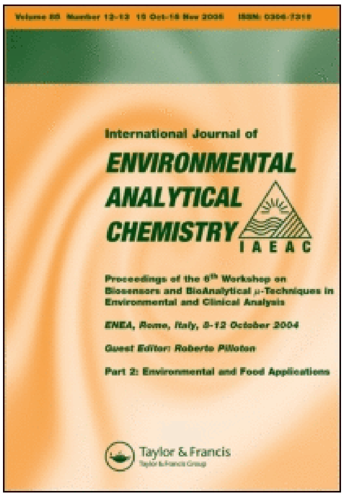

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Emission Spectrographic Determination of Arsenic, Antimony, Cadmium, Lead, Copper, and Zinc in Airborne Particulates Collected on Glass Fiber Filter

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KEY WORDS: Analytical method, emission spectrography, boiler cap electrode, trace elements, airborne particulates.

A fast, simple, precise, and direct emission spectrographic method has been developed for the determination of arsenic, antimony, cadmium, lead, copper, and zinc in airborne particulates collected on glass fiber filter. Sample discs, punched out from the glass fiber filter, are packed in a boiler cap electrode. Fifty microliters of an internal standard solution containing 10 mcg/ml of indium are added dropwise on the discs. After evaporating the solution, the electrode is subjected to DC arc excitation (current: 15 A, analytical gap: 2 mm, exposure time: 30 sec with no preburn). The precision of the method is consistently better than ±12%.

INTRODUCTION

Various methods for determining trace elements in airborne particulates have been reported in the literature. These include emission spectrography,[1-10] atomic absorption spectrometry,[11-20] X-ray fluorescence,[21,22] neutron activation analysis,[23-26] and spark source mass spectrometry.[27] Of these methods, emission spectrography has been used extensively for determining trace elements in airborne particulates, especially in large-scale survey work.

However, most sample preparation techniques for emission spectrographic analysis involve wet, dry or low-temperature ashing to destroy organic matter in airborne particulates, dissolution of elements in acid and concentration prior to analysis. These sample preparation steps are time-consuming and provide the opportunities for sample contamination and loss of sample constituents. Additionally, all elements are not necessarily dissolved in acid. It is anticipated that direct discharge of airborne particulates collected on filter media solves these problems.

Previously, Wheeler *et al.*[2] determined beryllium (collected on paper filters) spectrographically by a direct-sparking paper filter mounted on a silver rotating platform electrode. Lander *et al.*[6] determined Al, Ca, Cd, Cr, Cu, Fe, Pb, Mg, Ni, Si, Ti, and Zn on paper filter by a direct-reading spectrograph, using a push-up technique to introduce the sample paper filter directly into the analytical gap. We have reported direct spectrographic methods for determining Fe, Pb, Mn, V, Sn, Ni, and Cu in airborne particulates collected on glass fiber filter;[7] Mn and Pb on paper filter;[8] Si, Fe, Zn, Al, Mg, Ca, Pb, Mn, Cu, and V on membrane filter;[9] Hg on activated carbon filter.[10]

The present paper describes a fast, simple, precise, and direct emission spectrographic technique for determining four toxic elements; As, Sb, Cd, and Pb, and some other elements, including Cu and Zn in airborne particulates collected on glass fiber filter.

EXPERIMENTAL

Equipment and materials

A Shimadzu 1.7-m Ebert grating spectrograph (Type GE-170) equipped with 1,200 lines per mm grating having a reciprocal linear dispersion of 4.8 Å per mm in the first order was used. A Shimadzu Modular source (Type No. 280000) was used for direct current excitation. The unit has outputs of 5, 10, and 15 A at 200 V direct current. Spectral line density was measured with a Nippon Jarrel–Ash microphotometer (Type JM-3).

Shapes and sizes of high-purity graphite electrodes employed are shown in Figure 1. The necked electrode and counter electrode of the requisite dimensions are commercially available, as is the boiler cap with a 1-mm diameter orifice. In this laboratory, the orifice of the boiler cap is machined to 2.4 mm diameter.

