

Metals Determination in Atmospheric Particulates by Atomic Absorption Spectrometry With Slurry Sample Introduction

Alberto Fernández C.*, Raiza Fernández, Nereida Carrión, and Dulce Loreto
*Centro de Química Analítica
Facultad de Ciencias Universidad Central de Venezuela
Apartado 47102, Caracas 1041-A, Venezuela*

and
Zully Benzo and Rebeca Fraile
*Centro de Química Instituto Venezolano de Investigaciones Científicas
Apartado 21827 Caracas 1020-A, Venezuela*

INTRODUCTION

Atomic absorption spectrometry (AAS) has become a widely used analytical method for trace metal determination in atmospheric particulates, in particular in conjunction with electrothermal atomization (ETA-AAS). Its low detection limits, accuracy, wide applicability, high selectivity, and high sensitivity facilitates accurate evaluation of low-volume samples (1-7).

In AAS, airborne particulate samples collected on filters must be introduced in a soluble form, normally requiring some kind of pretreatment prior to analysis. This may cause filter destruction as well as blank problems, loss of analytes (8-10), and be very time-consuming. Acid extraction without destruction of the filter has been used in the determination of trace amounts of Cu, Pb, Zn, Al, Ca, Co, Cr, Fe, Mg, Mn, Ni (4,11-16). These methods use the solution from the acid treatment for analysis and to simplify the procedure, the residue is usually discarded. However, it has been found that this residue often contains significant amounts of metals like V and Al (6,16,17). Such methods can be used for the analysis of acid-extracted metals in airborne particulates, but not for the determination of total concentration of some metals.

ABSTRACT

An investigation has been carried out to establish a rapid method for the determination of total V, Cd, Ni, Cu, Pb, Fe, and Mn in atmospheric particulates using electrothermal atomization atomic absorption spectrometry and flame atomic absorption spectrometry with slurry sample introduction. To evaluate the accuracy of the proposed method, standard reference material Urban Particulate Matter NBS 1648 was analyzed accordingly. Results obtained and certified values did not show statistically significant differences. The precision of the method, when applied to real samples, was in the range of 1 to 3% expressed as RSD %. The results are compared with a standard dissolution procedure.

In an attempt to reduce blank levels and to establish environmental monitoring programs, several workers reported the collection of atmospheric particulates in containers especially designed for use in electrothermal atomizers (6,10,18-22). The advantages of this method are that no pretreatment steps are required, the risk of losses or contamination as well as tedious, time-consuming work is reduced. However, equipment for the direct collection is not yet commercially available, and analytical standardization is difficult to achieve. For the determination of Cd and Pb in airborne particulates,

some authors (9,10,22,23) inserted the filter paper directly into the graphite furnace. This method has matrix problems, and interelement interferences together with poor precision and calibration standards is not easily available.

Direct analysis of solid samples with the slurry technique offers the ability to use solid and liquid sampling (24-27). Previously, we described an AAS method for the determination of metallic elements in pine samples (28,29) and in four different types of plant tissues (30). The aqueous slurries of the powdered samples were pipetted directly into the electrothermal atomizers (slurry AAS). The pretreatment step was reduced to a minimum, and the slurry does not require special tools or equipment. Reproducibility, precision, and accuracy are similar to that of conventional methods. A number of authors have successfully used slurry AAS for the determination of several metals in sediments (31,32), rocks and minerals (33), soils (34-36), plant leaves (29,30,37), plant tissues (32,38), food (39), coals (40,41), sewage sludges (42), pigments (43), and others.

The aim of this investigation was to evaluate the applicability and accuracy of a rapid AAS method with slurry sample introduction for the determination of total Cd, Ni, Cu, Pb, Fe, Mn, and V in airborne particulate matter. The elements Ni, Cd, V, Cu, and Pb are mainly found in fine particulates emitted from

* Corresponding author.

anthropogenic activities (i.e., industrial, transport) and their contribution to the atmosphere seems to be higher than the one produced by natural sources (44,45). Iron and manganese are mainly found in the natural composition of the earth's crust and may be released into the atmosphere by soil erosion (44,46,47).

