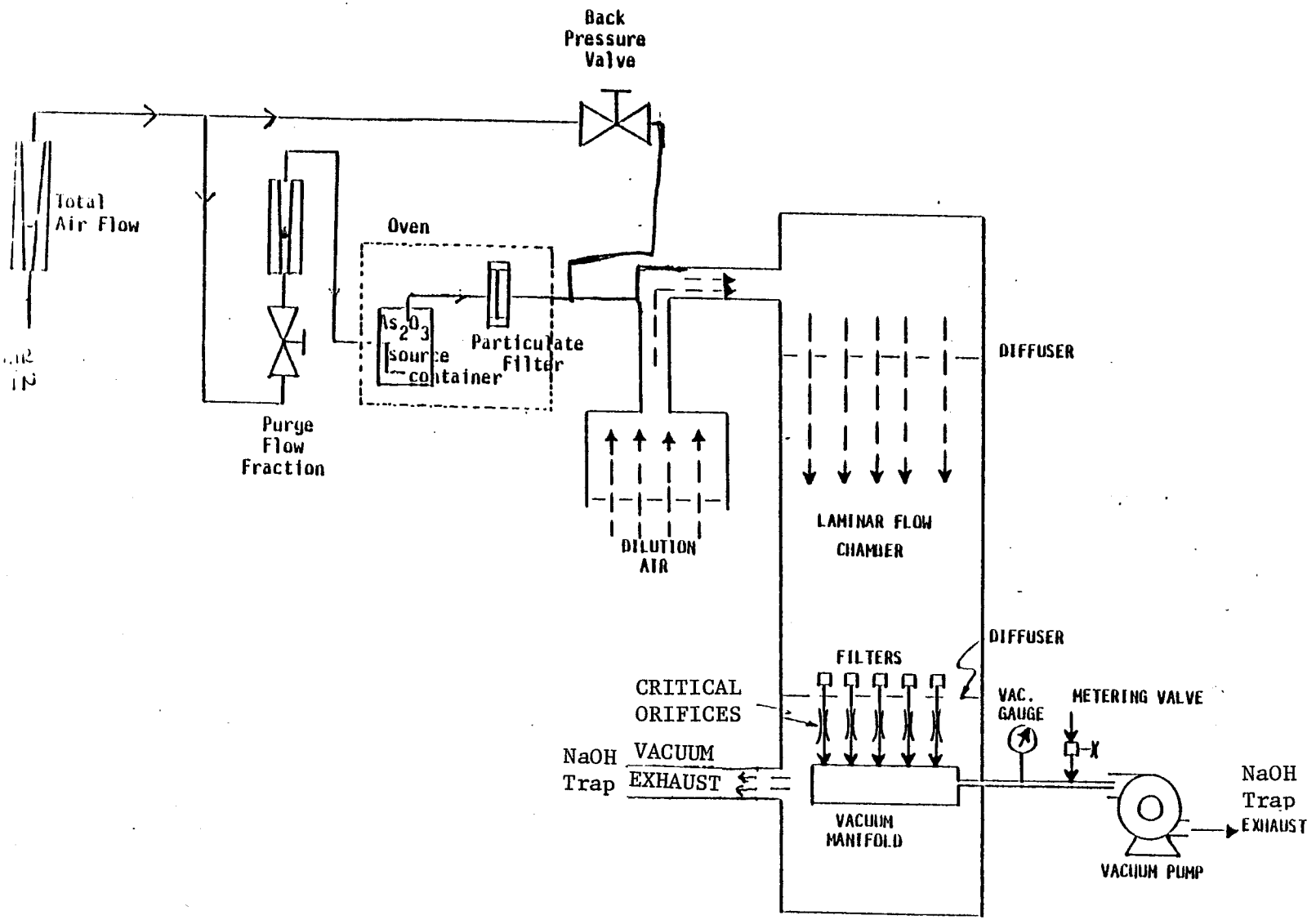

Figure A-4. As_2O_3 generation system.

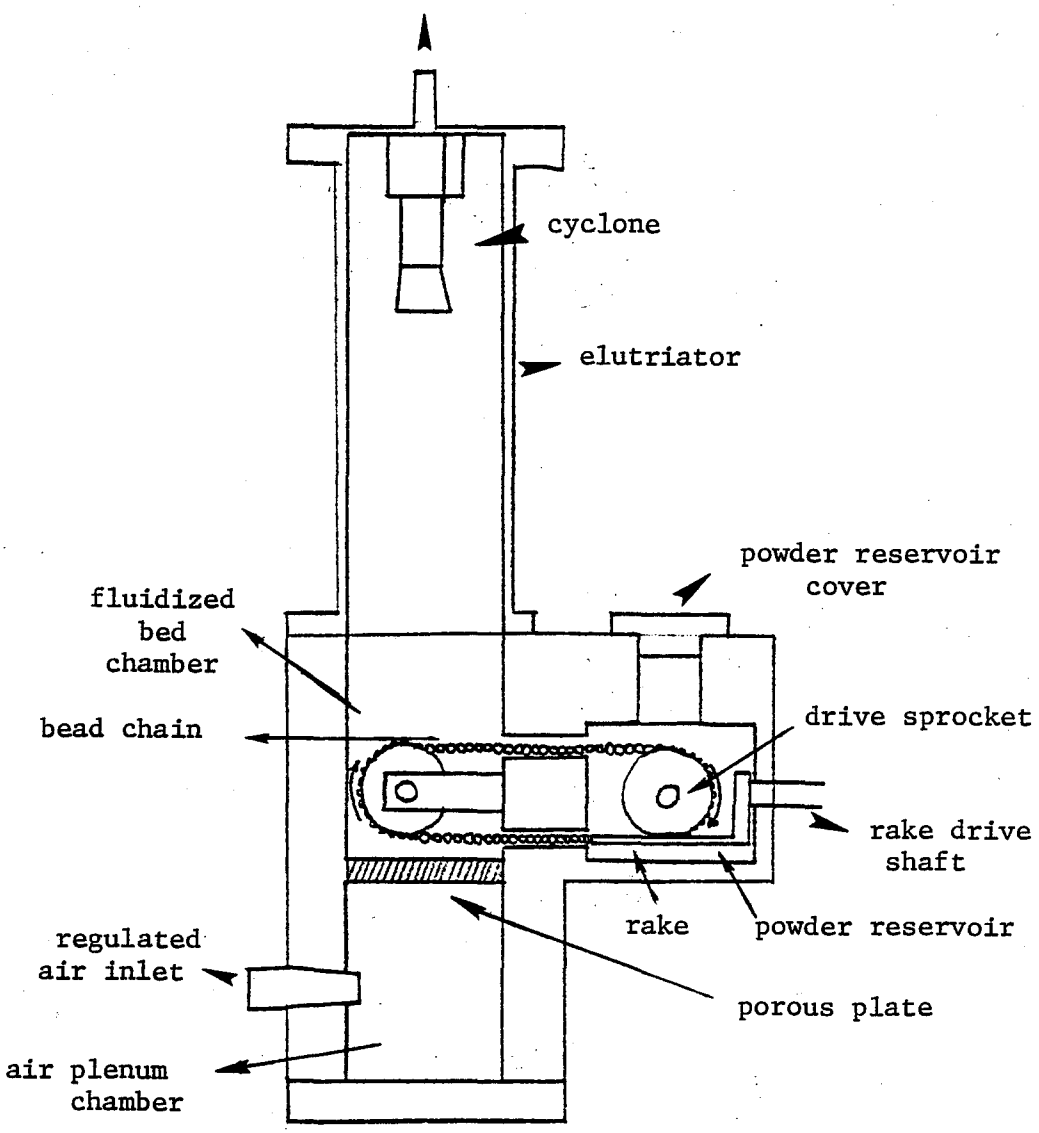

Figure A-5. Fluidized bed dust generator.
(Adapted from TSI Instruction Manual, Figure 2)

aerosol filter cassettes. The bottom half of the laminar flow chamber has a 45.7 x 45.7-cm opening with a clear acrylic door for convenient inserting, changing and viewing of the cassettes. Part of the flow of aerosol can be either collected by the twenty-five filters or pass through the bottom screen to the exit plenum. After the exit plenum, the flow of aerosol is filtered by another high efficiency HEPA filter and passes through a flow monitoring and flow control device before being exhausted through a high capacity blower. The purpose of this second HEPA filter is to remove the particles from the flow stream prior to being exhausted into the laboratory fume hood, thus minimizing contamination for the laboratory personnel as well as the environment. The exhaust flow is controlled so that the aerosol flow just above the filter cassettes is approximately isokinetic. Isokinetic sampling reduces turbulence in the laminar flow chamber, minimizes the probability of particle loss through aerodynamic size differentiation, and promises even mass deposition for each filter cassette independent of its position in the chamber.