A high-volume air sampler manufactured by the Kimoto Electric Co. was used to collect airborne particulates. Air was drawn through a Whatman GF/A glass fiber filter or Toyo GB-100R glass fiber filter (8 in. × 10 in.) at a flowrate of about 1.5 M^3/min for 24 hr, and airborne particulates were collected on the filter. The Whatman GF/A filter was usually used. However,

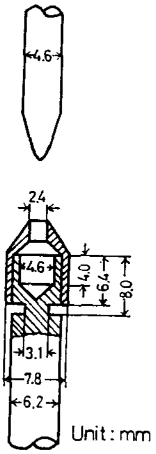

FIGURE 1 Shapes and sizes of electrodes.

the filter is not suitable for zinc analysis because of its high zinc content. For zinc analysis, the Toyo GB-100R filter was used because of its low zinc content (0.64 mcg/in.^{2}), although the filter contained a considerably high concentration of arsenic and was not suitable for arsenic analysis. Both filters are fairly good for analysis of antimony, cadmium, lead, and copper in airborne particulates.

Indium stock solution was prepared by dissolving 0.100 g of reagent-grade indium metal in a minimum volume of nitric acid and diluting to a liter with distilled water. An internal standard solution was prepared by diluting a portion of this indium stock solution to 10 times its volume with distilled water. Each stock solution of As, Sb, Cd, Pb, Cu, and Zn was prepared by dissolving a weighted portion of the reagent-grade metal in a minimum volume of nitric acid and diluting to standard volume in a volumetric flask. Requisite amounts of the solutions were then mixed and diluted with distilled water to make a series of standard solutions. The amounts are based upon the estimated amounts of elements in airborne particulates and the desired range to be covered. Each standard solution also contains 10 mcg/ml of indium as the internal standard. All other chemicals used were commercially available and of reagent-grade.

PROCEDURE

Necked graphite electrodes are warmed 10 min in an oven at 80°C. The crater portion of each electrode is briefly immersed into a 5% solution of paraffin in carbon tetrachloride and then oven-dried for a few minutes. Using a stainless steel cork borer, sample discs of 4 mm in diameter are punched out at random from a sample glass fiber filter, on which airborne particulates were collected. The discs are packed in the crater of each electrode to the level of the lip of the electrode. This requires 10 discs of Whatman GF/A glass fiber filter, or 6 discs of Toyo GB-100R glass fiber filter. Approx. 20 mcl of methyl alcohol is added dropwise on the filter discs to distribute the indium internal standard solution, which is subsequently added, evenly in the electrode. A micropipette is used to deliver 50 mcl of the internal standard solution to the discs in each electrode yielding an amount of 0.5 mcg of indium per electrode. The solution in the electrode is evaporated to dryness in an oven. A boiler cap is put on the electrode. Standard sample electrodes are prepared in the same manner by adding dropwise the standard solutions on the discs of unused glass fiber filter packed in the electrode. The electrodes thus prepared are discharged under the conditions given in Table I.

TABLE I

Experimental conditions

Excitation source	:	15 A DC arc
Sample electrode	:	Hitachi NE-1205 (Necked electrode) Hitachi BC-1601 (Boiler cap)
Counter electrode	:	Hitachi CTE-2001
Analytical gap	:	2 mm
Pre-burn time	:	None
Exposure time	:	30 sec
Slit width	:	20 microns
External optics	:	Quartz cylindrical lens, imaging source on grating
Step filter	:	3 step filter (Transmission : 4, 20, and 100%)
Detector	:	4 × 10-in. Kodak SA-1 plates
Spectral region	:	2400–3600 Å, first order

The photographic plate is developed in D-19 for 4 min, stopped for 10 sec in 5% acetic acid, fixed in Fuji-Fix for 5 min and washed in running water for 10 min.

