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The Accurate Measurement of Cadmium in Airborne Particulates†

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KEY WORDS: Atomic absorption; air; cadmium; analysis; particulates

The accurate and rapid measurement of cadmium in airborne particulates is described, with particular reference to so-called high-volume air samples collected on glass fibre filters. The method involves the acid digestion of a part of the filter followed by analysis using atomic absorption spectroscopy. The use of both conventional flame atomic absorption and atomic absorption with a graphite furnace atomizer was investigated.

It was found that the cadmium determinations were free of matrix error and that small interferences by other elements could be accurately taken into account. For a typical air sample of 2000 m³, the cadmium amount can be determined with accuracy down to about 2 ng/m³. Determinations below this level are possible at the expense, however, of the speed and simplicity of the method. The possibility of a non-uniform distribution of cadmium on the exposed filter, and the chance of accidental contamination of the filter or prepared sample by traces of cadmium are also discussed.

INTRODUCTION

The accurate measurement of cadmium in airborne particulates has been of increasing interest, particularly in recent years. Cadmium is known to have a high lethal potential and is absorbed quite efficiently through respiration. It has been estimated¹ that respiratory absorption is about ten times more efficient than absorption by the gastrointestinal route, and hence airborne cadmium can pose a serious health hazard, especially near cadmium sources.

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Cadmium is often found in nature associated with zinc, and it resembles zinc in its chemical properties. Most commercial zinc contains some cadmium and hence the widespread use of zinc has led to dispersal and release of cadmium to the environment. Cadmium is also used directly for plating and in alloys, as well as in pigments, batteries and fungicides. Measurable amounts of cadmium can now be found in water, air and organic materials from most industrialized areas.^{2,3}

A number of methods have been used for the analysis of small amounts of cadmium, including spectroscopic,⁴⁻⁶ wet chemical⁴ (dithizone) and electrochemical methods.⁷ Most of the work has been on trace analysis of cadmium in biological materials with only limited work referring to air samples.^{4,6} The most commonly used method for cadmium analysis is atomic absorption spectroscopy, and this method is discussed in this paper. The method is sensitive and has few complications when applied to air analysis.

METHOD DEVELOPMENT

Apparatus and reagents

An atomic absorption spectrophotometer (Perkin Elmer 403) with air acetylene burner and with HGA-70 furnace was used. Glass fibre filters, 8 × 10 in., Gelman A, were used for air sampling and Whatman No. 41 filter paper was used for filtering the digests. Water was distilled at least twice from glass. The reagents were hydrofluoric acid, 49 %, J. T. Baker analyzed and nitric acid, 71 %, J. T. Baker analyzed.

Sample preparation

The preparation of the glass fibre filters prior to use, the actual air sampling and the digestion of the filters for analysis have all been described in detail in a previous publication.⁸ The method is briefly as follows. The filters are first washed with hot distilled water to remove water-soluble impurities and then dried. Sampling is done with a conventional high-volume sampler which draws about 2000 m³ air in a 24-hr period.

An area aliquot, usually two 36-mm diameter circles, is cut from the exposed area of the filter and digested. This includes dissolving the filter with hydrofluoric acid, fuming at low heat to dryness and then adding 1–2 ml of nitric acid which is evaporated to about 0.5 ml. Ten millilitres of distilled water is added, the mixture is brought nearly to boiling and then filtered through Whatman 41. The beaker is further washed with hot water and the total filtrate is made up to 25 ml and stored in a screw-cap polyethylene bottle.

Flame AA measurements

With an analyzing wavelength of 228.8 nm and the other instrument settings as suggested by the manufacturer, a number of calibration curves were obtained for standards prepared in distilled water and various other matrices. Figure 1 shows the results. Line 1 was obtained using the water standards and was found to be linear up to a concentration of 1.0 mcg/ml. Line 2 shows the results for standards diluted in filter blank. The filter blank was obtained

