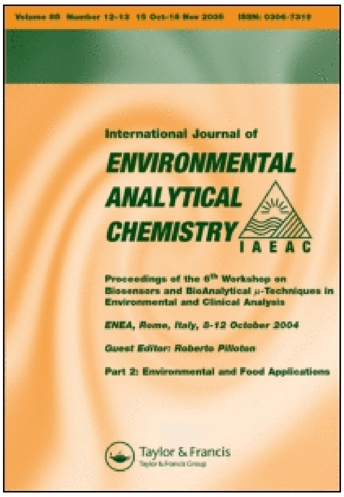

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The Accurate Measurement of Lead in Airborne Particulates

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The accurate and rapid measurement of lead in airborne particulates is discussed with particular reference to so-called high-volume air samples. By standard addition analysis, it was found that there is no significant matrix error in measurements of lead taken on glass high-volume filters, within the range of concentrations investigated. This applies to varying or fixed amounts of the glass filter matrix. Recovery of standard added lead is quantitative. Although glass fibre sheet is much too impure for the analysis of most airborne metals, it is possible to analyze lead since the blank is reasonably uniform and since the amounts of lead on such a filter are large in comparison to the blank. Some additional corroboration has been obtained that the distribution of lead is uniform across the total exposed area of the filter. The final error of the lead measurement, as reported, is likely to be more largely a function of sampling problems such as time and flow measurements and particulate fall off and disturbance in sampling, transit and storage.

INTRODUCTION

Due to its toxicological importance, there is a voluminous literature on the measurement of lead. There is an increasing realization that the danger from inhalation may be greater than that from ingestion. Although the amount ingested in food and drink is much larger than that inhaled, the air absorption route may be more open and direct. Before going on to discuss atomic absorption (AA) as an analytical method, some of the other methods will be briefly mentioned.

(*a*) Polarography
(*b*) Anodic stripping voltammetry
(*c*) X-ray fluorescence

Polarographic methods for measurement of lead in air have been published by Levine[1] and by Dubois and Monkman.[2] The method is sensitive and accurate but the polarographic wave may be interfered with seriously if sample preparation is incomplete. Anodic stripping voltammetry is a very promising technique. It has been reviewed by Neeb[3] and some applications to the analysis of air samples have been given by Matson.[4]

X-ray fluorescence (XRF) has been suggested as a useful technique for the measurement of lead in airborne particulates which have been taken on dry filter media.[5] An advantage of XRF may be the minimal sample preparation where an aliquot disc of the filter is placed in the X-ray sample holder without the need for a wet digestion procedure. A disadvantage of XRF is the inherent and appreciable matrix error. This error could be reduced if air samples were consistently taken on organic filter media. This is not the case at the present time, however, as high-volume air sampling networks in North America are set up on the basis of glass fibre filters. The matrix error due to the use of this very impure material is serious and not to be compensated for unless the standards can be made up in a background identical to the air samples. It is not sufficient, for example. to calibrate by comparing lead standards prepared in boric acid against airborne lead taken on a glass fibre filter. The calibration of an XRF method is likely to be tedious and somewhat difficult. In their work, Leroux and Mahmud[5] compared XRF measurements of lead against measurements already made by AA on the same samples, accepting the AA measurement as being correct.