The density differences of the analytical line pairs listed in Table II are measured to determine the amount of each element present in the sample discs. The working curves shown in Figure 2 are obtained by applying the above-mentioned procedure to the standard electrodes. The concentration of each element in the atmosphere is calculated from a knowledge of the filter area and the volume of air sampled.

TABLE II

Analytical line pairs and concentration ranges

	Range (mcg/M^3)
As I 2780.197 Å /In I 3256.090 Å[b]	0.016 ~ 0.32[c]
Sb I 2877.915 Å /In I 3256.090 Å[b]	0.016 ~ 0.32[c]
Cd I 3261.057 Å /In I 3256.090 Å[b]	0.006 ~ 0.13[c]
Pb I 2823.189 Å[a]/In I 3256.090 Å[b]	0.32 ~ 6.4[c]
Cu I 2824.369 Å /In I 3256.090 Å[b]	0.16 ~ 3.2[c]
Zn I 3282.333 Å[a]/In I 3256.090 Å[b]	0.26 ~ 5.2[d]

[a] Spectrum at 20% transmittance part of step filter.
[b] Spectrum at 4% transmittance part of step filter.
[c] Based on a 2,000 M^3 air sample collected on Whatman GF/A glass fiber filter.
[d] Based on a 2,000 M^3 air sample collected on Toyo GB-100R glass fiber filter.

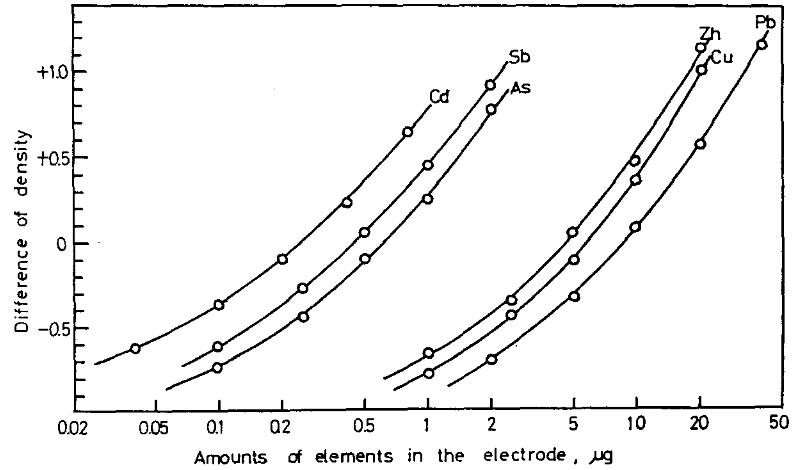

FIGURE 2 Working curves.

RESULTS AND DISCUSSION

Arsenic, antimony, cadmium, lead, copper, and zinc have a poor spectrographic sensitivity. A highly sensitive method is necessary especially for the determination of arsenic, antimony, and cadmium which are present in minute amounts in the atmosphere. Use of a boiler cap electrode is one of the highly sensitive methods for the determination of these volatile elements.[28,29] Spectroscopic variables associated with the application of the boiler cap electrode for the determination of trace elements in airborne particulates are discussed below.

The effect of variation in arc current on volatilization pattern of each element was studied. As an example, a spectral line density-time curve for lead is given in Figure 3. At the arc current of 15 A, lead was completely volatilized after 30 sec. In addition, a maximum line-to-background ratio was obtained at this current. Volatilization of arsenic, antimony, cadmium, copper, and zinc, which maybe classified as the volatile element group, was similar to that of lead. However, selective volatilization was strongly in evidence. Elements such as silicon, iron, aluminum, magnesium, manganese calcium, barium and so forth, which may be divided into volatility groups of medium volatile or involatile, tended to delay in volatilization, and vaporization of these elements continued more than 90 sec.