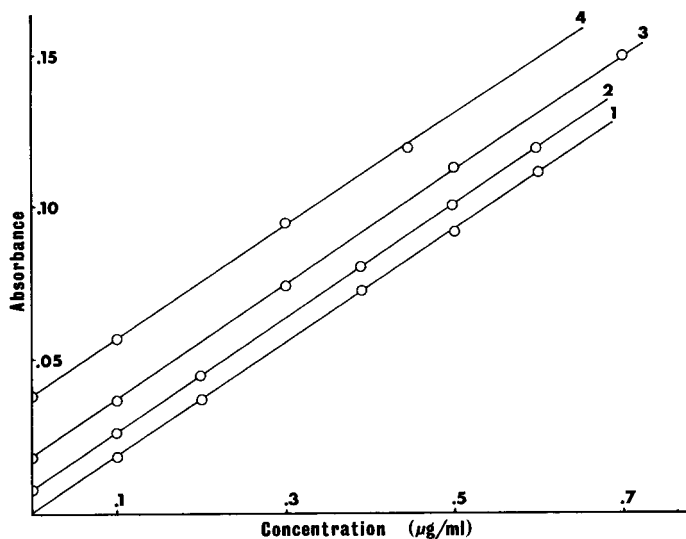


FIGURE 1 Comparison of calibration curves for the flame mode. Line 1, standards in distilled water; 2, standards in filter blank; 3 and 4, standards in sample solutions.

by digesting two unexposed 36-mm circles as described under Sample Preparation. The result indicates that the filter blank gives a small cadmium reading, but that there is no effect of the background on the added cadmium since the lines are parallel. The source of the background is discussed later. Lines 3 and 4 were obtained by measuring standards diluted with actual sample solutions. Each of the samples contained some cadmium and had a high loading of particulates (total cadmium was kept in the linear response region). The lines are parallel to the other two, indicating that the presence of particulate matter does not affect the determination.

To rule out matrix effects completely, a dilution test was carried out. A sample high in cadmium content was diluted with water and the concentration and total cadmium were measured. Table I shows the results and indicates that the total cadmium measured is the same within experimental error.

TABLE I
Cd dilution test

Aliquot 2797 (ml)	Water (ml)	Total vol. (ml)	Cd (mcg/ml)	Total Cd (mcg)
5.0	0.0	5.0	0.57	2.85
5.0	1.0	6.0	0.46	2.76
5.0	2.0	7.0	0.41	2.87
5.0	3.0	8.0	0.36	2.88
5.0	4.0	9.0	0.32	2.88
5.0	5.0	10.0	0.28	2.80
				Av. = 2.84 ± 0.05

The dilution of the background matrix by a factor of two should take into account any matrix variations encountered in samples. This experiment rules out possible interactions of cadmium with other cations and anions present. Such interactions, when present, can affect the results considerably, e.g., the signal enhancement of vanadium by aluminum.⁹

The origin and magnitude of the filter blank value were examined. It was known from previous analyses that the elements Na, Al, Si, Ba, Zn, Ca, and K are present in appreciable concentrations. Table II shows the measured interferences of the ions at 1000 mcg/ml, their approximate concentration in the blank, and the expected interference. From this treatment, the expected blank reading is about 0.028 mcg/ml. A solution was made up containing all the interfering ions at the concentration of the blank and this gave 0.027 mcg/

TABLE II
Interfering ions (mcg/ml)

Ion	Interference as Cd (± 0.005)	Concentration in blank	Estimated interference
Na ^a	0.025	400	0.010
Al	0.025	200	0.005
Si	0.020	400	0.008
Ba	0.005	300	0.001
Zn	—	180	—
Ca	0.020	200	0.004
K	—	150	—
			0.028

^a All ions assayed at 1000 mcg/ml.

ml, showing that the interferences are indeed additive and that no significant interactions are taking place.

A number of glass fibre filter blanks were prepared and analyzed for cadmium. It was found that 15 blanks from a number of different batches of filters gave a blank reading of 0.023 ± 0.004 mcg/ml. This value is comparable to the artificial blank and would suggest that the blank reading arises primarily from the effect of interfering ions. A semi-quantitative analysis of the blank using anodic stripping voltammetry shows that a small amount of cadmium is present, but probably less than 0.01 mcg/ml. It is possible that

TABLE III
Cd addition to filters

Sample	Amount added (mcg)	Amount recovered (mcg)
1165	12.5	12.3
1228	12.5	12.0
1136	7.5	7.5
981	7.5	7.3
904	2.5	2.5
967	2.5	2.7
Total	45.0	44.3

the small amount of cadmium is an impurity of the zinc, which is present at about 180 mcg/ml. It appears, therefore, that the blank reading is caused by cadmium and other interfering ions from the filter; the important thing is that the background is small, constant, and does not cause unwanted matrix effects.