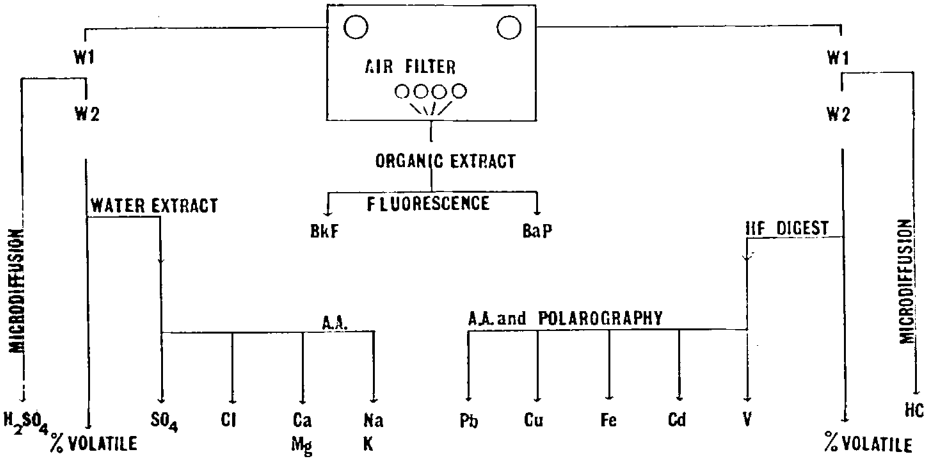

FIGURE 1 Analytical scheme for air filter analysis

Emission spectrography also suffers from matrix error and the associated need for lengthy calibration and carefully standardized conditions. Lead is not one of the elements best analyzed by emission spectrography. According to Morgan, AA is superior to emission spectrography.[6] While remembering that the emission spectrograph has been in use for a long time and is of classical respectability, a change in emphasis may now be noted, in that emission spectrography and XRF are now being used as scanning techniques for the preliminary assessment of a sample, by means of which a rough idea as to amounts and relative proportions of elements is obtained. After this, quantitative measurements are made by AA.

Figure 1 shows the procedure followed for the complete analysis of an air sample taken on glass filters. A description of the AA method used in our laboratory to measure lead in these samples will follow.

EXPERIMENTAL

Reagents

Air, compressed, in cylinders. Acetylene, compressed, in cylinders. Glass filters, 8 × 10 in., Gelman A. Filter paper, ashless, Whatman No. 41. Water, distilled at least twice from glass. Hydrofluoric acid, 49%, J. T. Baker Analyzed. Nitric acid, 71%, J. T. Baker Analyzed.

Apparatus

Atomic absorption spectrophotometer. Büchner funnel, polypropylene, 8½ × 10½ in. Beakers, PTFE, 100-ml capacity.

PROCEDURE

Before using the glass filters for air sampling, the impurities present may be leached out by means of boiling distilled water. A special Büchner funnel, rectangular rather than circular, was constructed of polypropylene by Bel Art Products, Pequannock, New Jersey. This was designed to hold one box of 8 × 10 in. Gelman A filters. To improve the access of the hot distilled water, spacers (Teflon grids) are placed in the pile at intervals of every ten filters. The pile of filters is covered with boiling water, allowed to steep for 30 min and the water is withdrawn by suction. This process is repeated. The washed glass filters are allowed to air-dry in a dust-free location.

The glass filter is mounted in a conventional high-volume sampler. The air to be sampled is drawn through the filter at a flow rate of 40–50 cubic feet/min for 24 hr. The total volume of air sampled amounts to approximately 2000 m^3. Area aliquots are cut from the exposed area of the filter by means of a circular metal disc. One convenient area aliquot is a disc of 47-mm diameter. In preparation for analysis, one or more 47-mm discs are placed in a Teflon beaker. The glass filter matrix is dissolved by the drop-wise addition of 1 ml of hydrofluoric acid. The contents of the beaker are gently fumed at low heat until the hydrofluoric acid is evaporated. At this point, 1–2 ml of nitric acid is added and gentle heating is continued until a few drops of HNO_3 are left. About 10 ml of distilled water is added, brought close to the boiling point and the sample is filtered through Whatman No. 41. The beaker is rinsed down with 10 ml distilled water, which is similarly heated and filtered. The combined filtrates are transferred to a 25-ml volumetric flask and made up to volume and also stored in screw-cap polyethylene bottles. The sample is now ready for measurement.