Filter Sampling System

The sampling filter cassettes are connected by thick-wall plastic tubing to a vacuum manifold and then to a vacuum pump. Sample flows are carefully regulated by an in-line critical orifice located just downstream of the filters. Vacuum levels are monitored and controlled by a vacuum gauge and a metering valve. The filter cassettes used are transparent plastic filter holders (Millipore Corporation Model No. MAWP 037 A) Aerosol Analysis Monitors, preassembled with a 37-mm diameter filter composed of appropriate filter material and a backup pad if needed. Each plastic cassette consisted of a removable top section, and a removable middle retaining ring which seals the filter to the bottom section. The top and the bottom sections each have female Luer fittings which are used as the inlet and outlet ports. The bottom outlet is connected to a male Luer fitting that serves as an adapter between the cassette and the Tygon tubing leading to the vacuum manifold and serves as a holder for the flow regulating critical orifice. Twenty-five cassettes are thus mounted on the bottom perforated screen in the laminar flow chamber. After a sampling run is completed, the Luer fitting openings in the top and bottom sections are plugged with plastic stoppers, thus sealing and protecting the exposed filters from contaminants.

The critical orifices used in the filter sampling system are rated at 2.0 Lpm ± 10% with a minimum required vacuum of 12" of Hg. (Millipore Cat. No. XX50 000 20). However, in order to control the sample flows to greater accuracies, each individual orifice is calibrated with representative samplers in line, and quality control checks are made periodically. The downstream vacuum is also regulated at 20" of Hg to minimize flow variation due to vacuum level changes.

Size Distribution Measurements

The aerosol size distribution in the laminar flow chamber was monitored by continuous aerosol sizing instruments. The electric aerosol analyzer and the optical particle counter were used for this. These two techniques are individually discussed below.

Electric Aerosol Analyzer

For the lower region of the particle size distribution where optical techniques do not have the required resolution, a Thermo-Systems Model 3030 Electrical Aerosol Analyzer (EAA) was used to measure particle number concentrations for particulate sizes ranging from about 0.007 microns to 1.0 microns in diameter. The EAA measures the concentration of aerosol particles in specific size increments, in situ, by drawing a continuous sample of aerosol into a steady flow system, and charging the particles to an electrical mobility which is a function of the size of the particles. The particles are classified according to their aerodynamic mobility and the concentrations for each size category are determined by measuring the net electrical charge carried by that aerosol. The electrical mobility of a particle is defined as the particle velocity in the direction of an electrical field per unit field strength.

Optical Particle Counter

For particles in the size range from 0.5 microns to approximately 5 microns, the Royco Model 220 Optical Particle Counter (OPC) was used to measure the particle number density in four size increments. The Royco 220 utilizes a right angle light-scattering optical system to detect particles drawn continuously through a viewing volume illuminated by a Tungsten lamp. A photomultiplier tube located 90 ° from the optical axis of the focused light beam detects the light scattered from the particles, and generates a voltage pulse for each particle which passes through the viewing volume. The amplitude of the voltage pulse is a measure of the particle size. By using the Nuclear Data Model 1100, 256 channel Pulse Height Analyzer System (PHA), the photomultiplier voltage pulses can be differentiated, analyzed and stored as pulse height distributions and displayed on a Teletype Terminal as well as a Cathode-Ray Tube. These voltage pulse distributions are then converted to equivalent particle number versus incremental size distributions from which particle surface and volume distributions may be calculated, assuming a spherical geometry.

The conversion from voltage pulse height distribution is based on a calibration curve generated by measuring a pulse height distribution for particles with known sizes. Two sources of calibration particles were used. The Thermo-System (TSI) Model 3050 Berglund-Liu Aerosol Generator produced monodispersed dibutyl phthalate particles with known diameters from about 1 micron to about 5 microns. The Royco Model 256 Aerosol Generator was also used to produce standard particles of polystyrene latex beads of very precise diameters in the range of 0.5 microns to about 2 microns.

References

1. Colovos, G., Eaton, W. S., Ricci, G. R., Shepard, L. S., and Wang, H. 1979. Collaborative Testing of NIOSH Atomic Absorption Method. DHEW (NIOSH) Publication 79-144.

APPENDIX B

INORGANIC ARSENIC

Methods Research Branch

Analytical Method

Analyte:	Arsenic	Method No.:	P&CAM 346
Matrix:	Air	Range:	0.67 - 32.2 $\mu g/m^3$
Procedure:	Treated filter collection, wet digestion, graphite furnace AAS	Precision:	$\overline{\% \text{ RSD}_T} = 7.5$
Date Issued:	August 24, 1981	Classification:	D (Operational)
Date Revised:			

1. Synopsis

1.1 A known volume of air is drawn through a Na_2CO_3 impregnated 0.8-µm pore size cellulose ester filter and cellulose backup pad to collect particulate arsenic and arsenic trioxide vapor.

1.2 The filter-backup pad pair is digested with HNO_3-H_2O_2 and nickel nitrate is added for matrix modification.

1.3 The samples are analyzed by graphite furnace atomic absorption spectrophotometry.

2. Working Range, Sensitivity and Detection Limit

2.1 The method was evaluated over the range 0.670 to 32.2 $\mu g/m^3$ for a 400-L air sample collected at 20 °C and 750 torr, corresponding to 0.268 to 12.8 µg/sample. The upper limit of the method may be extended by diluting the sample to a volume greater than 10.0 mL, such that 0.0005 to 0.008 µg As is injected into the graphite furnace.

2.2 The instrumental sensitivity at 193.7 nm is 0.000066 µg As/0.0044 absorbance units.

2.3 The 2σ detection limit at 193.7 nm is 0.0003 µg As/injection, corresponding to 0.15 µg/m^3 for a 400-L air sample dissolved in 10.0 mL of solution, and a 50-mL injection.

3. Interferences

3.1 Background absorption is overcome by the use of a deuterium background corrector.

3.2 Copper (II), nitrate, chloride, and sulfate have been shown specifically not to interfere with the determination at concentrations up to 50 times the As concentration.

3.3 The collection efficiency of the sampling device for arsine is unknown.

4. Precision and Accuracy

4.1 The percent relative standard deviation for the total sampling and analytical method in the range of 0.67 - 32.2 µg/m^3 of arsenic trioxide vapor and particulate arsenic was 7.51. Details of the statistical treatment may be found in Reference 11.1.

4.2 The analytical method percent recovery was determined to be 100.5 ± 2.0 at 6.5 µg/m^3. Collection efficiency was better than 0.939 in all cases. In stability studies of generated samples, the mean of samples analyzed after fourteen days was the same as that of samples analyzed after one day at the 95% confidence level.

5. Advantages and Disadvantages

5.1 The sampling device is small and portable, and the samples are easily collected.

5.2 With the base-treated filters, total arsenic, both particulate and vapor-phase, is collected and analyzed.

5.3 Samples may be analyzed quickly and easily.

5.4 The method is extremely sensitive for arsenic. Extreme care must be exercised in all stages of the analysis.

5.5 The analytical instrumentation required is relatively expensive.

6. Apparatus

6.1 Sampling equipment, consisting of filter unit (37-mm/0.8-µm cellulose ester membrane filter and cellulose backup pad treated with Na_2CO_3:glycerol solution) and personal sampling pump capable of sampling at 1.5 - 2.5 liters per minute. The impregnated filters may be prepared up to one week ahead of time. The pump must be

calibrated with a representative filter in line and its flow rate must be known to within ±5%. The pump must be capable of maintaining a maximum pressure drop of 20 inches of water across the impregnated filter-backup pad pair during a sampling period of 4 hours.

6.2 Atomic absorption spectrophotometer, equipped with a graphite furnace atomizer. Reproducible control of times and temperatures during the drying, charring, and atomization cycles is essential. Required accessories include an electrodeless discharge lamp for arsenic and EDL power supply, readout device (recorder or digital peak height analyzer), gas control system for argon purge gas, pipetting system (automatic or manual) and simultaneous deuterium background corrector.

6.3 Glassware (borosilicate)

6.3.1 Volumetric pipettes, 1.0-mL, 2.0-mL, 4.0-mL, 6.0-mL, 8.0-mL, 10.0-mL, 100.0-mL.

6.3.2 Volumetric flasks, 100.0-mL, 1000.0-mL.

6.3.3 Beakers, 50-mL.

6.4 Steambath

7.0 Reagents

All reagents used should be ACS reagent grade or better.

7.1 Water, distilled or deionized.

7.2 Nitric acid, 70% (w/w), redistilled in glass.

7.3 Hydrogen peroxide, 30%.

7.4 1000 µg/mL Ni^{++} in 1% HNO_3 solution. Dilute 4.95 gm Ni $(NO_3)_2$ to 1.0 L with 1% HNO_3. Alternatively, use a commercially prepared Ni standard prepared in 1% HNO_3.

7.5 Arsenic stock standard solution, 1000 µg/mL As. Use a commercially prepared standard.

7.6 Argon gas in a compressed gas cylinder.

7.7 9:1 1 M Na_2CO_3:glycerol solution to impregnate filter.

8. Procedure

8.1 Cleaning of Equipment. New glassware must be cleaned by soaking in hot, concentrated nitric acid, followed by thorough rinsing with distilled or deionized water. Then, after each use, the glassware should be washed with, in the following order, detergent solution,

tap water, dilute nitric acid (soak 4 hours or longer), and distilled water.

8.2 Collection and Shipping of Samples

8.2.1 Assemble the filter in the cassette and close firmly to ensure that a seal is made around the edge of the filter (the filter is supported by a cellulose backup pad). Apply a shrinkable cellulose band to the outside of the cassette.