EXPERIMENTAL

Apparatus

Graphite Furnace Atomic Absorption Spectrometer

A Jarrel Ash atomic absorption spectrophotometer Model 83000 was modified for this study. The original hollow cathode power supply control and analog portion of the signal processing circuit were replaced with a line reversal background corrector system constructed in our laboratory. The graphite furnace used was a Perkin-Elmer HGA-400 with an AS-40 autosampler. Pyrolytically coated graphite tubes were used for the determination of V and Ni, while a pyrolytically coated graphite tube together with a L'vov platform were used for the determination of Cd. Measurements were made in the integrated area mode using a data acquisition system (developed in our laboratory) that was connected to a Hewlett Packard Model 85 microcomputer. Intensity versus time during the atomization step was stored and the acquired data processed. The background-corrected absorbance versus time (atomization profile) was displayed on the computer screen. With this system, additional information such as maximum appearance time of the peak, peak area, and peak height readings can also be obtained.

Flame Atomic Absorption Spectrometer

The determination of Pb, Fe, and Mn was carried out by flame atomi-

zation using a Varian Model 875 atomic absorption spectrometer.

Reagents

All chemicals used were of analytical reagent grade. Deionized water (Milli-Q) was used throughout. Stock solutions (1000 mg/L) of Cd, Ni, V, Fe, Pb, Cu, and Mn (British Drug House) were diluted to provide working standard solutions.

Urban Particulate Matter Standard Reference Material (SRM) from the National Bureau of Standards (NBS) 1648 was used to assess the accuracy of the slurry method and for preparing the working standard suspensions.

Samples

Atmospheric particulates were collected over a one-week period using a low-volume sampler in different locations in the Caracas downtown area. The low-volume air sampler was constructed at the University of Hamburg, Germany, under VDI 2463 German official regulations. Particulates were collected on a cellulose acetate membrane filter (Schleicher and Schuell ST 69).

PROCEDURES

Slurry Preparation

The Urban Particulate Matter (SRM NBS 1648) slurry was prepared by suspension of 50 mg of the dried material in 100 mL 1% nitric acid solution and then homogenized with ultrasonic agitation. The working standard suspensions were made by dilution. The slurries can be prepared suspending up to 4 mg/mL in 1% nitric acid solution without agglomeration of solid particles.

The airborne particulate samples collected onto a filter were treated with 2.5 mL of 1:1 nitric acid in a clean test tube and left in an ultrasonic bath for 30 minutes at 90°C; the cellulose filter was completely

destroyed. The resulting slurry was diluted with water until 1% nitric acid concentration was obtained. Depending on analyte concentration, the slurry concentration varied from 0.4 to 0.1 mg/mL for the analytes determined by flame atomization and from 0.3 to 0.05 mg/mL for the analytes determined by electrothermal atomization. The sample blank was prepared by dissolving a new clean filter in the same amount of nitric acid.

All slurries were stirred with ultrasonic agitation for one minute before measurement.

Analytical Determination

Analytical determination by flame AAS or ETA-AAS was dictated by the concentration levels of the analyte under study. Lead, iron, and manganese concentrations were determined by flame atomization, while electrothermal atomization was used for copper, nickel, vanadium, and cadmium determination.

Reference Method

Sample wet acid digestion was used as the reference method (16). The airborne particulate samples were digested in an HF-HCl-HNO₃ mixture (1:1:2) and heated at 80°C for four hours.

RESULTS AND DISCUSSION

Measuring Conditions

For the elements determined by flame AAS, the following parameters were optimized: aspiration rate, flame type, and background correction using suspended and aqueous standards. The effect of the aspiration rate was checked by measuring the absorption signal at different aspiration rates. Maximum absorption was at a rate of 2-3 mL/minute. To find the optimum flame atomization conditions, the effect of flame composition, air-acetylene and nitrous oxide-acetylene on absorption of Pb, Mn, and Fe was investigated. The analyte absorption signal

was not affected by flame composition. Both measurements with and without background corrector gave identical signals for all elements. Therefore, background correction was not found to be necessary. All flame measuring conditions are the same for aqueous and suspended standards.