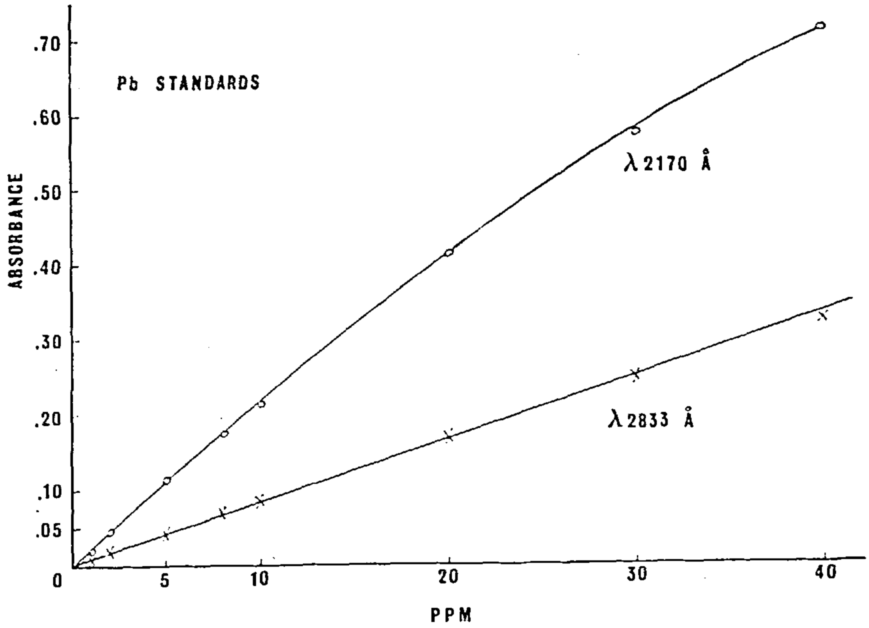

FIGURE 2 Aqueous standard lead curves at two wavelengths.

Figure 2 shows the calibration curves obtained at 2833 Å and 2170 Å with a commercially available AA instrument, PE403, using standards diluted with distilled water. Curve 1 of Figure 3 is the calibration curve obtained again at 2833 Å with standards diluted in the filter blank. This filter blank was obtained by digestion with HF and HNO_3 of a 47-mm disc, as described previously, and subsequent dilution to 25 ml with distilled water. Since this second curve intersects the Y axis, this intercept value can be considered as the amount of lead present in the filter, or as the amount of lead and other interfering materials giving a response as lead.