8.2.2 Remove the top plug from the cassette and inject 300 µL of 9:1 1 M Na_2CO_3:glycerol solution. Replace the plug, rotate the cassette carefully to completely cover the surface of the filter with solution, and allow the filter to dry overnight.

8.2.3 Remove the plugs from the cassette and attach to the personal sampling pump by means of flexible tubing. Clip the cassette, face down, to the worker's lapel. Air should not pass through any hose or tubing before entering the cassette.

8.2.4 Take the sample at an accurately known flow rate as close as possible to 1.7 L/min. A sample size of 400-L is recommended. Check the pump frequently during sampling to ensure that the flow rate has not changed. If sampling problems preclude the accurate measurement of air volume, discard the sample. Record the sampling time, flow rate, and ambient temperature and pressure.

8.2.5 With each batch of ten samples or less, submit one filter as a blank. Blanks should be from the same lot used for sampling, and should have been subjected to steps 8.2.1 and 8.2.2 of this procedure.

8.2.6 Ship the cassettes so as to prevent excessive vibration or jarring of the cassettes.

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the filter and backup pad with tweezers; transfer both to a 50-mL beaker.

8.3.2 To each beaker, add 15 mL 70% HNO_3. Cover with a watchglass and allow to sit on a hotplate at 150 °C until the volume has been reduced to ~1 mL. Rinse each watchglass with deionized water and add 6 mL 30% H_2O_2 to each beaker. Place each beaker on a steam bath and allow the solution to go to dryness. Cool the beakers; add 10.0 mL of 1000 µg/mL Ni^{++} 1% HNO_3 solution and sonicate for 30 minutes in an ultrasonic bath.

8.3.3 Inject samples into the graphite furnace and operate in accordance with the manufacturer's instructions with the following limitations:

Aliquot size:	10 or 50-µL, depending on the concentration of the sample.
Readout maode:	Peak height in absorbance mode (3 x scale) is most precise.
Wavelength:	193.7 nm.
Background correction:	Simultaneious D_2 background correction is recommended.
Dry cycle:	100 °C, 70 sec.
Char cycle:	1300 °C, 30 sec.
Atomize cylce:	2700 °C, 10 sec.
Graphite atomizer:	Non-pyrolytic tube.

9. Calibration and Standardization

9.1 Dilute stock (1000 µg/mL) arsenic standard solution 1:100 with 1000 µg/mL Ni in 1% HNO_3. The resulting standard solution contains 10 µg/mL As.

9.2 Make a further 1:10 dilution of the 10 µg/mL As solution with 1000 µg/mL Ni in 1% HNO_3 solution to give a 1 µg/mL As stock.

9.3 Make working standards by dilution of these two stock solutions with 1000 µg/mL Ni in 1% HNO_3 solution, e.g., 2:100, 4:100, 6:100, and 8:100 dilutions of the 1 µg/mL As stock will give 0.02, 0.04, 0.06, and 0.08 µg/mL As working standards for a 50-µL injection of sample. Working standards for a 10-µL injection of sample are prepared by 2:100, 4:100, 6:100, and 8:100 dilutions of the 10 µg/mL As stock giving concentrations of 0.20, 0.40, 0.60, and 0.80 µg/mL As. These working standards should be prepared weekly.

9.4 The calibration curve is constructed from the absorbance measured for the standard solutions (Section 7.6) analyzed under the same instrumental conditions as the samples.

10. Calculations

10.1 From the calibration curves obtained in Section 9, calculate for each sample the amount of arsenic in µg.

10.2 In the event that a filter blank is found, a correction for the blank must be made for each sample.

$$W = S-B$$

where

W = net sample weight (μg)

S = weight found in sample filter (μg)

B = weight found in blank filter (μg).

10.3 For personal sampling pumps with rotameters only, the following volume correction should be made.

$$V = \frac{f \cdot t}{1000} \left[\frac{P_1}{P_2} \cdot \frac{T_2}{T_1} \right]^{\frac{1}{2}}$$

where

V = the corrected volume (cubic meters) of air sampled

f = flow rate sample (liters/min)

t = sampling time (min)

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (K)

T_2 = temperature of air sampled (K).

10.4 Calculate the arsenic concentrations (C) in the air sample ($\mu g/m^3$) using the formula:

$$C = \frac{W}{V}$$

11. References

11.1 Backup Data Report for Inorganic Arsenic, prepared under NIOSH Contract 210-79-0060.

11.2 P&CAM 286, NIOSH Manual of Analytical Methods, Volume 5 (NIOSH Publication 79-141).

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APPENDIX C

INORGANIC NICKEL, METAL AND COMPOUNDS (AS Ni)

Methods Research Branch
Analytical Method

Analyte:	Nickel	Method No.:	P&CAM 298
Matrix:	Air	Range:	0.57-30.7 $\mu g/m^3$
Procedure:	Filter collection, acid digestion, graphite furnace AAS	Precision:	$\overline{\%RSD_T}$ = 7.5
Date Issued:	July 2, 1979	Classification:	B (accepted)
Date Revised:	August 24, 1981		

1. Synopsis

1.1 A known volume of air is drawn through a 0.8-μm pore size cellulose ester filter.

1.2 The filter and sample are digested with a HF-HNO_3 mixture, taken to dryness and diluted to a known volume with dilute HCl.

1.3 The samples are analyzed by graphite furnace atomic absorption spectrophotometry.

2. Working Range, Sensitivity, and Detection Limit

2.1 This method was evaluated over the range 0.57 μg Ni/m^3 to 30.7 μg Ni/m^3 for a 400-L air sample collected at 20 °C and 750 torr, corresponding to 0.228 to 13.2 μg Ni per sample. The upper limit of the method may be extended by diluting the sample to a volume greater than 10.0 mL, so that 0.00010 μg Ni to 0.0040 μg Ni is injected into the graphite furnace.

2.2 The instrumental sensitivity at 232.0 nm is 0.000625 μg Ni/0.0044 absorbance units.

2.3 The 2σ detection limit at 232.0 nm is 0.000188 μg Ni/injection, corresponding to 0.094 $\mu g/m^3$ for a 400-L air sample dissolved in 10.0 mL of solution, and a 50-μL injection.

3. Interferences

3.1 Background absorption may be overcome by the use of a deuterium background corrector.

3.2 Iron is a positive interference in the analysis for nickel when present at high concentration ratios, beginning at about 100:1 Fe:Ni. When the approximate concentration of iron in a sample is known, it is advisable to add a corresponding quantity of iron to the calibration standard.

3.3 Nitrate, sulfate, copper, molybdenum, and calcium have been shown not to interfere with the determination at concentrations up to 200x the nickel concentration.

3.4 Nickel carbonyl is not collected on the filter and therefore does not interfere.

4. Precision and Accuracy

4.1 The total precision of the sampling and analytical method is 7.48% RSD, based on six samples at each of three concentration levels.

4.2 The analytical method recovery was determined to be 101.9% at 0.5 times the NIOSH recommended standard. Collection efficiency was determined to be 1.00. In stability studies of generated samples, the mean of samples analyzed after 14 days was the same as that of samples analyzed immediately after generation, at the 95% confidence level; the means differed by 1.8%. Also at the 95% confidence level, the mean of samples analyzed by this method was the same as the mean of samples analyzed by instrumental neutron activation analysis. Details of this experiment are given in Reference 11.1.

5. Advantages and Disadvantages

5.1 The sampling device is small and portable, and the samples easily collected.

5.2 The analytical method is extremely sensitive for nickel.

5.3 Samples may be analyzed quickly and easily.

5.4 Large iron concentrations will cause high results.

5.5 The analytical equipment required is relatively expensive.

6. Apparatus

6.1 Sampling equipment, consisting of filter unit (0.8-μm cellulose ester membrane filter, and cellulose backup pad, 37-mm diameter, in a plastic cassette filter holder) and personal sampling pump capable of sampling at 1.5-2 L/min. The pump must be calibrated with a representative filter in line, using a soap-bubble flowmeter or wet- or dry-test meter, and its flow rate must be known accurately to within ± 5%.

6.2 Atomic absorption spectrophotometer, equipped with a heated graphite atomizing rod, tube, or furnace. Reproducible control of times and temperatures during the drying, charring and atomizing cycles is essential, and a minimum atomization temperature of 2700 °C is required. Accessories needed for the spectrometer are: hollow cathode lamp for nickel, readout device (recorder or digital peak height or peak area analyzer), gas control system for Ar purge gas, pipetting system (automatic or manual, 5-50-µL, as appropriate to atomizer size), and background correction system (simultaneous correction is preferred).

6.3 Glassware (borosilicate).

6.3.1 Volumetric pipettes, 1-, 2-, 3-, 4-, 5-, 6-, 10-, 15-, 20-, 25-mL.

6.3.2 Volumetric flasks, 10-, 25-, 50-, 100-, 250-, 1000-mL.

6.4 Teflon beakers, 100-mL, with watchglass covers.

6.5 Adjustable, thermostatically-controlled hotplate capable of reaching a surface temperature of 200 °C.

6.6 Steam bath.

7. Reagents

All reagents used should be ACS reagent grade or better.

