

Determination of Airborne Particulate Cadmium by Atomic Absorption Spectrophotometry

1. INTRODUCTION

Cadmium is a relatively rare metal that occurs mainly as minerals in zinc, lead-zinc, copper-zinc and lead-copper-zinc ores. Cadmium is found in nearly all ores containing zinc and it has been suggested that there is a direct concentration relationship between these two elements. Cadmium is produced as a byproduct in the refining of other metals, particularly zinc. There are no economic cadmium ores as such. Refining processes involving zinc, copper and lead are the production sources which emit cadmium into the atmosphere.

Cadmium in air and biological materials may be measured by dithizone methods. These methods suffer from pH dependency and instability of developed colors. Polarography may be used, but unless the test sample is very carefully prepared to eliminate all traces of organic materials, the cadmium wave may be masked and cadmium thought to be absent. Methods using anodic stripping voltammetry show promise but more practical experience must be obtained. The sensitivity of methods using emission or X-ray spectrography is low and the accuracy is affected by matrix error. The measurement of cadmium by the Weisz ring oven on paper tape samples, is simple and sensitive. The limit of identification, per individual assay, is given as 0.05 micrograms of cadmium as the element (12.1).

In the method to be described, airborne particulates are collected by drawing the air through a filter. The filter, or an areal aliquot, with collected particulates, is digested to prepare a test sample. Preparation of this sample is simple and rapid. The aqueous acidic sample is scrutinized by an atomic absorption spectrophotometer at the wavelength 228.8nm and the cadmium is calculated by referring the absorbance found to the appropriate calibration curve. By the use of a graphite furnace, additional sensitivity may be achieved beyond that of the usual flame mode. The cadmium values found are expressed in micrograms per cubic metre of air sampled. Some practical details of accuracy and precision obtainable will be found under the section "Expression of Results" (9).

2. FIELD OF APPLICATION

The method is applicable to the measurement of the levels of suspended particulate cadmium found in either ambient or industrial atmospheres. Based upon the flame mode, washed glass filters and a nominal air sample

volume of 2,000 cubic metres, cadmium is measurable to 0.0025 micrograms per cubic metre. If the sample is taken on analytical grade cellulose the minimum quantity measurable is also 0.0025 micrograms per cubic metre. For the same test sample, the use of the flameless mode increases the sensitivity by up to two orders of magnitude. As levels of cadmium in urban air are low and since cadmium levels in the laboratory may be rather high by comparison every care must be taken to ensure that the cadmium being measured is actually due to the air sample.

3. PRINCIPLE

A prepared test sample containing the inorganic constituents in aqueous acidic solution is atomized in a flame or heated graphite tube. The absorption of light of characteristic wavelength by the atoms of the element of interest is used to measure the concentration of that element.

4. REACTIONS

The most important reactions relate to the complete dissolution of the particulate sample in acid media to form a homogeneous test sample. As microgram quantities of material may be involved, losses due to incomplete solution, volatility or adsorption must be avoided. Again care must be taken in preparation to avoid airborne cadmium in the laboratory air and equipment and apparatus which is cadmium plated.

5. REAGENTS

5.1 *Air, compressed*

In pressure cylinders or online.

5.2 *Acetylene, compressed*

In pressure cylinders.

5.3 *Glass filters*

Commercially available material is exhaustively washed prior to use, in size 203 by 254mm.

5.4 *Cellulose filters*

Ashless, acid washed, analytical grade, in size 203 by 254mm.

5.5 *Water*

Distilled at least twice from glass or quartz.

5.6 *Hydrofluoric acid*

49%. Reagent grade, in polyethylene containers.

5.7 *Nitric acid*

71%. Reagent grade.

5.8 *Standard solution of cadmium*

Dissolve 1 gram of cadmium metal in the minimum volume of 50% hydrochloric acid and dilute to 1 litre with water. 1ml of this stock solution contains 1,000 micrograms of cadmium, Cd.

6. APPARATUS

6.1 *Spectrophotometer, atomic absorption*

With meter, recorder or digital readout and monochromator with wavelength dial reading to 0.1 nanometre.

6.2 *Pipettes, glass*

Millilitre capacities, "to deliver".