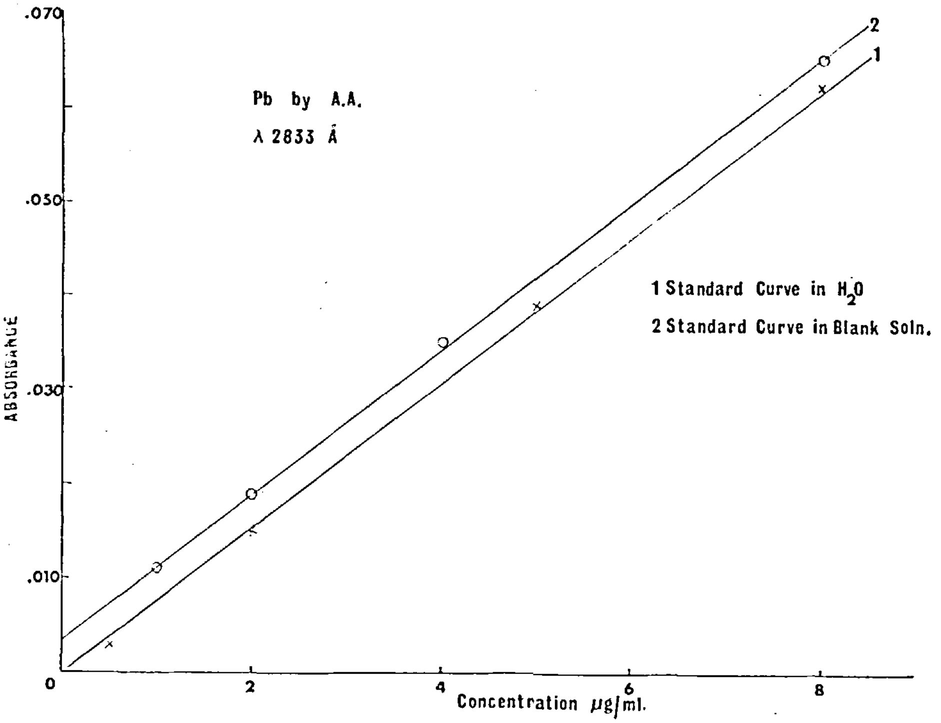

FIGURE 3 Standard lead curves in water, and filter matrix.

Repetitive analysis of 40 different filters, 20 washed filters and 20 unwashed, gave respectively an average value of 0.19 mcg/ml and 0.24 mcg/ml for a total of 4.75 mcg and 6.0 mcg for a 47-mm disc. The values are given in Table I. It should be noted, however, that these values are related to a given batch of filters only and values as high as 0.40 mcg were observed with a different batch of filters. Results obtained in the following experiments were calculated from the calibration curve prepared with the standards diluted in distilled water.

One aspect of the practical reproducibility obtained by this method is illustrated by Table II which shows the satisfactory agreement obtained for a group of ten replicates cut from one particular high-volume filter. The agreement is so good that in most cases differences are only evident in the second decimal of micrograms. The uniformity of these values supports the theory that the distribution of lead across the filter is also uniform.

TABLE I

Lead blanks of washed and unwashed glass filters

	Washed		Unwashed	
	No.	Lead (mcg/ml)	No.	Lead (mcg/ml)
	1	0.13	11	0.14
	2	0.28	12	0.25
	3	0.20	13	0.18
	4	0.18	14	0.19
	5	0.24	15	0.27
	6	0.16	16	0.23
	7	0.19	17	0.29
	8	0.15	18	0.21
	9	0.23	19	0.25
	10	0.24	20	0.20
	21	0.26	31	0.27
	22	0.24	32	0.27
	23	0.25	33	0.25
	24	0.14	34	0.25
	25	0.06	35	0.22
	26	0.17	36	0.26
	27	0.15	37	0.22
	28	0.12	38	0.27
	29	0.18	39	0.28
	30	0.17	40	0.22
n	20	- -	20	- -
Mean	- -	0.19	- -	0.24
Low	- -	0.13	- -	0.14
High	- -	0.28	- -	0.29

In the analysis of air samples taken on an 8 x 10 in. glass fibre filter, it is taken for granted that the distribution of the contaminant is uniform across the whole exposed area. This is implicit in the methods of sample preparation which are usually based on the preparation of a portion of the filter. The calculation of the total quantity of contaminant is made by prorating the aliquot area and total exposed area. This seems a dangerous assumption to make; however, experiments carried out by Dubois *et al.*[7] indicated that there was no significant difference in the lead levels obtained by analyzing aliquot discs taken from different portions of the filter. Since only one aliquot size was considered in this work, it may be that significant differences would begin to appear if the aliquots were sufficiently reduced in size. It is also necessary to remember that, if the high-volume filter is overloaded, classification may occur and particulates may be lost by fall off. The latter situation will result in analytical results lower than the truth. This possibility is probably best prevented by standardizing sampling conditions at a lower flow rate or for a shorter time period.