7.1 Distilled or deionized water.

7.2 Nitric acid, 70% (w/w), redistilled in glass.

7.3 Hydrochloric acid, 38% (w/w).

7.4 Hydrofluoric acid, 50% (w/w).

7.5 Dilute hydrochloric acid, 1% (w/w). Add 26.5 mL of 38% HCl_3 to distilled or deionized water and dilute to 1000 mL.

7.6 Nickel stock standard solution, 1000 ppm Ni. Dissolve 1.000 gm pure Ni metal in a minimum volume of 70% HNO_3 and dilute to 1 liter with 1% HCl. Alternatively, commercially prepared standard may be used.

7.7 Argon gas in compressed gas cylinder.

8. Procedure

8.1 Cleaning of Equipment. New glassware must be cleaned by soaking in hot, concentrated nitric acid, followed by thorough rinsing with distilled or deionized water. Then, after each use, the glassware should be washed with, in order, detergent solution, tap water, dilute

nitric acid (soak four hours or longer), and distilled or deionized water.

8.2 Collection and Shipping of Samples.

8.2.1 Assemble the filter in the cassette and close firmly to ensure that a seal is made around the edge of the filter (the filter is supported by a cellulose backup pad). Apply a shrinkable cellulose band to the outside of the cassette.

8.2.2 Remove the plugs from the cassette and attach to the personal sampling pump by means of flexible tubing. Clip the cassette, face down to the worker's lapel. Air should not pass through any hose or tubing before entering the cassette.

8.2.3 Take the sample at an accurately known flow rate as close as possible to 1.7 L/min. A sample size of 400-L is recommended. Check the pump frequently during sampling to ensure that the flow rate has not changed. If sampling problems preclude the accurate measurement of air volume, discard the sample. Record the sampling time, flow rate, and ambient temperature and pressure.

8.2.4 With each batch of ten samples or less, submit one filter as a blank. Blanks should be from the same lot used for sampling, and should have been subjected to step 8.2.1.

8.2.5 Ship the cassettes so as to prevent excessive vibration or jarring to the cassettes.

8.3 Analysis of Samples.

8.3.1 Open the cassette filter holder and carefully remove the cellulose membrane filter with tweezers and transfer it to a Teflon beaker. Discard the cellulose backup pad.

8.3.2 To each beaker containing a filter, add 10 mL 70% nitric acid. Cover with a watchglass and allow to sit on a hotplate at 150 °C for four hours or until the volume has been reduced to 1 mL. Rinse each watchglass with deionized water and add 4 mL of 1:3 70% HNO_3-50% HF to each beaker. Place the beakers on a steam bath and allow the solution to go to dryness. Cool the solutions, redissolve the residue and dilute to 10.00 mL with 1% HCl. Sonicate for 30 minutes in an ultrasonic bath.

8.3.3 Inject samples into the graphite atomizer and operate in accordance with the manufacturer's instructions within the following limitations:

Aliquot size:	10- or 50-μL, depending on the concentration of the sample.

Readout mode:	Peak height in absorbance mode (3 x scale) is most precise.
Wavelength:	232.0 nm.
Background correction:	Simultaneous D_2 background correction is recommended.
Dry cycle:	150 °C, 50 seconds for a 50-µL aliquot.
Char cycle:	1300 °C, 10 seconds.
Atomize cycle:	2700 °C, 10 seconds.
Graphite atomizer:	Pyrolytic tube.

9. Calibration and Standardization

9.1 A 10-µg/mL Ni standard solution is prepared by dilution of the 1000-µg/mL stock solution with 1% HCl. This solution is stable for several months if stored in a polyethylene bottle and is used to prepare fresh weekly the working standards which should cover the range 0.01-0.4 µg/mL Ni (e.g., 0.01, 0.02, 0.03, 0.04, and 0.06 µg/mL Ni in 1% HCl for a 50-µL injection and 0.06, 0.10, 0.20, 0.30, and 0.40 µg/mL Ni in 1% HCl for a 10-µL injection).

9.2 The calibration curve is constructed from the absorbances measured for the standard solutions (Sec. 7.7) analyzed under the same instrumental conditions as the samples, as described in Section 8.3.3.

9.3 If the sample is known to contain iron, at a concentration greater than 100 times the nickel concentration, iron should be added to the standard solutions to match the sample matrix.

10. Calculations

10.1 From the calibration curves obtained in Section 9 calculate for each sample the amount of nickel in µg.

10.2 In the event that a filter blank is found, a correction for the blank must be made for each sample.

$$W = S-B$$

where,

W = net sample weight (µg)

S = weight found in sample filter (µg)

B = weight found in blank filter (µg)

10.3 For personal sampling pumps with rotameters only, the following volume correction should be made.

$$V = \frac{f \cdot t}{1000} \left[\frac{P_1}{P_2} \cdot \frac{T_1}{T_2} \right]^{\frac{1}{2}}$$

where,

V = the corrected volume (cubic meters) of air sampled

f = flow rate sample (liters/min)

t = sampling time (min)

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (K)

T_2 = temperature of air sampled (K).

10.4 Calculate the nickel concentrations (C) in the air sample ($\mu g/m^3$) using the formula:

$$C = \frac{W}{V}$$

11. References

11.1 Backup Data Report for Inorganic Nickel, prepared under NIOSH Contract 210-79-0060.

11.2 P&CAM 298, NIOSH Manual of Analytical Methods, Volume 5 (NIOSH Publication 79-141).

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APPENDIX D

INORGANIC TUNGSTEN, SOLUBLE AND INSOLUBLE

Methods Research Branch

Analytical Method

Analyte:	Tungsten	Method No:	P&CAM 271 (Revised)
Matrix:	Air	Range:	0.42-2.0 mg/m^3 for soluble tungsten 0.84-19.74 mg/m^3 for insoluble tungsten
Procedure:	Filter collection, Water extraction for soluble, Acid digestion for insoluble, Flame AAS	Precision:	$\overline{\%RSD_T}$ = 7.9, soluble $\overline{\%RSD_T}$ = 7.6, insoluble
Date Issued:	December 5, 1977	Classification:	B (accepted)
Date Revised:	November 26, 1981		

1. Synopsis

1.1 A known volume of air is drawn through a 0.8-μm cellulose ester filter.

1.2 The filter and sample are extracted with deionized water to remove soluble tungsten species, digested with HNO_3-HF to solublize other species, taken to dryness, extracted with dilute HCl to remove interfering species, and re-digested with HNO_3-HF for insoluble tungsten species.

1.3 The soluble fraction and the insoluble fraction are analyzed separately by flame atomic absorption spectrophotometry.

2. Working Range, Sensitivity, and Detection Limits

2.1 The method for soluble tungsten was validated over the range 0.42 to 2.00 mg/m^3 for a 400-L air sample collected at 20 °C and 750 torr; corresponding to 0.168 to 0.800 mg/sample. The method for insoluble tungsten was validated over the range 0.84 to 19.74 mg/m^3 for a 400-L air sample collected at 20 °C and 750 torr, corresponding to 0.336 to 7.896 mg/sample. The upper limit of the method may be extended by diluting the sample to a volume greater than 10 mL for soluble tungsten or 25 mL for insoluble tungsten.

2.2 The instrumental sensitivity at 255.1 nm is 17.6 μg W/1% absorbance.

2.3 The 2σ detection limit at 255.1 nm is 1.97 μg/mL, corresponding to 0.0049 mg/m^3 for a 400-L air sample dissolved in 10 mL of solution.

3. Interferences

3.1 Nickel, molybdenum, vanadium, manganese, chromium, cobalt, and iron were shown specifically not to interfere with the determination at concentrations up to 50 times the tungsten concentration.

3.2 A dilute HCl extraction is included in the procedure for the removal of large concentrations of potentially interfering metals.

4. Precision and Accuracy

4.1 The percent relative standard deviation for the total sampling and analytical method for soluble tungsten in the range 0.40-2.00 mg/m^3 was 7.9. The percent relative standard deviation for the total sampling and analytical method for insoluble tungsten in the range 0.84-19.74 mg/m^3 was 7.6. Details of the statistical treatment may be found in Reference 1.

4.2 The analytical method recovery was determined to be 0.963 at 1.2 mg/m^3 soluble tungsten and 0.995 at 9.0 mg/m^3 insoluble tungsten. Collection efficiency was determined to be 1.00. In stability studies of generated samples, the mean of samples analyzed after fourteen days was the same as that of samples analyzed immediately after generation for both soluble and insoluble tungsten at the 95% confidence level. Also, at the 95% confidence level, the mean of samples analyzed by this method was the same as the mean of samples analyzed by neutron activation analysis. Details of this experiment are given in Reference 1.

5. Advantages and Disadvantages

5.1 The sampling device is small and portable, and the samples easily collected.

5.2 The analytical method is extremely sensitive for tungsten.

5.3 The extraction and digestion procedure results in effective separation of the soluble and insoluble tungsten species.

5.4 The analytical equipment required is relatively expensive.

5.5 The method ensures satisfactory recovery of insoluble tungsten compounds from alloys and steels and so extends P&CAM 271 (original version).