6.3 *Volumetric flasks*

Borosilicate with ground glass stopper, 25ml capacity.

6.4 *Bottles, polyethylene*

Screw cap, for storage of test samples, 30ml capacity.

6.5 *Beakers, teflon*

Griffin form, 100ml capacity.

6.6 *Beakers, borosilicate*

Graduated, Griffin form, with teflon coated rim, 150ml capacity.

6.7 *Hot plate*

Electric, with temperature control, thermostat, and ceramic heating surface.

6.8 *Büchner funnel*

Polypropylene, custom made, with sintered false bottom and vacuum connection, 216 by 267 by 85mm.

6.9 *Graphite furnace*

One suitable instrument is available commercially to the Massmann design.

6.10 *Strip chart recorder*

To display and record the response from the furnace.

6.11 *Pipettes, automatic*

Eppendorf design, with capacities 10 to 100 microlitres.

7. SAMPLING AND SAMPLES

7.1 *Air Sampling*

7.2 *Preparation of the laboratory sample*

Cellulose filters (5.4) may be used without further treatment. Glass fibre filters (5.3) are purified by placing a group of 100 such filters in the special Büchner funnel, and extracting repetitively with distilled water. Mount the filter in a conventional high volume or other sampler head. Draw air through the filter at a flow rate between 1.13 and 1.60 cubic metres per minute, for an appropriate period, such as 24 hours. The resistance to flow offered by the cellulose filter is much greater than for glass and an appreciably smaller total volume of air will be taken with cellulose. Calculate and record the total volume of air sampled, in cubic metres, as the product of mean flow rate and time.

7.3 *Preparation of test sample*

Cut areal aliquots from the exposed surface of a filter using a circular metal punch. The cutting edge of the punch is carefully wiped with lens tissue between each use to prevent carry over of contamination from one sample to another. Place one or more such discs in a teflon beaker. Initiate the dissolution of the filter matrix by the dropwise addition of 1ml of hydrofluoric acid (5.6). Gently warm the contents of the beaker, at low

heat, until the hydrofluoric acid is almost completely evaporated. At this point, add 1 to 2ml of nitric acid (5.7) and continue to heat gently until a few drops of nitric acid are left. Add about 10ml of water, bring gently to the boil and filter through a Whatman 41 filter into a glass beaker (6.6). Transfer to a 25ml volumetric flask (6.3). Rinse down the teflon beaker with another 10ml quantity of water, warm and filter into the same beaker. Transfer to the 25ml volumetric flask and make up test sample to mark at 25°C. Mix the contents of the volumetric flask thoroughly after adjustment to volume. Transfer contents of volumetric flask to polyethylene storage bottle (6.4). The test sample is now ready for analysis. The above method applies to the digestion of glass fibre filters. Cellulose filters can be digested or extracted using nitric acid.

8. PROCEDURE

8.1 *Safety precautions*

Follow normal precautions for the handling of compressed gases. Observe manufacturer's instructions on lighting and extinguishing flame. TEST GAS SUPPLY SYSTEM FOR LEAKS BEFORE USE AND EACH TIME A CYLINDER OF FUEL IS REPLACED.

8.2 *Test Portions*

8.2.1 Test portions, flame

Introduce the test portion into the flame by *continuous* aspiration, through polyethylene tubing, of an *unmeasured* portion of the test sample. Aspirate distilled water into flame, between the introduction of each test portion, to prevent cross contamination.

8.2.2 Test portions, furnace

Measure and insert in the furnace, test portions of 10 to 100 microlitres of the test sample using an automatic pipette (6.11).

8.3 *Calibration Curves*

8.3.1 Calibration curves, flame

Using "to deliver" pipettes, prepare known concentrations of cadmium by dilution of standard solution (5.8) to cover the range of 0.1 to 1.0 micrograms of cadmium per ml. Install in the spectrophotometer and align, if necessary, the hollow cathode source for cadmium. Set the wavelength of the monochromator at 228.8nm. Using an air-acetylene flame, aspirate an unmeasured portion of each dilute standard cadmium solution for 10

seconds (8.2.1). At the same time, aspirate into the flame a blank of distilled water. From the instrumental responses obtained, prepare a calibration curve of absorbance against concentration of cadmium, in micrograms per ml. Such a representative calibration curve is given in Figure 1 (Page 23).