Optimum Furnace Heating Conditions

Optimization of heating conditions was carried out with suspended standards containing 3 µg/L Cd and 30 µg/L Ni, and with aqueous standards containing 80 µg/L V and 5 µg/L Cu. The optimum conditions found for the

aqueous standards did not differ significantly from those obtained for suspended standards. The heating conditions are shown in Table I.

Use of Aqueous Standards

To evaluate the use of aqueous calibration standards in slurry analysis, calibration curves were obtained for all elements to be determined using standard solutions and standard suspensions made of NBS SRM. Table II shows the regression line coefficient and concentration range for calibration curves obtained for V, Cu, Pb, Fe, and Mn with both types of standards. It was observed that there were no statistically significant differences in the

slope and interception point for V, Pb, Fe, Cu, and Mn in the working range studied. Therefore, aqueous standard calibration can be successfully used.

Figure 1 shows the calibration curves obtained for Ni and Cd. Their deviation from linearity was observed in the calibration curves for suspended standards beginning with 5 µg/L and 50 µg/L, respectively. An increase in atomization temperature did not improve the linear range in the calibration curves for suspended standards. For Ni and Cd in the range of 10–50 µg/L and 1–5 µg/L, respectively, the differences in slope and

TABLE I
Furnace Heating Conditions for the Determination of Cd, Ni, V, and Cu

Elements	Dry		Step 2		Char		Atomize ^a	
	Step 1		Step 2		Temp (°C)	Time (s)	Temp (°C)	Time (s)
	Temp (°C)	Time (s)	Temp (°C)	Time (s)				
Cd	80	5	120	10	300	30	1400	3
Ni	80	5	120	10	800	30	2400	5
V	80	5	120	10	1000	30	2650	6
Cu	80	5	120	10	1000	20	2500	4

^a Stop flow.

TABLE II
Regression Line Coefficient and Concentration Range for Solution and Standard Suspensions

	Concentration range		Regression line A = mc + b		Correlation coefficient (r ²)	
	Solution	Slurry	Solution	Slurry	Solution	Slurry
V (µg/L)	20–120	20–120	0.029C+0.004	0.032C+0.002	0.9982	0.9979
Cu (µg/L)	10–80	10–80	0.052C+0.005	0.049C+0.003	0.9972	0.9969
Pb (mg/L)	1–15	1–15	0.088C+0.002	0.087C+0.003	0.9998	0.9993
Fe (mg/L)	1–10	1–10	0.057C+0.001	0.059C+0.001	0.9997	0.9997
Mn (mg/L)	1–7	1–7	0.025C+0.002	0.027C+0.001	0.9996	0.9995