6. Apparatus

6.1 Sampling equipment, consisting of filter unit (0.8-μm cellulose ester membrane filter, and cellulose backup pad, 37-mm diameter, in a plastic cassette filter holder) and personal sampling pump capable of sampling at 1.5-2 L/min. The pump must be calibrated with a representative filter in line, using a soap-bubble flowmeter or wet- or dry-test meter, and its flow rate must be known accurately to within ±5%.

6.2 Atomic Absorption Spectrophotometer, with burner head for nitrous oxide - acetylene flame, hollow cathode lamp for tungsten, and read-out device (recorder or digital peak height or peak area analyzer).

6.3 Glassware (borosilicate).

6.3.1 Volumetric pipettes, class A, 1.0-mL, 2.0-mL, 4.0-mL, 6.0-mL, 8.0-mL, 10.0-mL, 15.0-mL, 20.0-mL, 25.0-mL, 100.0-mL

6.3.2 Volumetric flasks, class A, 10.0-mL, 25.0-mL, 100.0-mL, 200.0-mL, 1000.0-mL

6.3.3 Beakers, borosilicate glass, 50-mL

6.3.4 Millipore filtering apparatus or equivalent, including funnel, clamp, frit, holder, belljar, and baseplate

6.4 Teflon beakers, 100-mL, with watchglass covers.

6.5 Adjustable, thermostatically-controlled hotplate capable of reaching a surface temperature of 200 °C.

6.6 Steam bath.

7. Reagents

All reagents used should be ACS reagent grade or better.

7.1 Water, distilled or deionized.

7.2 Nitric acid, 70% w/w, redistilled in glass.

7.3 Hydrochloric acid, 38% w/w.

7.4 Hydrofluoric acid, 50% w/w.

7.5 Dilute hydrochloric acid, 1% w/w. Add 26.5 mL 38% HCl to deionized water and dilute to 1000 mL.

7.6 Sodium hydroxide, 0.5M. Dissolve 20.0 gm NaOH in 1 L of deionized water.

7.7 Sodium sulfate, 20% w/w, dissolve 20 gm Na_2SO_4 in deionized water and dilute to 100.0 mL.

7.8 Stock standard tungsten solution, 1000 ppm W. Dissolve 1.5985 gm dried reagent grade Na_2WO_4 in 1.00 L 1% NaOH. Alternatively use commercial standard.

7.9 Working standards. Prepare working standards at 250, 200, 150, 100, 80, 60, 40, 20, and 10 mg/mL W by dilution of the stock. The final matrix should be 2% Na_2SO_4.

8. Procedure

8.1 Cleaning of Equipment. New glassware must be cleaned by soaking in hot, concentrated nitric acid, followed by thorough rinsing with distilled or deionized water. Then, after each use, the glassware should be washed with, in order, detergent solution, tap water, dilute nitric acid (soak four hours or longer), and distilled or deionized water.

8.2 Collection and Shipping of Samples.

8.2.1 Assemble the filter in the cassette and close firmly to ensure that a seal is made around the edge of the filter (the filter is supported by a cellulose backup pad). Apply a shrinkable cellulose band to the outside of the cassette.

8.2.2 Remove the plugs from the cassette and attach to the personal sampling pump by means of flexible tubing. Clip the cassette, face down, to the worker's lapel. Air should not pass through any hose or tubing before entering the cassette.

8.2.3 Take the sample at an accurately known flow rate as close as possible to 1.7 L/min. A sample size of 400 L is recommended. Check the pump frequently during sampling to ensure that the flow rate has not changed. If sampling problems preclude the accurate measurement of air volume, discard the sample. Record the sampling time, flow rate, and ambient temperature and pressure.

8.2.4 With each batch of ten samples or less, submit one filter as a blank. Blanks should be from the same lot used for sampling, and should have been subjected to step 8.2.1 of this procedure.

8.2.5 Ship the cassettes so as to prevent excessive vibration or jarring of the cassettes.

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the cellulose membrane filter with tweezers and transfer it to a filtering apparatus (6.3.4) with a 47-mm/0.45-μm cellulose ester

filter, with 50-mL beaker to catch filtrate. Add 3.0 mL deionized water and allow it to stand for three minutes; repeat. Draw the extract through the filter; transfer it to a 10.0-mL volumetric flask; add 1.0 mL 20% Na_2SO_4; dilute it to volume with distilled water. The solution is analyzed for soluble tungsten.

8.3.2 Digest filters and residue in a Teflon beaker with 10 mL 1:1 $HF-HNO_3$. Reduce the volume to 2 mL on a 150 °C hotplate; no filter residue should be visible in solution.

8.3.3 Extract the residue with manual agitation with 10 mL 1% cold HCl; filter through a 47-mm/0.45-μm cellulose ester filter in a filtering apparatus (6.3.4) and set filtrate aside. The filtrate may be analyzed for cobalt.

8.3.4 Digest filter and residue in a Teflon beaker with 10 mL 1:1 HNO_3-HF; reduce the volume to 2 mL on a 150 °C hotplate; no filter residue should be visible in solution. Take to dryness on a steam bath.

8.3.5 Dissolve residue with 2.5 mL 0.5 M NaOH and 2.5 mL 20% Na_2SO_4; place solution on a steam bath for 15 minutes; transfer to a 25.0-mL volumetric flask; dilute to volume.

9. Calibration and Standardization

9.1 The calibration curve is constructed from the absorbances measured for the standard solutions (see 7.9) analyzed under the same conditions as the samples.

9.2 A minimum of five working standards (prepare fresh weekly) should be used to prepare the calibration curve.

10. Calculations

10.1 From the calibration curves obtained in section 9, calculate for each sample the amount of tungsten in mg.

10.2 In the event that a filter blank is found, a correction for the blank must be made for each sample.

$$W = S - B$$

where

W = net tungsten in sample (mg)

S = tungsten found in sample (mg)

B = tungsten found in blank (mg)

10.3 For personal sampling pumps with rotameters only, the following volume correction should be made.

$$V = \frac{f \cdot t}{1000} \left(\frac{P_1}{P_2} \cdot \frac{T_2}{T_1} \right)^{\frac{1}{2}}$$

where

V = the corrected volume (cubic meters) of air sampled

f = flow rate, sample (liters/min)

t = sampling time (min)

P_1 = pressure during calibration of sampling pump

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (K)

T_2 = temperature of air sampled (K)

10.4 Calculate the tungsten concentrations (C) in the air sample (mg/m^3) using the formula:

$$C = \frac{W}{V}$$

11. Reference

11.1 Backup Data Report for Inorganic Tungsten, prepared under NIOSH Contract 210-79-0060.

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APPENDIX E

VANADIUM: SOLUBLE FUME AND INSOLUBLE DUST

Measurements Research Branch

Analytical Method

Analyte:	Vanadium	Method No.:	P&CAM 290 (Revised)
Matrix:	Air	Range:	Soluble: 0.01-0.10 mg/m^3 Insoluble: 0.2-2.5 mg/m^3
Procedure:	Filter collection, wet extraction & digestion graphite furnace AAS	Precision:	$\overline{\%\ RSD_T}$ = 6.0 (soluble) $\overline{\%\ RSD_T}$ = 11.1 (insoluble)
Date Issued:	May 25, 1979	Classification:	Soluble & fume: B (accepted)
Date Revised:	November 26, 1981		Insoluble dust: E (proposed)

1. Synopsis

1.1 A known volume of air is drawn through a cellulose ester filter.

1.2 The filter is extracted with water, filtered through a second cellulose ester filter and the filtrate is made alkaline with KOH.

1.3 The solution is analyzed for soluble vanadium by graphite furnace atomic absorption spectrophotometry.

1.4 Both filters are digested in concentrated nitric acid and the samples are brought to a final matrix of dilute KOH.

1.5 The samples are analyzed for insoluble vanadium by graphite furnace atomic absorption spectrophotometry.

2. Working Range, Sensitivity and Detection Limit

2.1 The method was validated for soluble vanadium over the range 0.0105 to 0.0953 mg/m^3 for a 25-L sample collected at 20 °C and 750 torr, corresponding to 0.26 to 2.4 µg V/sample. The method was evaluated over the range 0.214 to 2.45 µg/m^3 for a 400-L air sample collected at 20 °C and 750 torr, corresponding to 85.6 to 980 µg/sample. This often required dilution of the final samples to greater than the specified volume with 0.01 N KOH before analysis.

2.2 The instrumental sensitivity at 318.4 nm varies from analysis to analysis because of a large dependence on the characteristics of the particular pyrolytically coated graphite tube being used. The sensitivity is approximately 0.02 to 0.03 μg V per absorbance unit.

2.3 The 2σ detection limit for soluble vanadium at 318.4 nm is 0.084 μg V/injection, corresponding to 0.67 mg/m^3 for a 25-L air sample dissolved in 10.0 mL of solution and a 50-μL injection. The 2σ detection limit for insoluble vanadium is 0.084 μg V/injection, corresponding to 0.21 mg/m^3 for a 400-L air sample dissolved in 50 mL.

3. Interferences

3.1 Background absorption is overcome by the use of a deuterium background corrector.

3.2 Sulfate, nitrate, and aluminum have been shown specifically not to interfere at up to 200 times the V concentration.

3.3 Iron does not interfere at up to 50 times the vanadium concentration but shows a negative interference at higher levels. Matching the iron concentration in the standards to that of the sample is recommended.