TABLE II

Ten replicate lead analyses from one filter

First aliquot	First reading (mcg/ml)	Second reading (mcg/ml)	Difference
A	1.65	1.67	0.02
B	1.78	1.87	0.09
C	1.73	1.85	0.12
D	1.67	1.64	0.03
E	1.75	1.81	0.06
F	1.47	1.58	0.11
G	1.67	1.69	0.02
H	1.62	1.61	0.01
I	1.73	1.78	0.05
J	1.61	1.73	0.12
Arithmetic mean	1.67	1.72	0.06
S.D.	0.085	0.096	0.04
Coefficient of variation	5.08	5.56	- -

Taking two instrumental readings on the same prepared sample, as in Table II, gives an indication of the reproducibility of the AA instrument quite independently of the chemical treatment of the sample. A typical example of the reproducibility of the method is shown in Table III, where 62 air samples were analyzed in duplicate. Two separate 47-mm discs were cut from each filter, separately digested and the duplicate prepared samples were independently assayed for lead by AA. The arithmetic means and standard deviations of the differences between measurements are given in micrograms per ml of prepared sample. The difference in the average lead concentrations

TABLE III

Duplicate lead analyses of 62 different air filters

Sample No.	First measurement (mcg/ml)	Second measurement (mcg/ml)	Difference
1	1.64	1.70	0.06
2	1.57	1.53	0.04
3	2.76	2.88	0.12
4	11.08	10.74	0.34
5	5.15	5.28	0.13
6	5.46	5.44	0.02
7	8.30	8.24	0.06
8	7.65	7.50	0.15
9	1.96	2.01	0.05
10	2.71	2.86	0.15
11	1.61	1.65	0.04
12	0.72	0.79	0.07
13	2.01	1.53	0.48
14	1.85	1.79	0.06
15	1.68	1.73	0.05
16	1.27	1.26	0.01
17	2.73	2.69	0.04
18	4.66	4.66	0.00
19	4.06	3.99	0.07
20	2.08	2.14	0.06
21	1.45	1.43	0.02
22	1.33	1.30	0.03
23	2.02	2.08	0.06
24	2.78	2.58	0.20
25	3.25	3.16	0.09
26	2.15	2.07	0.08
27	5.22	5.37	0.15
28	2.11	2.02	0.09
29	2.73	2.72	0.01
30	1.08	1.06	0.02
31	2.65	2.62	0.03
32	6.14	5.92	0.22
33	1.98	1.86	0.12
34	1.72	1.72	0.00
35	4.22	4.08	0.14
36	1.96	1.98	0.02
37	1.73	1.83	0.10
38	8.29	8.14	0.15
39	1.72	1.71	0.01
40	1.63	1.85	0.22

TABLE III—*cont.*

Sample No.	First measurement (mcg/ml)	Second measurement (mcg/ml)	Difference
41	3.96	3.84	0.12
42	1.71	1.76	0.05
43	3.81	3.85	0.04
44	6.50	6.52	0.02
45	0.87	0.88	0.01
46	1.82	1.94	0.12
47	1.42	1.25	0.17
48	1.22	1.24	0.02
49	2.13	2.17	0.04
50	2.17	2.19	0.02
51	0.82	0.95	0.13
52	2.19	2.39	0.20
53	1.50	2.01	0.51
54	1.74	1.91	0.17
55	4.44	4.45	0.01
56	4.91	4.96	0.05
57	1.37	1.53	0.16
58	5.39	5.70	0.31
59	5.61	5.02	0.59
60	1.19	1.15	0.04
61	2.60	2.66	0.06
62	2.04	2.02	0.02
Arithmetic mean	2.99	3.00	0.11
S.D.	2.12	2.07	0.11

of the two separate groups of 62 assays is 0.11 mcg/ml on a mean value of 3.00 mcg/ml.

Based upon the statistical analysis of the lead values found in 38 air samples Burnham *et al.*[8] concluded that "it is necessary to utilize the standard additions technique to overcome matrix effects". Experiments carried out by us on blank glass filters, on air samples taken on such filters and on aqueous lead standards, are summarized in Figure 4 which does not support this statement. Figure 4 represents, firstly, lead standards in water run at 2833 Å; secondly, lead standards added to an air sample having a particulate loading of 36 mcg/m^3, and, thirdly, lead standards added to an air sample having a particulate loading of 143 mcg/m^3.