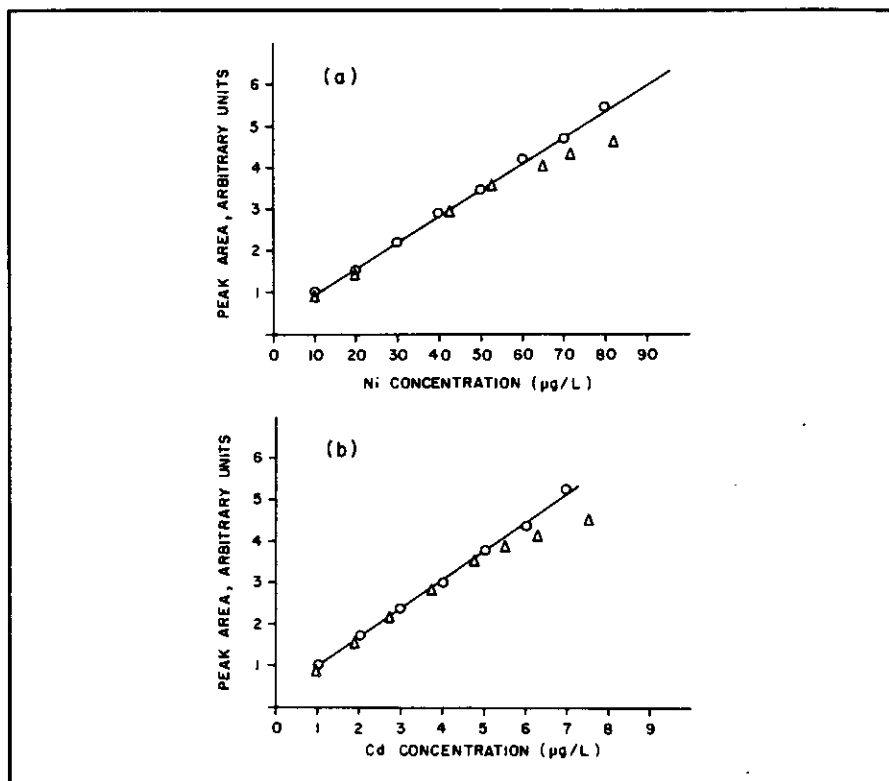


Fig. 1. Calibration graphs for (a) nickel and (b) cadmium.
 Δ Suspended standards
 \circ Aqueous standards

intercept for both calibration methods were not statistically significant when a Student *t*-test (48) was applied for a confidence level of 95%. Therefore, aqueous standard calibration can be successfully used.

Analysis of Urban Particulate Matter

To test the accuracy and feasibility of the metal trace determination using AAS with the slurry sample introduction method, the NBS SRM 1648 Urban Particulate Matter was analyzed using aqueous standards. Table III shows the results of five replicate analyses for this sample as well as the certified values. Comparison of the experimental mean with a certified value using the Student *t*-test for a confidence level of 95% proved that there were no statistically significant differences between the observed and certified values (48). This result shows the applicability of the proposed method for total metal trace determination in atmospheric particulates.

TABLE III
 Determination of Cd, Ni, Cu, V, Mn, Fe, and Pb in SRM NBS 1648 (\pm SD)

Element	Cd (mg/g)	Ni (mg/g)	V (mg/g)	Cu (mg/g)	Mn (mg/g)	Fe (%)	Pb (%)
Found ^a	75 \pm 3	82 \pm 5	140 \pm 6	610 \pm 10	840 \pm 10	3.90 \pm 0.07	0.650 \pm 0.007
RSD (%)	4	6	4.6	1.6	1.2	1.8	1.1
Certified	75 \pm 7	82 \pm 2	140 \pm 3	609 \pm 27	(860) ^c	3.9 \pm 0.1	0.655 \pm 0.008
Found ^b	77 \pm 1	79 \pm 3	104 \pm 9	612 \pm 15	830 \pm 15	3.87 \pm 0.06	0.647 \pm 0.007
RSD (%)	1.3	3.8	8.7	2.5	1.8	1.6	1.1

^a Direct introduction slurry process.

^b Extracted solution.

^c Not certified value.

Analysis of Particulates Collected onto Filter

The particulate airborne samples collected onto filters are subjected to further destruction as described in the Experimental section. The SRM samples were digested using the proposed method for filter dissolution and the clean solution was analyzed. The aim of this study was to verify if the elements under consideration had been extracted or remained suspended as part of an insoluble phase as a result of the filter treatment.

Table III shows the results obtained in the extraction analysis for the determination of Cd, Ni, Cu, Pb, Fe, Mn, and V. Statistically significant differences were not found between observed and certified values for all elements, except vanadium, when the Student *t*-test was applied for a confidence level of 95%. The results show that only vanadium was not totally solubilized with this treatment. The value found for vanadium is nearly 26% less than the certified value.