3.4 Molybdenum gives a positive interference at greater than 10 times the vanadium concentration. Use of an alternate wavelength for vanadium is recommended.

3.5 Titanium gives a positive interference at levels greater than 10 times the vanadium concentration until the titanium concentration is great enough to cause precipitation. Eliminate by analyzing in 2 % HNO_3 matrix.

3.6 V_2O_3 distributes between the soluble and insoluble fractions and is measured in both, resulting in biased readings.

4. Precision and Accuracy

4.1 The relative standard deviation ($\overline{RSD}_{Ts}$) for the total sampling and analytical method for soluble vanadium in the range 0.011 to 0.095 mg/m^3 was 0.060. The relative standard deviation ($\overline{RSD}_{Ti}$) for the total sampling and analytical method for insoluble vanadium in the range 0.21 to 2.5 mg/m^3 was 0.111. Details of the statistical treatment may be found in Reference 11.1.

4.2 The analytical method recovery was determined to be 0.971 ± 0.018 at 1.1 times the NIOSH-recommended standard for soluble vanadium and 0.982 ± 0.036 at 1.0 times the NIOSH-recommended standard for insoluble vanadium. Collection efficiency was better than 0.986 in all cases for soluble vanadium and was 1.00 for insoluble vanadium. In stability studies of generated samples for both species, the mean of samples analyzed after 14 days was the same as that of samples

analyzed after 1 day at the 95% confidence level. At the 99% confidence level, the mean of samples analyzed by this method was the same as the mean of samples analyzed by instrumental Neutron Activation Analysis. Details of this experiment are given in Reference 11.1.

5. Advantages and Disadvantages

5.1 The sampling device is small and portable and the samples are easily collected.

5.2 Both soluble and insoluble vanadium can be determined separately from the same sample.

5.3 Samples may be analyzed quickly and easily.

5.4 Larger insoluble vanadium particulates tend to be collected in the center of the filter and may not be well impacted. Care must be taken in transferring the filter.

5.5 The analytical instrumentation required is relatively expensive.

5.6 V_2O_3 does not fit into the soluble or insoluble vanadium category, but appears in both the extracted and digested fractions. The compound is not quantified effectively by this procedure.

5.7 This procedure extends the capability of previous procedures for vanadium; P&CAM 290 (vanadium oxides), S 388 (vanadium oxides-fumes) and S 391 (vanadium oxides-dust), by including soluble and insoluble vanadium compounds in addition to the oxides, and by providing for the separation and analysis of the two categories of compounds.

6. Apparatus

6.1 Sampling equipment, consisting of a filter unit (37-mm/0.8-μm cellulose ester membrane filter and cellulose backup pad) and personal sampling pump capable of sampling at 1.5-2.5 liters per minute. The pump must be calibrated with a representative filter in line and its flow rate must be known to within ±5%.

6.2 Atomic absorption spectrophotometer, equipped with a graphite furnace atomizer. Reproducible control of times and temperature during the drying, charring, and atomization cycles is essential. Required accessories include pyrolytically coated graphite tubes, a hollow cathode lamp for vanadium, a readout device (recorder or digital peak height analyzer), gas control system for argon purge gas, pipetting system (automatic or manual) and a simultaneous deuterium background corrector.

6.3 Glassware (borosilicate)

6.3.1 Volumetric pipettes, Class A, 1, 2, 3, 5, 7, 10, 15, and 50-mL.

6.3.2 Volumetric flasks, Class A, 10, 25, 100, and 1000-mL.

6.3.3 Beakers, 50-mL.

6.4 Steam bath.

6.5 Hot plate, 140-150 °C.

6.6 Eppendorf pipet, 10, 50, and 100-μL.

6.7 Filters, cellulose ester 47-mm/0.1-µm pore size.

6.8 Filtration apparatus, Millipore #XX1004700.

6.9 Bell jar.

6.10 Vacuum line.

6.11 Parafilm, 4" wide.

6.12 Watchglasses, non-ribbed.

7. Reagents

All reagents should be ACS reagent grade or better.

7.1 Distilled or deionized water.

7.2 Nitric acid, 70% (w/w), redistilled in glass.

7.3 Potassium Hydroxide, pellets.

7.4 Stock standard vanadium solution, 1000 µg/mL vanadium. Use a commercially prepared standard.

7.5 Argon gas in a compressed gas cylinder.

8. Procedure

8.1 Cleaning of Glassware. All glassware must be cleaned after each use by soaking in 1N KOH, followed by rinsing with 10% (v/v) nitric acid and then rinsing with distilled or deionized water.

8.2 Collection and shipping of samples.

8.2.1 Assemble the filter and backup pad in the cassette and close firmly to ensure that a seal is made around the edge of the filter. Apply a shrinkable cellulose band to the outside of the cassette.

8.2.2 Remove the plugs from the cassette and attach to the personal sampling pump by means of flexible tubing. Clip the cassette,

face down, to the worker's lapel. Air should not pass through any hose or tubing before entering the cassette.

8.2.3 Take the sample at an accurately known flow rate as close as possible to 1.7 L/min. A 15-minute sample is to be used for detection of ceiling concentrations. A 4-hr sample should be used in determining time-weighted averages. Check pump frequently during sampling to ensure that the flow has not changed. If sampling problems preclude the accurate measurement of air volume, discard the sample. Record the sampling time, flow rate, and ambient temperature and pressure.

8.2.4 With each batch of ten samples or less, submit a filter as a blank. Blanks should be from the same lot used for sampling, and should have been subjected to step 8.2.1.

8.2.5 Ship the cassette so as to prevent excessive vibration or jarring of the cassettes.

8.3 Analysis of the samples.

8.3.1 Place a 47-mm/0.1-μm cellulose ester filter on the glass fritted bottom portion of a Millipore filtration apparatus XX100-4700. Clamp the top in place and place the funnel into the top of a bell jar containing a 50-mL beaker to catch liquids. Place the system under vacuum and add water to seat the filter. While the vacuum is still running, unclamp and remove the upper portion of the filtration apparatus. Turn off the vacuum and replace the beaker in the bell jar with a clean 50-mL beaker.

8.3.2 Open the cassette filter holder and carefully remove the filter with forceps and place it on the center of the seated 47-mm filter. Clamp the top back into place. Place 3 mL of deionized water onto the filters and allow to sit for 4 minutes. Apply vacuum. When solution has filtered, release the vacuum and place an additional 3 mL water on the filters and allow to sit for 2 minutes. Apply vacuum. When solution has drained, release the vacuum and place 2 mL of water on the filters. Wait one minute and apply vacuum. While the system is under vacuum, remove the upper portion of the filtration assembly and place it on its side. Release the vacuum. Transfer and rinse the contents of the beaker in the bell jar into a 10-mL volumetric flask which contains 100 μL of 1.0 N KOH. Fill the volumetric flask to the mark with deionized water. The soluble vanadium fraction is now ready for analysis.

8.3.3 Rinse the surface of the upper portion of the filtration apparatus that came into contact with the sample into a fresh 50-mL beaker with 10% (v/v) HNO_3 to wash off any clinging insoluble vanadium particulates.

Add the 37/47-mm filter pair to this beaker and take to dryness on a 100 °C steam bath. When dry, add 15 mL concentrated HNO_3 into the beaker, cover with a non-ribbed watchglass and place on a 140-150 °C hot plate until the volume is reduced to 2 mL. Transfer the beaker to a 100 °C steam bath and rinse the watchglass into the beaker with a small portion of 10% HNO_3 and remove the watchglass. Take the solution in the beaker to dryness. Allow the beaker to cool and add 50 mL 0.01 N KOH by pipet. Carefully cover the beaker with parafilm and place in an ultrasonic bath for 15 minutes. The insoluble vanadium fraction is now ready for analysis.

Inject samples into the graphite furnace and operate in accordance with the manufacturer's instructions with the folowing limitations:

Aliquot size:	10 or 50-µL, depending on sample concentration
Readout mode:	Peak height in absorbance mode (5x scale) is most precise.
Wavelength:	318.4 nm
Background correction:	Simultaneous D_2 background correction is recommended
Dry cycle:	150 °C, 35 sec
Char cycle:	1900 °C, 10 sec
Atomize cycle:	2800 °C, (or higher if attainable), 10 sec
Graphite atomizer:	Pyrolytically coated tubes

9. Calibration and Standardization

9.1 The calibration curve is constructed from the absorbance measured for the standard solutions (Section 7.5) analyzed under the same instrumental conditions as the samples.

9.2 Dilute the 1000 µg/mL vanadium standard stock solution 1:100 with 0.01 N KOH. The resulting standard solution contains 10 µg/mL vanadium.

9.3 Make a further 6:100 dilution of the 10 µg/mL vanadium to give a 0.6 µg/mL V stock.

9.4 Make working standards by dilution of these two stock solutions, e.g., 1:100, 3:100, 5:100, 7:100, 10:100, and 15:100 dilutions of the

0.6 µg/mL V stock will give 0.006, 0.018, 0.030, 0.042, 0.060 and 0.090 µg/mL V working solutions for a 50-µL injection of sample. Working standards for a 10-µL injection are prepared by 1:100, 3:100, 5:100, 7:100, and 15:100 dilutions of the 10 µg/mL V stock, giving concentrations of 0.1, 0.3, 0.5, 0.7, 1.0, and 1.5 µg/mL vanadium. These working standards should be prepared weekly.