A check of the digestion procedure was carried out by adding known amounts of cadmium directly to exposed filters and then digesting as described previously. The cadmium was added to the area aliquot in a cadmium chloride solution. Table III shows the results. The amount recovered was found by taking the difference of the cadmium readings of the area aliquots with and without added cadmium. The results indicate that added cadmium can be totally recovered. This is sometimes not the case for procedures where higher temperatures are used for ashing the filter and where volatilization of cadmium may occur.

The accuracy of any one determination can be judged by knowing the instrument precision and the blank variability. It is not practical in most cases to do a blank determination on each filter, although a number should be carried out for each filter batch. Instrument precision is 0.005 mcg/ml

using the "100 reading average" mode on the digital readout. Average blank variability, as determined previously, is 0.004 mcg/ml and hence any one reading should be accurate to about 0.01 mcg/ml. Using an area aliquot of two 36-mm diameter circles from an 8 × 10 in. filter and an air volume of 2000 m³, a concentration of 0.01 mcg/ml in the prepared sample corresponds to 2.5 ng Cd/m³. This amount also represents the minimum detectability.

To answer the question of repeatability, a number of repeat determinations were carried out on exposed filters. In each case a new area aliquot was taken from the filter and put through the digestion procedure. The results in Table IV indicate that the mean deviation of repeated determinations is 0.006 mcg/ml

TABLE IV
Repeatability of net Cd (mcg/ml)

Sample	First	Second	Third	Deviation
O 935	0.11	0.11	0.10	0.007
O 949	0.03	0.02	0.03	0.007
O 954	0.02	0.02	0.03	0.007
O 1011	0.02	0.02	0.01	0.007
N 2827	0.02	0.02		0.000
N 2624	0.03	0.03		0.000
N 2990	0.09	0.08		0.010
N 2797	0.51	0.50		0.010
				Average 0.006

(for the case where three determinations were made, the three deviations were averaged). This deviation reflects errors introduced by the digestion method as well as the instrument reading. It is apparent that individual determinations are good to at least 0.01 mcg/ml, as predicted above, and that by carrying out duplicate determinations the deviation can be reduced to about 0.006 mcg/ml, corresponding to 1.5 ng Cd/m³ in air. The assumption implicit in using area aliquots from the filter is that the metal is uniformly distributed. The fact that cadmium amounts can be accurately repeated (Table IV) using different portions of the filter supports this assumption. It has already been confirmed experimentally that lead is uniformly distributed.⁸

Some additional cadmium analyses, carried out after the main body of work for this paper had been completed, resulted in finding some examples of non-uniform distributions of cadmium on filters, and hence further investigations were done in this area. The filters of interest were obtained from a

sampling network in the province of Nova Scotia. It was found that exposed filters from three of the seven sampling stations in the area sometimes showed significant amounts of cadmium, and that the readings were not reproducible when a second or third area aliquot was taken. In order to clarify the situation, sections from different parts of the filter were analyzed and the non-uniform distribution of cadmium was confirmed. Figure 2 shows the findings for one such filter. Circles of 2.54 cm diameter were cut from the exposed filter area as indicated and analyzed; the results are given in Figure 2 in units