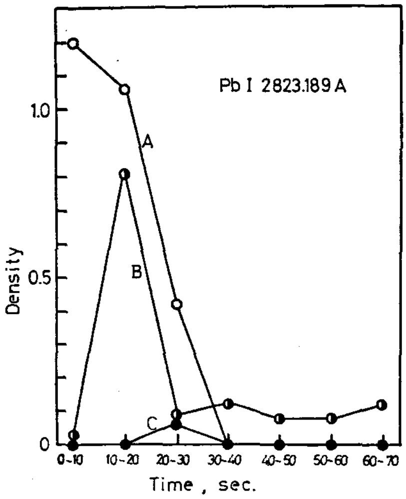

FIGURE 3 Spectral line density-time curves at various currents A, 15 A; B, 10 A; C, 5 A.

The orifice diameter of the boiler cap considerably affected the volatilization of elements out of the sample and the background. The density-time curve of Pb I 2823.189 Å and the background, adjacent to the line, are shown in Figure 4. For the spectral line, background correction was made by subtracting the background density from the total density. The volatilization tended to delay with decreasing diameter of the boiler cap orifice. In addition, a higher background was observed in the case of a smaller diameter of the orifice. A maximum line-to-background ratio was obtained for a 30-sec exposure with no preburn, using the boiler cap with 2.4 mm diameter orifice.

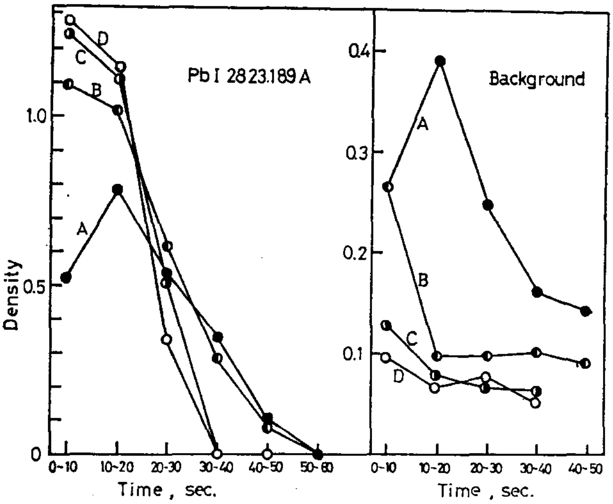

FIGURE 4 Effect of the diameter of the orifice of the boiler cap on the volatilization of element and the background. A, 1.0 mm; B, 1.8 mm; C, 2.4 mm; D, 3.0 mm.

The effect of the electrode gap on the line-to-background ratio was examined. The line-to-background ratio generally decreased with increasing electrode gap as a result of an increase in background continuum without a corresponding increase in line intensity. An electrode gap of 2 mm provided the best line-to-background ratio. In addition, the shortness of the electrode gap decreased the amount of arc wandering and led to better reproducibility.

To assess the effect of the electrode polarity on line-to-background ratio coupled with the cathode layer effect, the cathode and anode sample excitation were examined. The distribution of lengthwise gap intensity was studied by projecting the electrodes on the slit of the spectrograph by means of the optical system. Figure 5 shows the distribution of the density of spectral line Pb I 2823.189 Å and that of the background. The spectral line was considerably more intense near the cathode both in the cathode and anode excitation, as a result of cathode layer enrichment. The spectral line was more widely distributed in the arc gap in the cathode excitation than in the anode excitation. Indeed, in the anode excitation, the spectral line was observed only at the part of the cathode electrode, where the background was high. Background was more intense at the close-anode region than at the close-cathode region both in the cathode and anode excitation. The longitudinal intensity distribution of the other analytical elements, with the exception of arsenic, was similar to that of lead. Arsenic showed negligible cathode enrichment, presumably because of the high ionization potential (10.5 V). These results clearly favored the use of the cathode sample excitation. In this laboratory,

