Development of a Method for Sampling and Analysis of Metal Fumes

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Fine dusts and fumes of metallic compounds are produced as a result of material handling and thermal processing operations involving metals and ores. The mechanism of dust production is primarily by comminution and the resulting particles range from one to several micrometers in size. Thermal operations involving vaporization produce much finer fumes in the 0.01 to 1 micrometer range. These dust and fume particles remain suspended in the work-place atmosphere for long periods of time and expose workers to several health risks arising through inhalation of these particles.

Inhaled particles can deposit in the respiratory system. Larger particles (several micrometers in size) are deposited in the ciliated portion and are cleared from the respiratory system by muco-ciliary action into the gastronomical tract, but may produce systemic toxic effects by absorption in body fluids. Finer particles reach the lower non-ciliated portion of the lungs, are cleared very slowly, and are responsible for diseases such as pneumoconiosis and lung cancer. Metallic lead (Pb), tellurium (Te), selenium (Se), and platinum (Pt) are known to cause both systemic and respiratory toxicity in laboratory animals and several cases of acute and chronic poisoning among metal workers have also been documented.

A method for sampling and analysis of the metallic dusts and fumes is necessary to assess the exposure of workers to these dusts. Personal sampling devices are used to collect samples from the work-place atmosphere in a representative manner. The samples are then analyzed by convenient analytical techniques such as atomic absorption spectroscopy.

The purpose of the present study is to develop and validate a method for sampling and analysing metal fumes. The techniques under examination are several of those presently prescribed by the National Institute for Occupational Safety and Health (NIOSH); they include collection of particles of the substance from the air by filters, the acid digestion of the filters, and measurement of the residue using atomic absorption spectroscopy. The several components of the study are:

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- Determination of the instrumental detection limit of atomic absorption spectrometry and also precision as a function of concentration for the four elements listed.
- Verification that presently prescribed dissolution procedures will result in greater than 90 percent recovery of the elements deposited on the filters in the form of pure metals or compounds of the metal.
- Development of modified or new dissolution procedures to replace those not providing satisfactory recovery.
- Generation and collection of metal fumes and determination of collection efficiency.
- Characterization of the generated fumes, i.e., particles.
- Analysis of the collected fumes and determination of the overall accuracy and precision of sampling and analysis for each fume.

Experimental effort has been devoted in parallel to evaluate the sampling operation as well as the analytic procedure.

The sampling operation involves collection of an aerosol sample that is representative of the particle size distribution and concentration of the sampled atmosphere. The efficiency of particle transport and collection operations are dependent on the particle size, sampling velocity, the geometry of the sampling apparatus and the properties of the collection medium. In the present work, a 37 mm diameter membrane filter (0.8 μm pore size) is the primary collection medium under evaluation. The filter is housed in a standard filter cassette and effects of filter-holder inlet geometry are also being investigated.

The dissolution and measurement experiments start with attempts to dissolve a sample (300 μg or less) of a metal or metal compound species using the prescribed NIOSH procedure, followed by measurement using the NIOSH atomic absorption spectrometric (AAS) procedure. If 90 percent recovery of the metal is not achieved, the dissolution procedure is modified, or changed completely, to achieve 90 percent recovery. From previous studies, it is expected that the metal oxides, and selenium generally, would pose problems. The NIOSH-AAS procedures are to be evaluated also, especially when the dissolution matrix is changed. The AAS detection limits using standards are determined through the measurement of blanks.

Experimental

1. Aerosol Sampling Studies. Metallic fumes can be formed by atomization of molten metals, by condensation of metal vapors, and by electric discharge (1). To realistically simulate the metal fumes expected from thermal processing and to cover worst-collection properties, a size range of 0.01 to 1 micrometers is most desirable as a target range in the selection of an appropriate generation technique. A condensation technique was selected in this study to generate fumes of Pb, Te and Se. Platinum was excluded from fume

studies due to high costs. A flow chamber was used to create a uniform aerosol atmosphere from which samples were taken for collection efficiency studies and to produce filters loaded with prescribed amounts of the aerosols for subsequent analytical studies. A schematic diagram of the experimental facility is shown in Figure 1. Details of the aerosol generation and the collection chamber are discussed below.