If a matrix effect exists, the effect can be either negative or positive, resulting in a decrease or increase in the measured lead value as compared with the truth. The curves of Figure 4 show that the slopes obtained with standard addition of lead are identical to the slope of the calibration curve obtained with lead standards made up in distilled water. In Figure 5 the same samples and standards are also analyzed at 2170 Å. The results obtained at 2170 Å are in complete agreement with those obtained at 2833 Å. An additional proof of no interference from the matrix can be derived from the results given in Table IV and V. In Table IV six separate identical volume aliquots were taken from prepared air sample No. 758. The volume aliquots were made up to differing total volumes. The values for total lead found are identical for each of the six assays, within experimental error. Similarly, in Table V, seven separate but differing volume aliquots were taken from prepared air sample No. 759. One hundred micrograms of standard lead were added to each of the aliquots, which were made up to total final volumes varying from 5.0 to 50.0 ml. Again, all lead assays are within experimental error, with the exception of one. In Table VI, ten replicate discs were taken from one air filter, these were prepared for analysis with the standard addition of 50.0 mcg of lead in each case. Three blank discs from three separate filters were prepared for analysis at the same time. The results of Table VI indicate not only the lack of matrix effect but the uniformity of distribution of lead particulates across the surface of the filter.

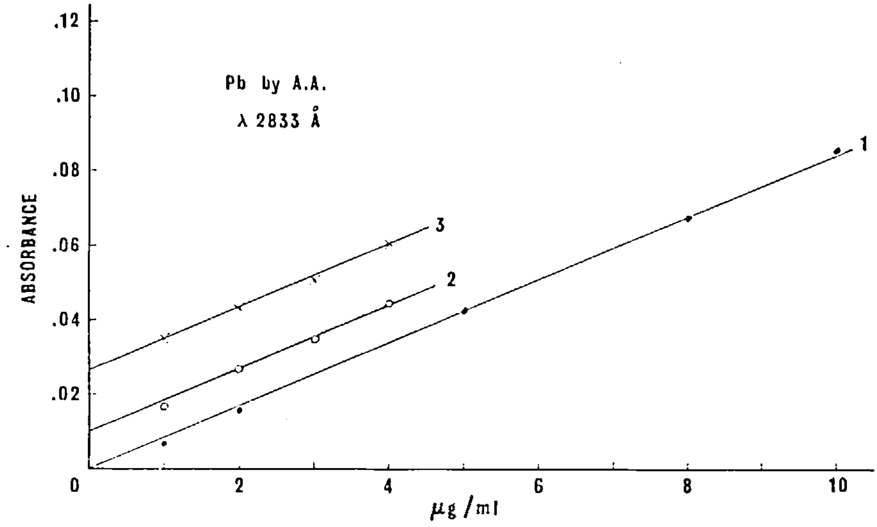

FIGURE 4 Lead standards in three different matrices at 2833 Å.

Burnham *et al.*,[8] working with air samples taken on glass fibre filters, also suggest that lead losses could occur due to the treatment of the sample. In their sample preparation, they make use of a dry ashing step at 500°C for 1 hr. Indeed, it is conceivable that lead may be lost by volatilization at this temperature, made unavailable by the formation of refractory oxides insoluble in nitric acid, or made unavailable by reaction with the glass fibre to form a lead glass. It is at least partly for reasons of this kind that we employ a wet ashing procedure at low temperatures.