9.5 Because of sensitivity changes, calibration curves should be run frequently, approximately every 10-15 samples.

10. Calculations

10.1 From the calibration curves obtained in Section 9, calculate for each sample, the amount of vanadium for each species in mg.

10.2 In the event that a filter blank is found, a correction for the blank must be made for each sample.

$$W = S-B$$

where

W = net sample weight (mg)

S = weight found in sample filter (mg)

B = weight found in blank filter (mg)

10.3 For personal sampling pumps with rotometers only, the following volume correction should be made.

$$V = \frac{f \cdot t}{1000} \left[\frac{P_1}{P_2} \cdot \frac{T_1}{T_2} \right]^{1/2}$$

where

V = the corrected volume (cubic meters) of air sampled

f = flow rate of sample (liters/min)

t = sampling time (min)

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled

T_1 = temperature during calibration of sampling pump (K)

T_2 = temperature of air sampled (K)

10.4 Calculate the vanadium concentrations (C) in the air sample (mg/m^3) using the formula:

$$C = \frac{W}{V}$$

11. References

11.1 Backup Data Report for Vanadium, prepared under NIOSH Contract No. 210-79-0060.

11.2 P&CAM 290, NIOSH Manual of Analytical Methods, Volume 5, (NIOSH Publication 79-141).

11.3 S 388, NIOSH Manual of Analytical Methods, Volume 4, (NIOSH Publication (78-175).

11.4 S 391, NIOSH Manual of Analytical Methods, Volume 3 (NIOSH Publication 77-157c).

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APPENDIX F

RESPIRABLE TALC

Methods Research Branch

Analytical Method

Analyte:	**Respirable Talc**	Method No.:	P&CAM 355
Matrix:	Air	Range:	200 - 4000 $\mu g/m^3$
Procedure:	Filter collection, low temperature ashing, Re-deposition on Ag filter, XRD	Precision:	$\overline{\%RSD}_1 = 5.3$ (analytical) $\overline{\%RSD}_T = 34$ (sampling and analytical)
Date Issued:	November 26, 1981	Classification:	E (proposed)
Date Revised:			

1. Synopsis

   1.1 A known volume of air is drawn through a 0.45-µm polyvinyl chloride filter.

   1.2 The filter and sample are radio-frequency ashed; the residue is suspended in 2-propanol and co-deposited with α-Al_2O_3 on a silver membrane filter.

   1.3 The samples are analyzed by X-ray diffraction.

2. Working Range, Sensitivity, and Detection Limit

   2.1 The method was evaluated over the range 50 to 4000 $\mu g/m^3$, corresponding to 10 to 800 µg/filter for a 200-L air sample collected at 20 °C and 750 torr.

   2.2 The instrumental sensitivity is 0.0053 µg/count for the 002 peak and 0.0083 µg/count for the 006 peak.

   2.3 The detection limit is approximately 12 µg/filter for the 002 peak and 10 µg/filter for the 006 peak. The lowest analytically quantifiable level is 50 µg/filter for the 002 peak and 30 µg/filter for the 006 peak.

3. Interferences

3.1 A preliminary, qualitative scan of the sample is performed and indicates **whether interferences are present.**

3.2 Either the 002 or 006 peak of talc may be used for analysis to assist interfering peaks such as the 310 peak of tremolite (006 peak of talc).

4. Precision and Accuracy

4.1 The precision of the analytical method is 5.3% RSD, based on six samples at each of three concentration levels. The total precision of the sampling and analytical method is 34%, based on six samples at each of three concentration levels. The poor precision was caused by **the inconsistent synthetic atmosphere generated during testing of the method.**

4.2 The analytical method recovery was determined to be 1.00 at 160 µg per filter. In stability studies of generated samples, the mean of samples analyzed after fourteen days was the same as that of samples after one day, at the 95% confidence level. Details of the experiment are given in Reference 1.

5. Advantages and Disadvantages

5.1 The sampling device is small and portable, and the samples easily collected.

5.2 The analytical method requires a skilled operator and expensive equipment.

5.3 When no interferences or only avoidable interferences are present, the method is highly specific for talc.

5.4 Compared to the alternates of electron or optical microscopy, the method is rapid and very specific.

5.5 Occasionally (rarely) talc peaks may be obscured totally by interferences.

6. Apparatus

6.1 Sampling equipment, consisting of filter unit (0.45-µm polyvinyl chloride filter with backup pad, 37-mm diameter, in a plastic cassette with 10-mm nylon cyclone) and personal sampling pump capable of sampling at 1.5 - 2 L/min. The pump must be calibrated with a representative filter and cyclone in line, using a soap-bubble flowmeter or wet- or dry-test meter, and its flow rate must be known accurately to within ±5%.

6.2 Silver membrane filters, 25-mm diameter and 0.45-μm pore size: Selas Flotronics, Huntingdon Valley, PA 19006.

6.3 Vacuum filtration apparatus with modified filtering tower. The bore of the filtering tower should be sized to yield the largest sample surface that can be optimally exposed to the X-ray beam without being shadowed by the sample holder at the low angle (9.45 ° 2θ) of the 002 talc reflection.

6.4 X-ray diffractometer equipped with broad focus copper target X-ray tube, rotating sample holder, secondary beam monochromator, scintillation detector, pulse height analyzer and digital printout capability. The diffractometer parameters should be set to provide high intensity at the expense of resolution. In addition to higher counting rates this will improve statistics by allowing a greater fraction of the talc crystallites to contribute to the peaks.

6.5 Micro-pipets with disposable tips (Eppendorf, Oxford or equivalent). Micropipets should be calibrated gravimetrically using 2-propanol. A variety of sizes covering the range from 0.20 mL to 1.00 mL will be required.

6.6 Glassware (borosilicate)

6.6.1 Volumetric flasks, class A, 100-mL.

6.6.2 Beakers, 30-mL.

6.6.3 Erlenmeyer flask, wide mouth, tapered stopper, 125-mL.

6.7 Ultrasonic Agitator

6.8 Low Temperature Asher.

6.9 Magnetic Stirrer and Teflon coated stir bars.

7. Reagents

7.1 2-propanol.

7.2 Hydrochloric acid, 38% (w/w).

7.3 Ammonium Hydroxide, 30% (w/w).

7.4 Dilute hydrochloric acid, 6 N. Add 50 mL HCl to 40 mL H_2O. Dilute to 100 mL.

7.5 α-Alumina (Alpha Micropolish, Buehler Ltd).

7.6 Talc, TA-99, MMD = 3.45 μm, MMAD = 5.5 μm, described in Reference 11.3.

7.7 Stock standard talc suspension; suspend 10 mg TA-99 talc in 100 mL 2-propanol in an **Erlenmeyer** flask containing a magnetic stir bar. Agitate ultrasonically for two minutes followed by two minutes of stirring.

7.8 Stock α-Al_2O_3 suspension; suspend 30 mg α-Al_2O_3 in 100 mL 2-propanol as described in Section 7.7.

8. Procedure

8.1 Cleaning of Equipment.

8.1.1 Glassware. New glassware must be cleaned by soaking in hot, concentrated nitric acid, followed by thorough rinsing with distilled or deionized water. Then, after each use, the glassware should be washed with, in order, detergent solution, tap water, dilute nitric acid (soak 4 hours or longer), and distilled or deionized water.

8.1.2 Silver membrane filters. If the qualitative scan described in Section 3 indicates use of the 006 talc peak at 28.59 °2 θ, it will be necessary to determine whether the silver filters contain any AgCl whose 111 peak at 27.83 ° 2 θ interferes. If so, the AgCl may be leached from the filters by soaking in concentrated NH_4OH for two hours followed by two rinses in 2-propanol and air drying.

8.2 Collection and Shipping of Samples

8.2.1 Assemble the filter in the cassette and close firmly to ensure that a seal is made around the edge of the filter (the filter is supported by a cellulose backup pad). Apply a shrinkable cellulose band to the outside of the cassette.

8.2.2 Attach nylon cyclone to cassette and remove cap. Remove the plugs from the cassette and attach to the personal sampling pump by means of flexible tubing. Clip the cassette, face down, to the worker's lapel. Air should not **pass through** any hose or tubing before entering the cassette.

8.2.3 Take the sample at an accurately known flow rate as close as possible to 1.7 L/min. A sample size of 200-L is recommended. Check the pump frequently during sampling to ensure that the flow rate has not changed. (If sampling problems preclude the accurate measurement of air volume, discard the sample.) Record the sampling time, flow rate, and ambient temperature and pressure.

8.2.4 With each batch of ten samples or less, submit one filter as a blank. Blanks should be from the same lot used for **sampling, and should have been subjected to step 8.2.1.**

8.2.5 Ship the cassettes so as to prevent excessive vibration or jarring to the cassette.

8.3 Analysis of Samples

8.3.1 Open the cassette filter holder and carefully remove the filter with tweezers and transfer it to a 30-mL glass beaker.