(a) Aerosol Generation. The condensation technique for aerosol generation has been used by several workers to produce spherical metallic particles in sizes ranging from 0.01 to several micrometers (2, 3, 4). The apparatus shown schematically in Figure 2 is similar to one used by Ranade, et al. (4) for generation of $PbCl_2$ aerosols. The material to be aerosolized is contained in a ceramic boat placed in a quartz tube heated by an electric furnace. A chromel-alumel thermocouple is used to monitor the temperature of the ceramic boat and also acts as a sensor for the furnace temperature controller. A constant flow of clean, dry N_2 gas is maintained through the quartz tube. The metal vapor is carried out of the furnace with N_2 and condensed to form a polydisperse aerosol. The primary aerosol is diluted by mixing with a filtered dry air stream. The diluted aerosol is then routed to the chamber as required and the excess aerosol is vented out through a glass fiber filter.

Effects of carrier gas flow rate, dilution flow rate, and the combustion boat temperature were studied by sampling the aerosol stream with an electrical aerosol analyzer to obtain the particle size distribution. Filter samples were taken for chemical analysis to determine mass concentrations. Aerosol samples were also collected in an electrostatic sampler for electron microscopic examination.

(b) Aerosol Characteristics. Initial tests were made with potassium chloride as a surrogate material and showed little influence of air flow rate on the size distribution in the flow rate range of 1 to 5 liters/min (Lpm). The aerosol output, however, depended on the flow rate. Temperature showed a major effect on the aerosol size distribution. In the aerosol generation experiments with Pb, Te, and Se, the N_2 carrier gas flow rate was therefore kept constant at 3 Lpm. A dilution air flow was maintained at 8 Lpm.

Effect of temperature was studied by stepwise variation of the temperature accompanied by a size analysis using the electrical aerosol analyzer. The size distribution data for selected temperatures are shown in Figures 3 through 5 for Pb, Te, and Se, respectively. The particle size increases as the generation temperature is increased. An aging chamber was used with the Te aerosol in some tests and increase in size by coagulation in the aging chamber is also evident in Figure 4.

Stable aerosol generation is important to maintain a stable atmosphere in the chamber. Good stability of the aerosol size distribution and mass output was observed for Pb aerosol over