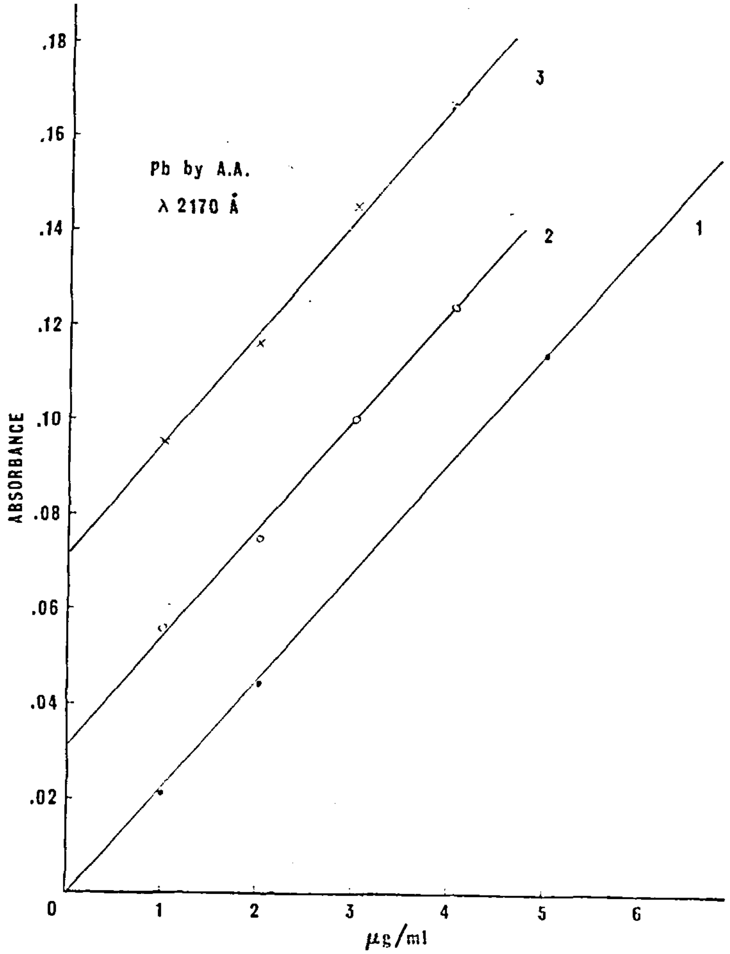

FIGURE 5 Lead standards in three different matrices at 2170 Å.

Hwang and Feldman[9] worked with air samples taken on organic membranes. Their results, for this reason, will be free of the "matrix" effects of glass fibre. According to them it is not possible to measure airborne lead by AA using aqueous lead standards because of matrix effects. In the work presented here, only aqueous lead standards were used.

Our present sample preparation includes the complete dissolution of the exposed glass filter aliquot by means of hydrofluoric acid which is followed by nitric acid. No excessive temperature or dry heat is used. Since approximately 60% of the disc is SiO_2, this part of the filter should disappear by volatilization during the HF treatment. Experiments were done with added lead to see if possible loss of lead could occur during this treatment of the filter. Results of Tables V and VI show complete recovery of the lead added. Interference from anions was not observed; hydrofluoric acid, as stated previously, is removed by heating, and nitric acid in the amounts used has no effect on the lead measurement.

TABLE IV

Replicate lead analyses in differing sample volumes (matrix and dilution errors, sample 758)

Aliquot 758 (ml)	Water (ml)	Total volume	Lead (mcg/ml)	Total Pb (mcg)
5.0	0.0	5.0	3.31	16.55
5.0	1.0	6.0	2.80	16.80
5.0	2.0	7.0	2.38	16.66
5.0	3.0	8.0	2.08	16.64
5.0	4.0	9.0	1.88	16.92
5.0	5.0	10.0	1.68	16.80

In Table VII the effect of different cations on the lead measurement is listed. The interferences from 1000 mcg/ml of a given added cation are expressed in mcg of Pb per ml. It is to be noted that none of these cations is present in so large a concentration in an air sample.

