

Determination of Airborne Particulate Zinc by Atomic Absorption Spectrophotometry

1. INTRODUCTION

Zinc is widely distributed in the earth's surface and occurs in small quantities in almost all igneous rocks. Underground mining accounts for most of the production. The reduction of zinc ores and concentrates is accomplished by electrolytic deposition of zinc from solution or by distillation in retorts. The primary sources of emissions of zinc compounds into the atmosphere are these zinc operations as well as lead and copper smelting. Zinc compounds are emitted in the production of steel. The quantities emitted are not thought to be economically recoverable, although probably significant with respect to air quality.

Zinc in air and biological materials may be measured by dithizone methods. These methods suffer from pH dependency and the calibration curve may differ from day to day. Polarography may be used, but unless the test sample is very carefully prepared to eliminate all traces of organic materials, the zinc wave may be masked and zinc thought to be absent. The sensitivity of methods using emission or X-ray spectrography is low and the accuracy is affected by matrix error. Losses of zinc may occur if sample preparation includes dry ashing at elevated temperatures. Zinc may be measured on cellulose filter samples to a limit of identification of 0.05 micrograms, using the Weisz ring oven (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 of 213.8nm and the zinc is calculated by referring the absorbance found to the appropriate calibration curve. The zinc 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 zinc found in either ambient or industrial atmospheres. Based upon the flame mode, cellulose filters and a nominal air volume of 1,000 cubic metres, one may determine down to 0.0050 microgram of zinc per cubic metre of air.

3. PRINCIPLE

A prepared test sample containing the inorganic constituents in aqueous acidic solution is atomized in a flame or heated graphite furnace. The amount of the element of interest is measured by making use of its property of absorbing light of characteristic wavelength when in the atomic state.

4. REACTIONS

The most important reactions relate to the complete dissolution of the particulate sample in acidic 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.

5. REAGENTS

5.1 *Air, compressed*

In pressure cylinders or online.

5.2 *Acetylene, compressed*

In pressure cylinders.

5.3 *Cellulose filters*

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

5.4 *Water*

Distilled at least twice from glass or quartz.

5.5 *Nitric acid*

71%. Reagent grade.

5.6 *Standard solution of zinc*

Dissolve 1 gram of metallic zinc in 5ml of nitric acid and make up to 1 litre with water. 1ml of this stock solution contains 1,000 μ g of zinc, Zn.

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, borosilicate*

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

6.6 *Hot plate*

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

7. SAMPLING AND SAMPLES

7.1 *Air Sampling*

7.2 *Preparation of the laboratory sample*

Cellulose filters (5.3) may be used without further treatment. Glass filters, whether washed or unwashed, have a very high zinc blank and are unsuitable for the measurement of zinc in air. Mount a cellulose, or other suitable zinc-free filter in a sampling head. Draw air through the filter at an appropriate flow rate. If a cellulose filter is used with a high volume sampler, it may be better to draw a total of only 1,000 cubic metres to minimize subsequent fall-off of particulates from the filter. Calculate and record the total volume of air sampled, in cubic metres, as the product of mean flow rate and time. The resistance to air flow offered by the cellulose filters is much greater than for glass and an appreciably smaller total volume of air will be taken with cellulose.

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 beaker (6.5) and add 2ml nitric acid (5.5). Gently warm the contents of the beaker, at low heat, to initiate digestion. When the amount of liquid reaches about one-half ml, add an additional 3ml acid and continue digestion until the volume is again about one-half ml. Add about 10ml water and bring nearly to a boil. The solution will not be clear at this point due to an incomplete digestion of the cellulose with this procedure. The solution should then be filtered with suction through Whatman 41 or other suitable membrane filter. Rinse the beaker and funnel with an additional 10ml of water, 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 digestion procedure has been checked for complete recovery of zinc. Extraction methods may also be used but experiments must be carried out in each case to ensure that added known amounts of zinc can be completely recovered from the filter.

8. PROCEDURE

8.1 Safety precautions

Follow normal precautions for the handling of compressed gases. Observe manufacturer's instructions on lighting and extinguishing flame.

8.2 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.

8.3 Calibration curves, flame

Using "to deliver" pipettes, prepare known concentrations of zinc by dilution of standard solution (5.7) to cover the range of 0.1 to 1.0 micrograms of zinc per ml. Install in the spectrophotometer and align, if necessary, the hollow cathode source for zinc. Set the wavelength of the monochromator at 213.8nm. Using an air-acetylene flame, aspirate an unmeasured portion of each dilute standard zinc solution for 10 seconds (8.2). 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 zinc in micrograms per ml. Such a representative calibration curve is given in Figure 1 (Page 32).

8.4 *Determination, flame*

Set the wavelength of the monochromator at 213.8nm. Observing conditions of 8.2 and 8.3, aspirate an unmeasured test portion of each unknown test sample into the flame. Record the response for each unknown. Aspirate distilled water into the flame between each unknown test portion to prevent cross contamination. Measure the zinc in all the unknown test samples which can be accommodated to the wavelength of 213.8nm and the corresponding calibration curve.

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 zinc and express blanks in micrograms of zinc per ml.

9. EXPRESSION OF RESULTS

9.1 *Blanks*

Although others have used glass fibre filters to sample and measure airborne zinc, it is difficult to see how such measurements can have any validity (12.2). The zinc blank in 8 x 10 inch glass fibre filters, whether washed or unwashed, is 0.1g. Glass can not, therefore, be recommended for sampling airborne particulate zinc. Cellulose filters contain about 50 micrograms zinc by comparison.

9.2 *Instrumental precision*

This is defined as the standard deviation of replicate determinations, expressed in micrograms per ml. For ten repeat measurements on a standard sample, the precision was found to be $0.50 \pm 0.003\mu\text{g/ml}$ (flame mode).

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 $0.01\mu\text{g}$ per ml in the case of zinc.

9.3.2 Concentration in air

This is based on a sample volume of 1,000 cubic metres and two aliquot discs 36mm in diameter. This minimum measurable concentration is 0.0050 micrograms of zinc per cubic metre, when cellulose filters are used.

9.4 *Calculations*

The zinc content of the test portion is expressed in micrograms per ml, X_1 . The blank, X_2 , in the same units, is subtracted from X_1 to get the corrected concentration of zinc in the test sample. Multiplication by the dilution factor, usually 25, gives the total quantity of zinc 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
Zinc 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 zinc is almost all between 1 and 3 microns according to Lee (12.3).

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.

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 rate 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 area aliquots can be very easily reproduced with accuracy. In the method described, a punch of stainless steel is used. No zinc contamination has been found to result from its use. As cellulose is more difficult to cut than glass fibre the die should be exceedingly sharp.

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 and cadmium measured on high volume filters (12.4, 12.5, 12.6). 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 (12.7).

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 (12.8).

10.8 *Operating conditions, flame*

The optimum operating conditions are as given:

Wavelength	=	213.8nm
Spectral band width	=	0.7nm
Source	=	Hollow cathode
Source current	=	As recommended
Oxidant	=	Air
Fuel	=	Acetylene
Flame	=	Oxidizing, lean, blue
Sensitivity	=	0.019 μ g/ml for 1% absorption

Change acetylene container before pressure drops below 50 psig.

10.9 Graphite furnace

Since the analytical sensitivity of the flame mode is so high and since the analytical response of zinc in the furnace seems anomalous, there is no point in recommending the furnace mode at this time. A representative curve for the measurement of zinc in the furnace is given in Figure 2 (Page 32).

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.

12. REFERENCES

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