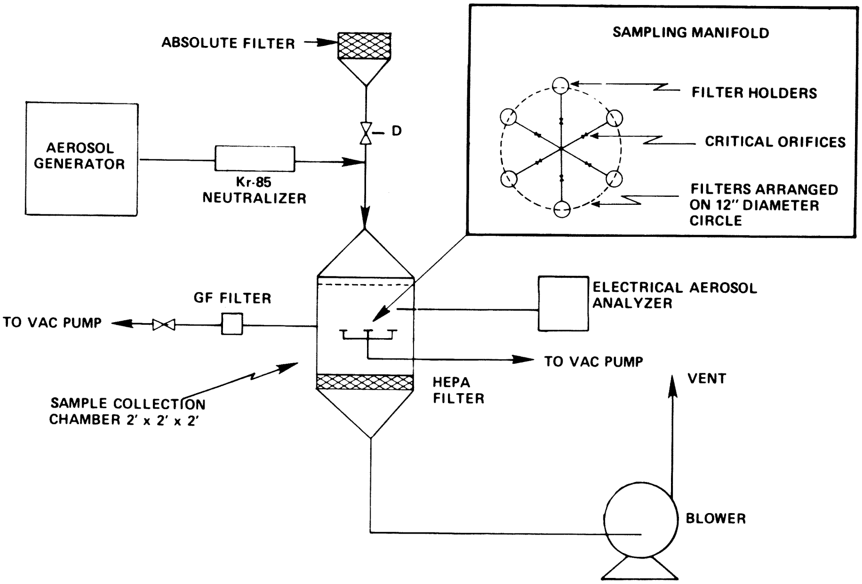


Figure 1. A schematic of the flow chamber for filter sample collection

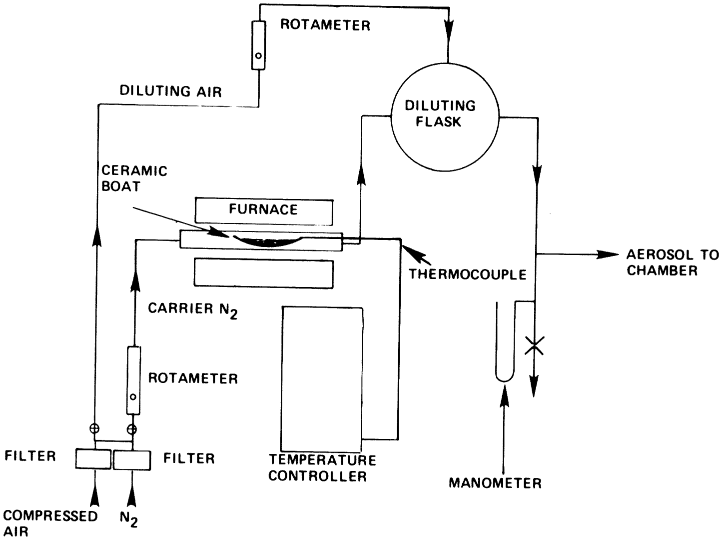


Figure 2. Lead chloride aerosol generator

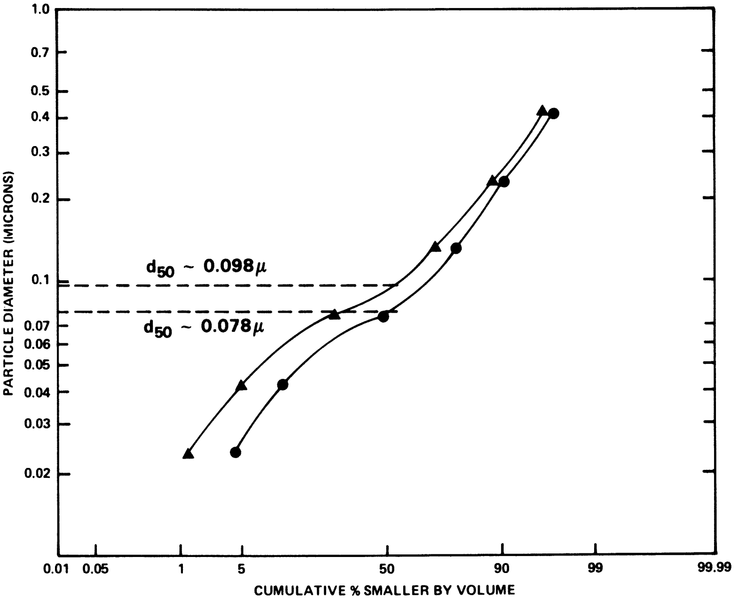


Figure 3. Particle-size distribution for lead aerosols: furnace temperature (●) —840°C, (▲) —895°C; carrier N_2 flow rate ~ 3 Lpm

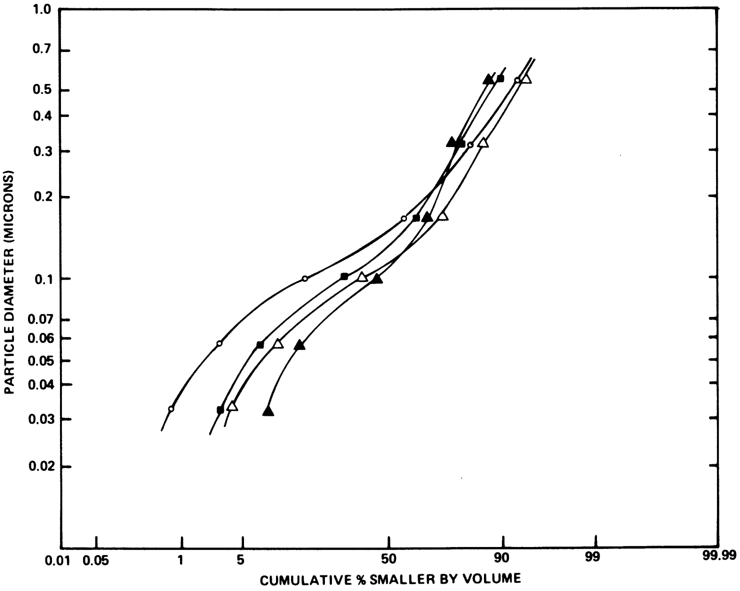


Figure 4. Particle-size distribution of tellurium aerosols at various conditions: (○) 500°C. (□) 455°C, (△) 500°C, (▲) 455°C; (○, □) with coagulation, (△, ▲) without coagulation