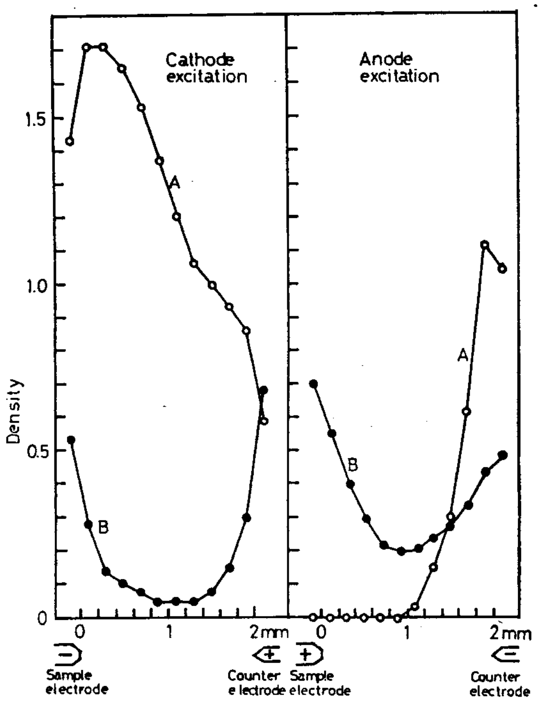

FIGURE 5 Longitudinal density distribution of spectral line and background. A, Pb I 2823.189 Å; B, Background.

to eliminate the background emitted from the parts of electrodes, a vignette mask passing the central 2 mm of the discharge is placed on a collimator mirror of the spectrograph.

The influence of co-existing elements in airborne particulates on the analytical line intensity was examined. The examined elements are iron, aluminum, calcium, magnesium, and sodium, which are common elements in airborne particulates. The electrodes for this experiment were prepared by adding dropwise 50 mcl of solutions of analytical elements, incorporating definite amounts of co-existing elements, on the discs of unused glass fiber filter packed in the electrodes. The ranges of amounts of the co-existing elements added to the electrodes are as follows: iron and aluminum: 20–500 mcg (equivalent to the atmospheric concentration of 4–80 mcg/M^3 on the basis of an air volume sample of 2,000 M^3), calcium, magnesium, and sodium: 10–250 mcg (2–40 mcg/M^3). The spectral line densities of the analytical elements were almost unaffected by these co-existing elements. Previously, Shaw *et al.*[30] have reported that the CN-band spectrum was reduced by buffering the sample with the salt of an alkali metal in the case of double arc furnace method, which resembled the boiler cap method in the principle of excitation. It was felt that line-to-background ratio would be improved by impregnating the boiler cap with salt of an alkali metal. The boiler cap, impregnated with sodium chloride, was prepared by heating it to redness in a crucible, followed first by immersion in a saturated solution of sodium chloride, and then by ovendrying. The background was reduced by impregnating the boiler cap with sodium chloride. However, the spectral line density was greatly reduced, and the line-to-background ratio which resulted, decreased the sensitivity of detection.

Indium was chosen as an internal standard element since the volatilization behavior of the element closely paralleled that of each element studied. In addition, indium tends to occur in insignificant amounts in most airborne particulates.

The standard sample electrodes were prepared by adding dropwise the standard solutions on filter discs and evaporating the solutions. In order to evaluate the spectrographic method, it is necessary to confirm that airborne particulate samples behave similarly to the evaporated standard solutions during the discharge step. For this experiment, sample discs, packed in the crater of the electrode were spiked by adding dropwise a solution containing known amounts of arsenic, antimony, cadmium, lead, copper, and zinc, and then analysed. Recoveries of the added elements ranged from 92.3% to 107% at levels approximating to their airborne particulate concentrations.

Table III shows the coefficient of variation of concentration for the elements determined and the concentration at which it was determined. In nearly all cases, the coefficient of variation was 12% or less: values which are generally acceptable for most air pollution analysis requirements.