8.3.2 Calibration curves, furnace

By means of an automatic pipette with polyethylene tip, place identical microlitre volumes of the dilute standard cadmium solutions and a distilled water blank in the furnace. Measure and record the response of each test portion following the predetermined measuring cycle. Cover the range 0.2 to 1.0 nanograms cadmium in steps of 0.2 nanograms (0.01 to 0.05 micrograms per ml for a 20 microlitre volume). Prepare a calibration curve of response, in arbitrary units, against concentration of cadmium in micrograms per ml. Such a representative calibration curve is given in Figure 2 (Page 23).

8.4 Determination

8.4.1 Determination, flame

Set the wavelength of the monochromator at 228.8nm. Observing conditions of 8.2.1 and 8.3.1, aspirate an unmeasured test portion of each unknown test sample into the flame. Record the responses for each unknown. Aspirate distilled water into the flame between each unknown test portion to prevent cross contamination. Measure the cadmium in all the unknown test samples which can be accommodated to the wavelength 228.8nm and the corresponding calibration curve.

8.4.2 Determination, furnace

Measure into the furnace, by automatic pipette, a similar test portion of each unknown test sample. Follow the drying and heating programmes previously established. Record the response for each test portion in arbitrary units. Derive the amount of cadmium present in the test sample by referring to the appropriate calibration curve, such as, for example, Figure 2 (Page 23).

8.5 Blank Tests

8.5.1 Reagents

In parallel with preparation of calibration curves, prepare a reagent blank of the acids and distilled water used in the preparation of calibration curves and test samples. Change or purify reagents, as necessary, if blanks are unsatisfactory.

8.5.2 Reagents plus filters

In parallel with the preparation of calibration curves and test samples, prepare areal test portions from unexposed filter media as described in 7.3. Measure cadmium and express blanks in micrograms of cadmium per ml.

9. EXPRESSION OF RESULTS

9.1 *Blanks*

The glass filter blank value for any element may vary considerably with the batch. This has been very noticeable with manganese and beryllium. For this reason, filter blanks should be determined regularly. Extreme care must be taken to isolate and eliminate cadmium interferences normally present in the laboratory. Part of the filter blank value is due to matrix interferences from elements present in larger amounts in the filter such as Na, Ba, Si, Ca, Zn, K and Al.

9.2 *Instrumental precision*

This is defined as the standard deviation of a number of replicate determinations and is expressed in micrograms per ml. Typical precisions for ten repeat determinations on standard samples are: $0.50 \pm 0.004 \mu\text{g/ml}$ for the flame mode; $0.02 \pm 0.00035 \mu\text{g/ml}$ for the flameless mode, on a 20 μl sample.

9.3 *Minimum measurable*

9.3.1 Concentration in test sample

This is taken as twice the blank deviation, or instrument precision, whichever is larger. This is 0.01 micrograms per ml in the case of cadmium, using the flame mode. For the flameless mode the blank deviation is the determining factor and this may vary for different filter batches. A typical value is 0.001 micrograms per ml.

9.3.2 Concentration in air

This is based upon a sample volume of 2,000 cubic metres and two aliquot discs 36mm in diameter. The minimum measurable concentration is 0.0025 micrograms per cubic metre for the flame mode and 0.00025 micrograms per cubic metre for the flameless mode. These values are the same for washed glass or cellulose filters.

9.4 *Calculations*

The cadmium content of the test solution is expressed in micrograms of cadmium per ml, X_1 . The blank, X_2 , in the same units, is subtracted from X_1 to get the corrected concentration of cadmium in the test sample in μg

per ml. Multiplication by the dilution factor, usually 25, gives the total quantity of cadmium in the test sample, in micrograms.