several hours as shown in Figure 6. Similar stability was observed for the Te aerosol. Preliminary tests with Se aerosols showed low mass output which decreased as generation was continued over several hours. Reasons for this occurance are being explored.

Based on these results, generation temperatures of 895°C and 500°C were chosen for Pb and Te, respectively. The aerosol characteristics are given below in Table I. Electron microscopic examination of the aerosol samples showed spherical particles in the 0.01 to 1.0 µm size range--in agreement with the electrical aerosol analyzer data.

Table I. Generation Temperature and Aerosol Characteristics

Metal	Temperature	Volume Median Diameter, µm	Mass Output, µg/min
Pb	895°C	0.10	47
Te	500°C	0.12	62
Se	375°C	0.40	-
Se	400°C	0.40	-

(c) Test Chamber and Collection Studies. A plexiglass chamber (2'x2'x2', active volume) was used as a test chamber (see Figure 1). The test aerosol is introduced at the top in a filtered air stream. The dilute aerosol is distributed across the chamber cross section via screens at inlet and outlet followed by a HEPA filter. A centrifugal blower is used to maintain a constant flow through the chamber as monitored by an orifice meter in the inlet section. The chamber is operated at a slightly negative pressure ($\approx$ 2" H_2O) to prevent leaks into the work area.

The sampling manifold shown in the insert in Figure 1 is designed to obtain six replicate samples on 37 mm filters in cassettes. Individual critical flow orifices are used to regulate the flow rate through each cassette. The chamber atmosphere is monitored using an electrical aerosol analyzer. Uniformity of the aerosol concentration was checked by obtaining six replicate samples of Pb aerosol followed by atomic absorption analysis. The results are shown in Table II and show good reproducibility.

The chamber is being used to produce replicate samples of Pb, Te, and Se at several loading levels for the analytical studies. Filter sampling and collection efficiencies are also being explored using Pb aerosols and by varying the sample flow rate through the 37 mm filter cassettes from 0.1 to 4.0 Lpm.

2. Dissolution Studies

(a) Experimental Apparatus. A Perkin Elmer Model 603 Atomic Absorption Spectrophotometer equipped with an HGA-2100 heated