8.3.2 Ash filter in low temperature asher for 45 minutes.

8.3.3 Add 2 mL 6 N HCl to residue; agitate ultrasonically for 30 seconds and let stand for 3 minutes.

8.3.4 Turn on the magnetic stirrer under the α-Al_2O_3 suspension and stir for one minute. Turn the stirrer off and immediately withdraw 2 mL of the suspension using a micropipet with disposable tip and transfer to the sample beaker. Agitate ultrasonically for 2 minutes.

8.3.5 Mount silver membrane filter under filtering tower. With vacuum off, add approximately one half inch 2-propanol to the filtering tower. Pour the contents of the sample beaker into the tower with a minimum of splashing and apply vacuum. As the liquid level in the tower permits, rinse the beaker into it with 2-propanol. As the level in the tower approaches the filter, wash down the sides of the tower with 2-propanol from a squeeze bottle being careful not to shoot the stream directly into the liquid. Add no more 2-propanol after the filter surface is exposed.

8.3.6 Let air continue to be pulled through the filter until the sample is dry before releasing the clamp and removing the filter.

8.3.7 Analyze the talc peak selected in Section 3 by step scanning the peak and integrating the counts. Count the background on each side of the peak for one half the time used for peak integration, and add the counts from each side to obtain an average background. The difference between the integrated peak counts and the average background counts is the net peak counts.

9. Calibration and Standardization

9.1 Prepare working standards by pipetting aliquots of the stock standard suspension onto polyvinyl chloride filters. Working standards should contain 0, 20, 50, 100, 200, 400, and 800 µg talc per filter, i.e., 0.20 mL, 0.50 mL, 1.00 mL, 2.00 mL, 4.00 mL, and 8.00 mL stock suspension. Subject all standards to the same procedure as the samples, steps 8.3.3 - 8.3.7.

9.2 Using a least squares linear regression (or higher order fit), generate calibration equations from the net peak counts and prepared

concentrations (μg talc) of the standards.

10. Calculations

10.1 From the calibration equations obtained in Section 9, convert the sample net peak counts to μg talc/sample (W).

10.2 For personal sampling pumps with rotameters only, the following volume correction should be made.

$$V = \frac{f \cdot t}{1000}\left(\frac{P_1}{P_2} \cdot \frac{T_2}{T_1}\right)^{\frac{1}{2}}$$

where

V = the corrected volume (cubic meters) of air sampled

f = flow rate sample (liters/min)

t = sampling time (min)

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (K)

T_2 = temperature of air sampled (K).

10.3 Calculate the talc concentrations (C) in the air sample ($\mu g/m^3$) using the formula:

$$C = \frac{W}{V}$$

11. References

11.1 Backup Data Report for **Respirable Talc, prepared under NIOSH Contract 210-79-0060.**

11.2 P&CAM 259, NIOSH Manual of Analytical Methods, Volume 5 (NIOSH Publication 79-141).

11.3 Data Summary for Talc (TA-99), prepared under NIOSH Contract 210-75-0043.

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APPENDIX G

WOOD DUST

Methods Research Branch

Analytical Method

Analyte:	Wood Dust	Method No.:	P&CAM 356
Matrix:	Air	Range:	1.4 - 4.4 mg/m^3
Procedure:	Filter collection, drying and equilibration, gravimetric analyses	Precision:	$\overline{\% \ RSD}_T = 7.49$
Date Issued:	November 26, 1981	Classification:	E (Proposed)
Date Revised:			

1. Synopsis

   1.1 Air is drawn through a glass fiber filter; the filter is dried, equilibrated, and weighed.

   1.2 A known volume of air is sampled through the filter.

   1.3 The filter is dried, equilibrated, and weighed.

2. Working Range and Detection Limit

   2.1 The method was validated over the range 550 to 1750 µg wood dust per sample, corresponding to 1.4 to 4.4 mg/m^3 for a 400-liter air sample collected at 20 °C and 750 torr.

   2.2 The detection limit is less than 80 µg/filter (0.2 mg/m^3). This is most dependent on the consistency of the controlled atmosphere during filter equilibration.

3. Interferences

   3.1 Any ambient particulate matter other than wood dust will create a positive interference.

4. Precision and Accuracy

4.1 The relative standard deviation ($\overline{\%\ RSD_T}$) for the total sampling and analytical method in the range 1.4 to 4.4 mg/m^3 was 7.49. Details of the statistical treatment may be found in Reference 11.1.

4.2 The analytical method recovery was determined to be 1.000 ± 0.0031 at 1.0 times the NIOSH-recommended standard for wood dust. Collection efficiency was better than 97.5% in all cases. In stability studies of generated samples, the mean of samples analyzed after 14 days differed by only 5.9% from the mean of samples analyzed after 1 day.

5. Advantages and Disadvantages

5.1 The sampling device is small and portable and samples are easily collected.

5.2 The method is non-destructive to the samples.

5.3 The method is not specific to wood dust. Results may be affected by interferences.

5.4 Depending on particle sizes, the wood dust on the filter may not be well impacted. Care must be taken in transferring the filter.

5.5 Results are greatly affected by changes in humidity during equilibration. A consistent weighing room environment must be maintained.

6. Apparatus

6.1 Sampling equipment, consisting of a filter (37-mm glass fiber filter), a cassette to hold the filter, and personal sampling pump capable of sampling at 1.5 - 2.5 liters per minute. The pump must be calibrated with a representative filter in line and its flow rate must be known to within ± 5%.

6.2 Analytical balance with a sensitivity of 0.1 µg.

6.3 Oven, capable of maintaining 105 °C ± 2 °C.

6.4 Glass petri dishes, Kimax 60-mm x 15-mm.

6.5 Filters, glass fiber, 37-mm (Gelman type AE or equivalent).

6.6 Climate-controlled weighing room, temperature 70 °F ± 2 °F, relative humidity 42% ± 2%.

7. Reagents

7.1 There are no reagents required.

8. Procedure

8.1 Filter preparation.

8.1.1 Assemble the filter in the cassette and close firmly to ensure that a seal is made around the edge of the filter. Apply a shrinkable cellulose band to the outside of the cassette.

8.1.2 Remove the plugs from the cassette and attach to a pump by means of flexible tubing.

8.1.3 Pull air which has not been exposed to wood dust through the filter for one hour at a flow rate as close as possible to 1.7 liters per minute.

8.1.4 Remove the filter from the cassette and place in a glass petri dish. Dry the filter in an oven for 16 hours at a temperature of 105 °C ± 2 °C.

8.1.5 Allow the filter to equilibrate in a controlled atmosphere (Section 6.6) for 12 hours.

8.1.6 Weigh the filter to the nearest 0.1 µg, using the procedure specified by the balance manufacturer.

8.2 Collection and Shipping of Samples

8.2.1 Assemble the filter in the cassette and close firmly to ensure that a seal is made around the edge of the filter. Apply a shrinkable cellulose band to the outside of the cassette.

8.2.2 Remove the plugs from the cassette and attach to the personal sampling pump by means of flexible tubing. Clip the cassette to the worker's lapel. Air should not pass through any hose or tubing before entering the cassette.

8.2.3 Take the sample at an accurately known flow rate as close as possible to 1.7 liters per minute. Check pump frequently during sampling to ensure that the flow has not changed. If sampling problems preclude the accurate measurement of air volume, discard the sample. Record the sampling time, flow rate, and ambient temperature and pressure.

8.2.4 With each batch of ten samples or less, submit three filters as blanks. Blanks should be from the same lot used for sampling, and should have sampled the same volume of air as the other filters, but should not have been exposed to wood dust.

8.2.5 Ship the cassettes so as to prevent excessive vibration or jarring of the cassettes.

8.3 Analysis of the Samples

8.3.1 Remove the filter from the sample cassette and carefully place in a glass petri dish. Dry the filter in an oven at 105 °C for 16 hours with the petri dish uncovered.

8.3.2 Allow the filter to equilibrate for 12 hours with the petri dish uncovered in a controlled atmosphere.

8.3.3 Weigh the filter to the nearest 0.1 µg, using the procedure specified by the balance manufacturer.

9. Calculations

9.1 Calculate the amount of wood dust in the sample:

$$W_S = W_F - W_I - W_{BF} - W_{BI}$$

where

W_S = weight of wood dust sample (mg)

W_F = final weight of filter (mg)

W_I = initial weight of filter (mg)

W_{BF} = final weight of blank filter (mg) (average of 3 or more)

W_{BI} = initial weight of blank filter (mg) (Average of 3 or more).

9.3 For personal sampling pumps with rotameters only, the following volume correction should be made.

$$V = \frac{f \cdot t}{1000}\left[\frac{P_1}{P_2} \cdot \frac{T_2}{T_1}\right]^{\frac{1}{2}}$$

where

V = the corrected volume (cubic meters) of air sampled

f = flow rate of sample (liters/min)

t = sampling time (min)

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled

T_1 = temperature during calibration of sampling pump (K)

T_2 = temperature of air sampled (K).

9.3 Calculate the wood dust concentration in the air sample (mg/m^3) using the formula:

$$C = \frac{W_S}{V} .$$

10. Reference

10.1 Backup Data Report for Wood Dust, prepared under NIOSH Contract No. 210-79-0060.

10.2 NIOSH Technical Report "Wood Dust Director's Review Draft."

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