For high volume filters of nominal size 203 by 254mm:

Total exposed filter surface	=	$4.159 \times 10^4 \text{ mm}^2$
Areal test portion, 2 x 36mm discs	=	$2,036 \text{ mm}^2$
Surface multiplication factor	=	20.43
Dilution factor	=	25
Volume of air sampled, cubic metres	=	V
Response, unknown test portion	=	X_1
Response, total blank	=	X_2
Cadmium concentration, in $\mu\text{g}/\text{m}^3$	=	T

$$T = \frac{(X_1 - X_2) \times 20.43 \times 25}{V}$$

10. NOTES ON PROCEDURE

10.1 *Collection efficiencies*

Little is known about actual collection efficiencies and in methods for the analysis of particulate metals, these efficiencies are usually ignored. The particle size of particulate cadmium is almost all between 1 and 3 microns according to Lee (12.2).

10.2 The effect of temperature and pressure during the sampling period has been largely disregarded in the past. Since these factors must have some effect on the measured air volume, it is recommended that these corrections be introduced routinely. There is increasing agreement that if standard conditions of temperature and pressure are to be used to correct the final volume, these conditions should be 25°C and 760mm Hg.

10.3 Although the method described is nominally based upon high volume samples taken for a 24-hour sampling period, there is no valid reason why samples may not be taken for shorter time periods, at slower flow rates, or both. If high volume samples are taken on cellulose, it is particularly appropriate to take air sample volumes of 1,000 cubic metres or less. The lower particulate loading, so obtained, minimizes particulate fall-off. This much more favourable blank resulting from the use of cellulose and the attendant increase in sensitivity should be borne in mind when the sampling procedure is being planned.

10.4 It is customary to assume that the decrease in air flow rate during sampling is linear and for usual purposes of calculation, the mean value of initial and final flow rates is taken. This is not correct, although the error introduced by this oversimplification is not ordinarily serious.

10.5 For the preparation of areal test portions, the use of a sharp circular metal die is to be preferred over the use of scissors or rectilinear templates of large perimeter. Areal test portions prepared by these latter are less likely to be identical in size. A circular die, of limited diameter, machined from solid metal, is very rigid and areal aliquots can be very easily reproduced with accuracy. In the method described, a punch of stainless steel is used. No cadmium contamination has been found to result from its use.

10.6 In the repetitive and consecutive areal test portions cut from an exposed high volume filter, the assumption is implicit that the element of interest is uniformly distributed across the exposed surface of the filter. This assumption is established as fact, at least in the case of lead (12.3, 12.4, 12.5) and cadmium (one exception was noted in 12.5) measured on high volume filters. This uniform distribution cannot be assumed in certain "membrane" type filters due to inherently high pressure drop and faulty geometry of commercially available filter holders. In the case of such filters, areal aliquotting cannot be used (12.6).

10.7 It is helpful, when it is possible, to have several calibration curves, relating to different sensitivities. This minimizes the possibility that the concentration of the metal, in the unknown test sample, will not match one or another of the curves. See method for lead in this series where two calibration curves are given for the flame and one for the furnace (12.7).

10.8 *Operating conditions, flame*

The optimum operating conditions are as given:

Wavelength	=	228.8nm
Spectral band width	=	0.7nm
Source	=	Hollow cathode
Source current	=	As recommended
Oxidant	=	Air
Fuel	=	Acetylene
Flame	=	Oxidizing, lean, blue
Sensitivity	=	0.026 μ g/ml for 1% absorption

Change acetylene cylinder before pressure drops to 50psig.

10.9 *Graphite furnace*

The calibration curve for the flame mode obeys Beer's Law up to 1.0 micrograms of cadmium per ml of test sample as illustrated by Figure 1. A representative curve for cadmium, measured by the graphite furnace, is given in Figure 2, which shows greatly increased sensitivity over the flame.

Furnace operating conditions:

Wavelength	=	228.8nm
Sample size	=	20 microlitres
Purging gas	=	Argon or nitrogen

Thermal decomposition = drying (15sec, 100°C)
charring (15sec, 330°C)
atomizing (10sec, 1,800°C)

The use of a deuterium lamp background compensator is recommended.

11. SCHEMATIC REPRESENTATION OF PROCEDURE

- 11.1 Draw laboratory air sample.
- 11.2 Cut areal test portion from exposed surface.
- 11.3 Digest areal test portion.
- 11.4 Adjust digest to volume to give test sample.
- 11.5 Aspirate test portion into flame.
- 11.6 Or, add test portion to furnace, measured by microlitre pipette.

12. REFERENCES

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