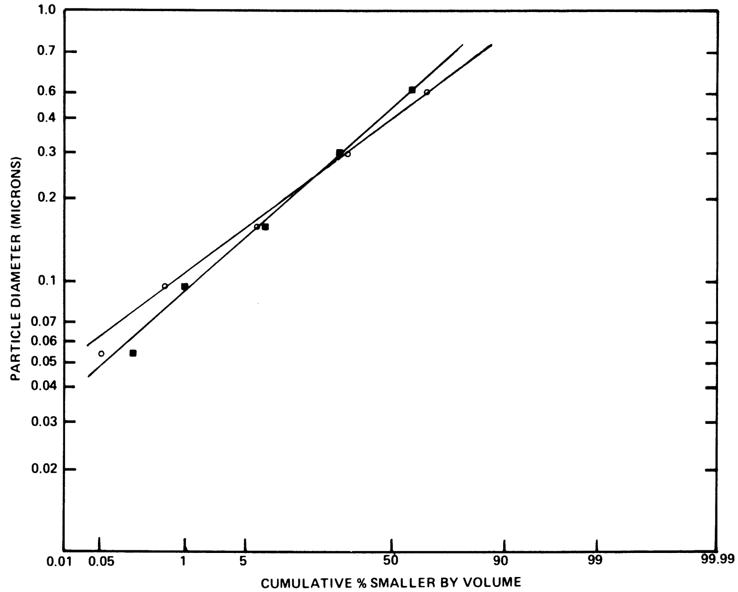
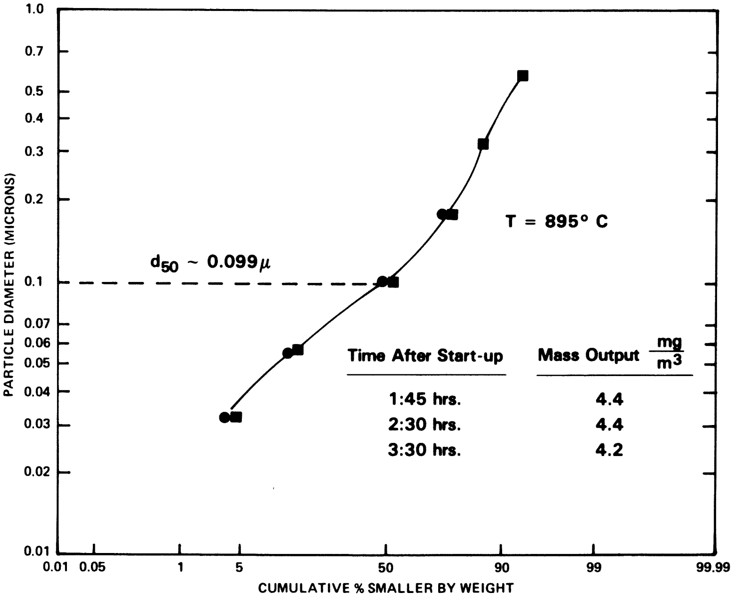


Figure 5. Particle-size distribution of selenium aerosols: (■) 400°C, (○) 375°C



Time After Start-up	Mass Output $\frac{mg}{m^3}$
1:45 hrs.	4.4
2:30 hrs.	4.4
3:30 hrs.	4.2

Figure 6. Particle-size distribution of lead aerosols at different times from start-up

Table II. Results of the Chamber Uniformity Tests

Position #	Pb Deposit, μg	Flow Rate Through Filter, Lpm	Normalized* Pb Deposit, μg
1	44	1.38	43.3
2	42	1.30	43.9
3	48	1.41	46.3
4	45	1.38	44.3
5	44	1.38	43.3
6	43	1.30	45.0
		1.36 avg.	44.4±1.1 avg., std. dev.

$$^{*}\text{Normalized Deposit} = \frac{\text{Actual Deposit x Average Flow Rate}}{\text{Actual Flow Rate}} .$$

Table III. Instrument Settings

Analyte	Wavelength (nm)	Slit (nm)	Background Correction	Element Source	Atomization
Pb	283.3	0.7	No	Electrodeless Discharge Lamp (EDL) at 10 watts	Air/ Acetylene Flame
Se	196.0	2.0	Yes	EDL at 6 watts	1) Ar/H_2[a] 2) Air/ Acetylene[b]
Te	214.3	0.2	Yes	EDL at 9 watts	Air/ Acetylene Flame
Pt	265.9	0.7	Yes	Hollow Cathode Lamp at 30 ma	Electrothermal Atomization[c]

[a] Used for all species except NBS-Se in steel.

[b] Used for NBS-Se in steel.

[c] Temp Program: Dry 110°C, 40 sec; Char 350°C, 20 sec; Atom 2750°C, 7 sec. 50 μL injection; 10 sec integration; argon purge gas.

graphite atomizer, a conventional flame atomizer including single slot and three-slot burner heads, a deuterium arc, background correction system, hollow cathode (HCL) and electrodeless discharge lamps (EDL) and a Model 56 recorder were used during the study. The graphite furnace was loaded manually using MLA microliter pipets. The instrument settings used for the vaious elements are shown in Table III.

(b) Sample Preparation. Initially, dissolution tests were to be made using test samples simulating real-world samples. Attempts were made to deposit species upon cellulose ester filters by spraying a slurry composed of the species in water. It was found difficult, however, to achieve a homogeneous slurry, even with the addition of surfactants. The mass of sample deposited on the filter could not be reliably related to the volume of slurry deposited. Due to the difficulty in obtaining a constant weight for the cellulose ester filters at the μg level, weighing could not be used to quantify the deposit and this work was discontinued. Depositions were then performed by weighing out the powder onto a 1-cm Teflon disk which was placed in the digestion flask with a filter. A minimum of six replicates were prepared in this manner for each species.