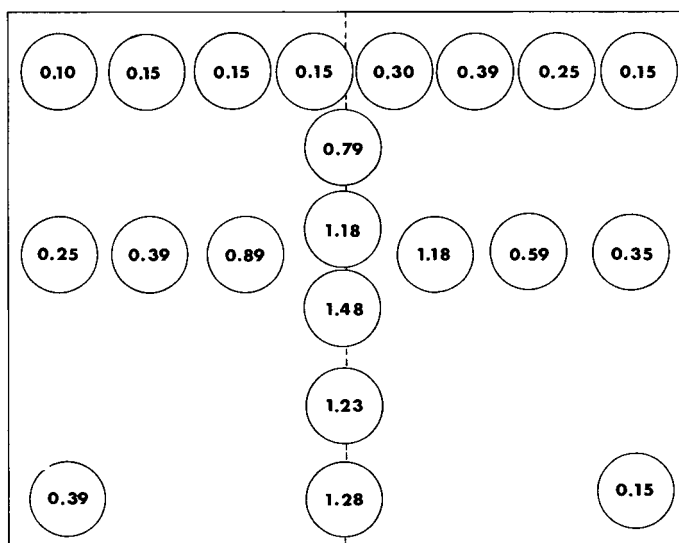


FIGURE 2 Example of filter showing non-uniform cadmium distribution. Cadmium is given in units of $\text{mcg}/\text{cm}^3 (\pm 0.05)$.

of $\text{mcg Cd}/\text{cm}^2 (\pm 0.05)$. It can be seen that the highest concentrations are present along the center fold (filters are usually folded along the dotted line shown in Figure 2 for transfer and storage) with a marked decrease in going to the right or left of the fold. Some decrease is also apparent in going from the center to the top and bottom of the filter.

The cause of the non-uniform distribution has not yet been determined. Contamination from the high-volume sampler is unlikely since not all filters showed cadmium. The possibility that the sampler was drawing air non-uniformly is also possible, although it was found that the lead present was distributed *completely uniformly*. Differences in the distribution of lead and cadmium could result, however, from differences in the particle size distributions of the metals. Lee *et al.*¹⁰ have found that the mass median dia-

meter for cadmium is about 20 times larger than for lead. A larger size for the cadmium particles could result in their being disturbed more easily in the handling of the filter with a possible concentration of particles at the center fold. Experiments to investigate the above possibilities are being carried out.

A further examination of filters listed in Table IV and others, all of which represent air samples from Ottawa or Montreal, revealed without exception only uniform cadmium distributions. The Nova Scotia samples are therefore unique in our investigations so far. Presumably the size and number of cadmium particles, the total loading of particulates, the type of sampler and the subsequent handling of the filters can all have some bearing on the uniformity of the distribution. The uniformity must therefore be checked for each set of samples and for the case that a non-uniform distribution exists, the cadmium concentration in air can only be determined exactly by digesting the entire filter.

Many air samples taken from rural or not heavily industrialized areas contain cadmium below 2 ng/m^3 . Of 333 samples taken at Tunney's Pasture in Ottawa in 1971, only 4% showed measurable amounts of cadmium. The first four samples in Table IV are examples from Ottawa in which the detectable cadmium content varies from 3.9 (0 1011) to 29.1 (0 935) ng/m^3 . From a limited number (74) of samples from Montreal air, about 33% showed detectable cadmium. The maximum found was 171 ng/m^3 (N 2797).

With the analysis described so far, some improvement in sensitivity can be made by sampling a larger volume of air and by treating more of the filter. The accuracy, however, is still limited by the instrument precision, and hence any significant improvement can only be achieved by different instrumentation. The "flameless" graphite furnace atomic absorption unit provides this additional sensitivity.

Furnace AA measurements

The recent development of the graphite rod atomizer for atomic absorption spectroscopy has pushed back detection limits for many metals by at least two orders of magnitude. Cadmium seems ideally suited for this method of analysis since no carbide formation or other undesirable interferences occur.

The instrument settings suggested by the manufacturer were found to give good results. Typical furnace conditions for aqueous solutions were: 15 sec drying at 95°C , 20 sec ashing at 330°C and 7 sec atomizing at 1900°C . A deuterium arc background corrector was in operation for all measurements. Figure 3 shows a calibration curve for standards diluted in water and in a glass fibre filter blank solution. The lines are parallel, indicating that the blank value, about 0.01 mcg/ml , does not affect the determination. The calibration curve was found to be linear up to 0.03 mcg/ml .