Two different samples collected onto filter were analyzed using the method with the solution and slurry introduction procedure. The comparative results obtained are given in Table IV. In general, there is good agreement for all elements and total recovery is obtained with the slurry AAS method using aqueous standards as calibration standards. To estimate the significant difference between the values obtained by the two methods, the Student's *t*-test for the mean and the *F*-test were applied. The results show that there is no statistically significant difference between the mean of both populations for a confidence level of 95% (48).

Results Obtained for Collected Atmospheric Particulates

To show the applicability of the proposed slurry method, samples from different locations in the Caracas valley were analyzed for V, Cd, Cu, Ni, Pb, Fe, and Mn. The results shown in Table V indicate that for the levels at which particulate pollutants in ambient air can be determined with good precision, the relative standard deviation varies from 1-3%.

CONCLUSION

The results obtained point to the feasibility of using slurry sample introduction and AAS for routine determination of V, Ni, Cd, Pb, Fe, Cu, and Mn in atmospheric particulates. The advantages of this method include simplicity of the procedure, less expense for use of reagents, shorter time required for analysis, less risk of contamination, and determination of total concentration of elements under investigation.

Use of aqueous solutions as calibration standards in the reported range simplifies the slurry technique even more. For real samples, reproducibility of the proposed method (as RSD %) varies from 1-3%. This range is similar to conventional methods using acid dissolution.

ACKNOWLEDGMENT

The support of this work by Research Grant CO321-86 from CDCH.UCV is gratefully acknowledged.

Received February 4, 1991.

TABLE IV
Comparative Results – Solution-AAS and Slurry-AAS Methods

	Sample A				Sample B			
	Solution	RSD(%)	Slurry	RSD(%)	Solution	RSD(%)	Slurry	RSD(%)
Cd (mg/g)	13.0	1.5	12.6	2.4	3.60	1.4	3.60	1.9
Ni (mg/g)	44.8	0.9	45.1	1.1	28.5	1.0	28.0	0.7
Cu (mg/g)	52.4	1.1	53.0	0.9	79.1	0.9	78.2	0.8
V (mg/g)	34.0	0.9	33.0	0.9	56.5	1.1	57.2	1.2
Mn (mg/g)	305	1.3	312	1.6	530	0.9	537	1.1
Fe (%)	1.73	1.6	1.68	1.7	1.45	1.5	1.48	1.3
Pb (%)	0.75	1.3	0.77	1.3	0.55	1.8	0.55	1.3

TABLE V
Results for the Determination of V, Cd, Cu, Ni, Pb, and Mn in Atmospheric Particulate
Collected in the Caracas Valley Using the Proposed Slurry Method

Sample	1	2	3	4	5	6	7	8
V ($\mu\text{g}/\text{m}^3$)	0.0209	0.0109	0.0292	0.0486	0.0116	0.0086	0.0307	0.0261
RSD (%)	1	2	3	1	1	1	2	1
Cd ($\mu\text{g}/\text{m}^3$)	0.0014	0.0017	0.0020	0.0037	0.0019	0.0010	0.0090	0.0028
RSD (%)	2	2	2	2	1	1	1	1
Cu ($\mu\text{g}/\text{m}^3$)	0.0525	0.0268	0.0566	0.0184	0.0889	0.0139	0.0016	0.0121
RSD (%)	2	2	3	1	1	2	2	3
Ni ($\mu\text{g}/\text{m}^3$)	0.0039	0.0069	0.0052	0.0076	0.0018	0.0042	0.0080	0.0027
RSD (%)	3	2	2	2	1	1	1	2
Pb ($\mu\text{g}/\text{m}^3$)	1.28	0.73	1.07	0.93	0.67	0.90	1.34	1.47
RSD (%)	1	1	2	1	1	1	2	1
Fe ($\mu\text{g}/\text{m}^3$)	2.02	1.27	1.07	1.55	1.74	2.57	3.62	1.60
RSD (%)	1	2	1	2	1	2	1	2
Mn ($\mu\text{g}/\text{m}^3$)	0.0638	0.1136	0.0417	0.0608	0.1837	0.0511	0.0679	0.0837
RSD (%)	1	2	2	2	1	2	2	2

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