(c) Dissolution and Measurement. The prescribed dissolution and measurement procedures for the Pb, Te, Se and Pt species were tested. Modifications were made when recoveries greater than 90 percent were not achieved. These modifications are described below and Table IV shows the recoveries obtained with the NIOSH procedures or modifications of these procedures.

Lead. The existing NIOSH analytical procedure for Pb in air, S-341, involving dissolution in nitric acid was developed using $Pb(NO_3)_2$ (5). This procedure was to be evaluated using Pb metal, PbO, PbO_2, PbS_2 and NBS-SRM 1579 (Pb in paint). The procedure yielded adequate recoveries and precision for all species except PbO_2. With the addition of 1 mL, 30 percent H_2O_2, the oxidation state of lead was converted from +4 to +2 and greater than 90 percent yields were then obtained for PbO_2.

Selenium. The NIOSH method for Se in air, S-190, describes an extraction procedure which utilizes 0.1 N HNO_3 (6). This procedure was developed for K_2SeO_3. The species Na_2SeO_4, Se metal, SeS_2, SeO_2 and NBS-SRM 339 (Se in steel) were to be tested in this study.

The NIOSH procedure was originally developed in order to avoid the matrix effects which arise from acid-digested, cellulose ester filters; these effects suppress the selenium signal approximately 20 percent when using the argon (Ar)/H_2 flame (7). In the extraction procedure, the filter remains complete and has no effect upon the analysis. However, while the extraction procedure gives excellent recoveries for a soluble selenium salt such as K_2SeO_3, it does not solubilize Se metal or NBS-SRM 339 (Se in steel). Therefore, a digestion procedure was reconsidered. Since nitric acid dissolves

Table IV. Recoveries Obtained using NIOSH or Modified NIOSH Procedures

Species	Digestion Procedure	% Recovery	% Coefficient of Variance
Pb	S-341	94.5±5.8	6.1
Pb	Modified*	103.3±3.4	3.3
PbO	S-341	92.9±3.5	3.8
PbS	S-341	92.6±4.9	5.3
PbO_2	S-341	81.6±2.9	3.5
PbO_2	Modified	99.8±1.3	1.2
Pb in Paint	S-341	94.5±2.7	2.9
Pb in Paint	Modified	93.9±5.2	5.5
Se	Modified	92.6±7.0	7.6
Na_2SeO_4	Modified	97.2±4.4	4.5
SeS_2	Modified	90.8±5.3	5.9
SeO_2	Modified	91.3±7.1	7.8
Se in Steel	Modified	90.6±1.5	1.6
Te	S-204	97.2±5.3	5.4
Te	Modified	99.9±5.4	5.4
Pt	Modified	94.2±9.2	9.7
$(NH_4)_2PtCl_4$	Modified	96.7±7.9	8.2
PtO_2	Modified	98.0±9.5	9.8

*Modified procedures were developed and used when one or more species of a particular element did not yield >90 percent recovery (see text).

only one of three forms of selenium metal, an aqua regia digestion was examined. It was decided that the filter interference could be dealt with by employing one of three possible procedures:

1. employing standard additions and Ar/H_2 flame;
2. digesting standards with filters added and using Ar/H_2 flame; or
3. utilizing the slightly less sensitive but hotter air/acetylene flame.

Since maximum sensitivity was desired, the first two procedures were considered. Standard additions proved slightly more time consuming in terms of both sample and data manipulations, thereby leaving the second option as the procedure of choice. This procedure yielded >90 percent recoveries for Se metal, Na_2SeO_4, SeS_2 and SeO_2. Recoveries for NBS-SRM 339 were <10 percent. It was quickly realized that the high iron matrix in the sample was playing a major role in signal depression, as the sample otherwise appeared completely solubilized. Although addition of iron to the standards improved the recovery to >90 percent, the sensitivity was still poor, ~5-10 percent of that obtained in an iron-free matrix. To reduce this effect, a hotter air/acetylene flame was chosen. Sensitivity proved to be only a factor of two lower than that obtained with the argon/hydrogen flame (in absence of interferences). Recoveries were still >90 percent. Consequently, should there be any questions regarding interferences in the sample, one could select the air/acetylene flame for any selenium-in-air analysis without sensitivity suffering significantly.