The procedure for the determination of trace elements in airborne particulates usually involves the initial destruction of organic matter in airborne

TABLE III

Coefficient of variation of analytical elements

Element	Coefficient of variation (%)	Amount in the electrode (mcg)	Air volume sampled (M^3)	Atmospheric concentration (mcg/M^3)	Number of determinations
As	11.1	0.11	1,870	0.019	8
Sb	12.3	0.20	1,870	0.034	8
Cd	10.9	0.15	1,870	0.026	8
Pb	7.6	7.8	1,870	1.3	8
Cu	8.5	1.7	1,870	0.29	8
Zn	9.2	3.6	2,056	0.93	8

particulates followed by acid dissolution of elements. Some investigators have reported losses of low-melting elements such as cadmium, lead, copper, and zinc during dry ashing of airborne particulates at high temperature.[15,17–19] These losses have been explained frequently by volatilization of the elements at high temperature. In contrast to this explanation, Kometani *et al.*[20] have recently reported that the losses during the dry ashing were mainly due to the formation of acid-insoluble compounds (metal silicates), as metal salts reacted with glass fiber filter. To make clear the losses of elements at high temperature, adjacent areas of airborne particulate samples collected on glass fiber filter were ashed under different conditions, and then arsenic, antimony, cadmium, lead, copper, and zinc on the glass fiber filter were determined by the proposed method (Table IV). The amounts of these elements on the glass fiber filters treated at ~100°C by low-temperature ashing, and at 400°C, 500°C and 600°C by dry ashing were all within the experimental error of each other, and were approximately in agreement with those on the glass fiber filter without ashing treatment. On the basis of these data, it seems reasonable to assume that volatilization of arsenic, antimony, cadmium, lead, copper, and zinc during the dry ashing at 400°C, 500°C and 600°C for 1 hr is negligible.

TABLE IV

Comparison of results[a] of airborne particulate samples[b] treated at various temperatures

	Element											
	As		Sb		Cd		Pb		Cu		Zn	
Ashing method	Sample		Sample		Sample		Sample		Sample		Sample	
	1	2	1	2	1	2	1	2	1	2	1	2
DA[c] 400°C	0.29	—	0.14	0.04	0.04	0.11	4.7	8.3	2.6	1.5	—	3.0
DA 500°C	0.26	—	0.14	0.04	0.04	0.08	5.2	7.4	2.7	1.3	—	3.0
DA 600°C	0.26	—	0.14	0.04	0.04	0.09	5.3	8.1	2.7	1.7	—	3.4
LTA[d] ~ 100°C	0.28	—	0.15	0.04	0.04	0.09	5.8	7.6	2.8	1.4	—	3.2
No treatment	0.29	—	0.18	0.05	0.04	0.11	5.9	8.1	3.1	1.5	—	3.0

[a] Expressed as mcg/cm² glass fiber filter; each value is the mean of quadruplicate determinations.
[b] Sample 1 was collected on Whatman GF/A glass fiber filter; sample 2 was collected on Toyo GB-100R glass fiber filter.
[c] DA: Dry-ashed for 1 hr in a muffle furnace.
[d] LTA: Low-temperature ashed for ½ hr in a Trapelo low-temperature asher, Model LTA-504.

Samples of airborne particulates were analyzed for arsenic, antimony, cadmium, lead, copper, and zinc by the described method. Table V shows the values obtained for the airborne particulate samples collected at 10 m above the ground in a commercial area of Osaka.

TABLE V
Analytical results

Sample No.	Concentration (mcg/M^3)					
	As	Sb	Cd	Pb	Cu	Zn
1[a]	0.014	0.031	0.014	1.64	0.20	—
2[a]	0.017	0.016	0.011	0.52	0.16	—
3[a]	0.029	0.058	0.008	1.26	0.25	—
4[a]	0.023	0.051	0.020	0.45	0.23	—
5[b]	—	0.029	0.042	1.48	0.40	0.83
6[b]	—	0.043	0.088	2.43	0.33	0.47

[a] Sample collected on Whatman GF/A glass fiber filter.
[b] Sample collected on Toyo GB-100R glass fiber filter.

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