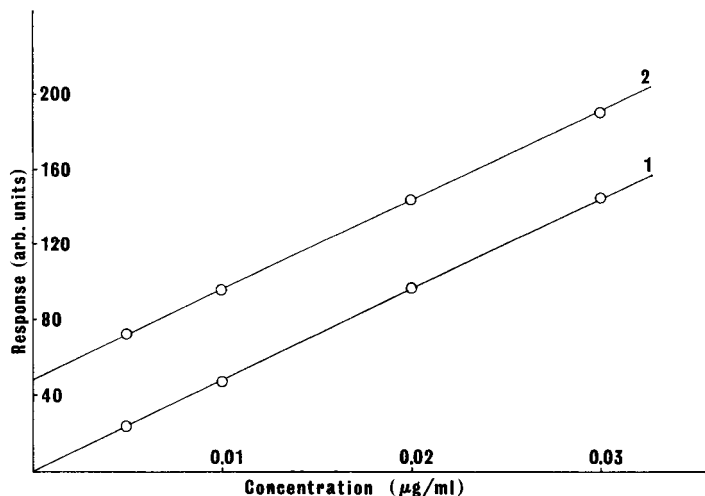


FIGURE 3 Comparison of calibration curves for standards in water (line 1) and filter blank (line 2) using graphite furnace atomizer.

A number of unexposed filters were analyzed to determine blank values and their variability for glass and cellulose filters. Table V shows the results. It was found that glass filters from different batches showed somewhat different average values and a deviation which is about 10% of the average. (The blank variation within any one filter was found to be no larger than the measurement precision.) This variation for filters from different batches was not detectable in the flame measurements because of the lower sensitivity. The precision of the measurements is considerably better than the blank variability. A set of measurements (10) on a standard 0.02 mcg/ml solution

TABLE V
Filter blank values obtained with furnace AA

Filter type	No. of blanks	Concentration (ng/ml)	
		Average	Deviation
Glass ^a , Batch 1	5	9.64	1.09
Glass, Batch 2	5	13.1	1.45
Glass, Batch 3	8	8.00	0.72
Cellulose ^b	5	7.29	0.36

^a Gelman A.

^b Schleicher-Schüll 2312.

(using a 20-mcl sample size) gave a standard deviation of 0.00035 mcg/ml, i.e., 1.8% coefficient of variation. The lower limit of detection was 0.0002 mcg/ml for a 20-mcl sample, representing 4 picograms Cd. This may be lowered to about one picogram by increasing the volume of sample injected to the maximum of 100 mcl.

Practical cadmium analysis is therefore limited by the blank variation. For an area aliquot of two 36-mm diameter circles and an air volume of 2000 m³, a lower limit of detection of about 0.2 ng Cd/m³ can be realized. This can be lowered by at least a factor of two if a separate filter blank determination is carried out for each exposed filter. The use of cellulose filters does not reduce the blank reading significantly, which may in part be due to impurities present in the fairly large amounts (10–15 ml) of concentrated nitric acid needed for digestion. Cellulose filters have disadvantages such as particulate fall-off for high loading, and hence appear to offer no great advantage.

The uniform distribution of cadmium over the filter surface determined by the flame mode was confirmed by the flameless mode for filters containing only small amounts of cadmium. It should be noted that there was complete agreement between analyses done with the flame or furnace, for concentrations where both instruments could be used.

DISCUSSION

The choice of the flame or flameless method of atomic absorption for the analysis depends chiefly on the accuracy desired. The time required for analysis may also be a factor. About 60 area aliquots can be digested and prepared in one day by one person. Subsequent analyses by the flame method can be done at 100 samples per hour, whereas analyses using the graphite furnace are considerably slower at 12 per hour. A gain in detectability of a factor of 10 is therefore balanced by a factor of 10 in time consumption.

Cadmium analyses, especially in the lower regions of detectability, must be carried out with care. Initial work in our laboratory was plagued by erratic cadmium results, the cause of which was soon traced to the presence in the laboratory of cadmium-plated objects such as oven grates and tongs. Physical contact of clean glassware with these objects was enough to cause contamination. Removal of all cadmium sources and thorough rinsing of all glassware just prior to use completely eliminated this source of error. An analysis of "rafter" dust found in various rooms in the laboratory showed an average of 184 mcg cadmium per gram of dust. This again serves to illustrate the generally frequent presence of cadmium in the surroundings and the care which must be taken to avoid contamination.

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