Tellurium. The NIOSH Method S-204 for analysis of Te in air was originally developed using $Te(OH)_2$ (8). RTI applied this procedure to the analysis of the pure metal. The procedure involves the use of both nitric and perchloric acids during the digestion. Recoveries were excellent, ~97 percent. An additional set of samples were subjected to a digestion involving no perchloric acid, i.e., nitric acid only. This digestion yielded recoveries averaging 99.9 percent. Since the analyst may wish to avoid the use of perchloric acid wherever possible, he might opt for the latter procedure.

Platinum. The NIOSH Method S-191 was developed for soluble Pt salts in air (9). The digestion involves the use of nitric and perchloric acids which are ineffective with Pt metal. Therefore, it was decided to use a nitric-hydrochloric acid digestion procedure. Pt and $(NH_4)_2PtCl_4$ were recovered satisfactorily but PtO_2 appeared inert to the dissolution mixture and recoveries for PtO_2 were less than 5 percent. However, PtO_2 is converted to a mixture of Pt metal and PtO at temperatures greater than 380°C (10). Therefore, a series of six replicates were prepared in quartz crucibles. The samples (with filters included) were first wet ashed in the crucibles which were then placed in an oven and heated to 500°C. The residue was then treated with aqua regia as before. Recoveries subsequently averaged >90 percent with a precision of about ±10 percent.

The electrothermal AAS measurement of Pt is linear to approximately 2 µg/mL using 50 µL injections, above which a high-point-density calibration curve is absolutely necessary. Poorer precision for platinum species is probably related to some degree to the graphite furnace analysis. More specifically, the graphite tube degradation affects the sensitivity, thereby necessitating frequent standard injection--on the order of one standard every three or four samples. Generally, pyrolytic graphite tubes have greater lifetimes than uncoated tubes.

(d) Detection Limits. Instrumental detection limits were determined for each of the elements using standard solutions prepared and measured according to the modified procedures described above. The detection limits were calculated as corresponding to twice the standard deviation of the blanks, and are presented in Table V.

Table V. Instrumental Detection Limits Based on Twice the Standard Deviation of the Blank

Element	Standard Curve Concentration Range, µg/mL	Detection Limit Determined with Standard Solutions, µg/mL
Pb	0-80	0.27
Pt	0-0.20	0.0030
Se	0-40	0.20
Te	0-40	0.29
Se (in steel)	0-64	1.8

Summary and Conclusions

Sampling and analysis of several metal fumes were investigated in order to develop a reliable method for monitoring work place atmospheres. Significant results are listed below.

1. Lead, tellurium, and selenium aerosols in 0.01 to 1 micrometer size range could be generated using a condensation aerosol technique. The particle size is dependent on the generation temperature. The aerosol output is dependent on both the generation temperature and the carrier gas flow rate.
2. The stability and reproducibility were excellent for lead and tellurium aerosols. Selenium aerosol output decreased with time at a given temperature.
3. The uniformity of aerosol concentration in the sample collection chamber was excellent.

4. A nitric acid/hydrogen peroxide digestion was found to satisfactorily solubilize all lead species in the study.

5. In order to dissolve adequately all selenium species including selenium metal and selenium in steel samples, an aqua regia digestion procedure was used in lieu of the existing NIOSH extraction method.

6. For platinum compounds, the nitric/perchloric acid digestion mixture used in NIOSH procedure S-191 was replaced with aqua regia to solubilize platinum metal. Platinum dioxide was solubilized by first heating the compound to >380°C to convert the PtO_2 to the aqua regia-soluble forms of platinum metal and platinum monoxide.

7. Tellurium metal was found to be recovered adequately not only with the NIOSH procedure using nitric acid/perchloric acid but also with a simple nitric acid procedure.

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