The precision of lead determinations as carried out by Burnham *et al.*[8] and in this laboratory is compared in Table VIII. In both cases the Pb absorption at 2170 Å was used. The results of Burnham *et al.* were obtained with a Perkin-Elmer 303 spectrophotometer, whereas the results from this laboratory were obtained using the Perkin-Elmer 403 spectrophotometer with digital readout. The table shows that our coefficient of variation is still less than 2% for a 1-ppm solution using the 100 average mode. This is a

TABLE V

Replicate lead analyses with constant added lead and varying matrix†

Aliquot 759 (ml)	Total volume	Lead found (mcg/ml)	Total Lead	Less standard	Blank lead (mcg/ml)
4.0	5.0	26.80	134.00	34.00	8.50
9.0	10.0	18.25	182.50	82.50	9.17
14.0	15.0	15.30	229.50	129.50	9.25
19.0	20.0	14.00	280.00	180.00	9.47
24.0	25.0	12.91	322.75	222.75	9.28
49.0	50.0	11.15	557.50	457.50	9.34
50.0	50.0	9.30	465.00	465.00	9.30

†100 mcg lead standard added to each aliquot.

TABLE VI

Ten replicate lead analyses with constant added lead and constant matrix

Sample No.	First reading (mcg/ml)	Second reading (mcg/ml)	
1	2.36	2.34	
2	2.45	2.43	
3	2.33	2.31	
4	2.42	2.43	
5	2.29	2.27	
6	2.41	2.50	
7	2.30	2.33	
8	2.37	2.42	
9	2.24	2.32	
10	2.41	2.49	Total mean = 2.37
11 Blank	0.31	0.42	
12 Blank	0.31	0.39	
13 Blank	0.40	0.40	Total mean = 0.37

By subtraction 2.00 mcg/ml
Lead found 2.00 × 25 = 50.00 mcg
Lead added = 50.0 mcg

TABLE VII

Ion	Interference as Pb (mcg ml)	Concentration in extract (mcg/ml)	Estimated interference
Na	0.04	400	0.02
Al	0.15	200	0.03
Si	0.08	400	0.03
Ba	0.00	300	0.00
Zn	0.03	150	0.00
Ca	0.10	200	0.02
K	0.00	150	0.00
Mg	0.00	10	0.00

†Interfering ions assayed at concentration of 1000 mcg/ml.

TABLE VIII

Precision of lead determinations

Conc. (ppm)		Average absorbance	S.D.	% Coeff. of variation	No. of analyses
H_2O Blank	A†	0.0093	0.0020	21.5	9
	B	0.0001	0.0003	—	10
	C	0.0003	0.0009	—	10
1	A	0.0176	0.0034	19.3	9
	B	0.0292	0.0005	1.7	10
	C	0.0287	0.0011	3.8	10
2	A	0.0362	0.0017	4.7	5
	B	0.0567	0.0006	1.1	10
	C	0.0553	0.0012	2.2	10

†A C.D. Burnham *et al.*
B This lab, using the 100 average mode on digital readout
C This lab, using the 10 average mode on digital readout.

considerable improvement over the results of Burnham *et al.*, which already show a 19.3% variation for this concentration. Comparison of measurements B and C indicates that the standard deviation decreases by about a factor of 2 when the total number of readings is increased by a factor of 10. This is in approximate agreement with statistics, which predict a decrease by a factor of $\sqrt{10} = 3.2$.

DISCUSSION

Our method of measuring lead in airborne particulates taken on glass fibre sheet is accurate and free of interferences in the range of 0–20 mcg of lead per ml of prepared solution, the average difference between measurements being 0.11 mcg/ml. This is true for areal sample sizes from 4–8% of the exposed area of an 8 × 10 in. filter. The overall accuracy of the measurement of lead in air is the sum of individual accuracies, or otherwise expressed, the overall error is the sum of the individual errors. These sources of error include the analytical error and the error in measuring the volume of air sampled.

Lead levels in air are usually expressed in micrograms per cubic metre of air sampled. To get this number, it is necessary to divide the analytical result (in micrograms) by the volume (in cubic metres). The errors in the volume are made up of the error in measuring the flow rate and the error in the time measurement. Although no experimental results have been obtained on the experimental errors associated with sampling, it is appropriate to say that the chemical measurements, as described previously, contribute a minimum to the overall error of the lead measurement in air samples.

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