

Determination of Airborne Particulate Beryllium by Atomic Absorption Spectrophotometry

1. INTRODUCTION

Inhalation of beryllium or its compounds can cause a systemic disease in men and animals with associated pulmonary damage. The element is widely distributed but constitutes only 0.006% of the earth's crust. Beryl is the only commercial source of beryllium, but beryl is only obtained as a by-product of the production of other minerals. The processes of extracting, refining and machining of beryllium and its alloys produce considerable quantities of airborne beryllium. Dusts are produced in emitting and grinding operations. These emissions from extractive and metallurgical operations produce the toxic manifestations. Air concentrations at 100 air sampling stations in the USA are said to be of the order of 0.5 nanograms per cubic metre.

Beryllium in suspended particulates may be measured by fluorimetric methods. One of these methods utilizes the fluorescence emitted by beryllium fused into a bead of sodium fluoride. Another method is based upon the bright yellow fluorescence produced when beryllium reacts with morin. The measurement of beryllium by the Weisz ring oven on paper tape samples is simple and sensitive. The morin reaction is used and the limit of identification, per individual assay, is given as 0.01 micrograms of beryllium 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 234.8nm and the beryllium 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 beryllium 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 beryllium 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, beryllium is measurable to 0.0025 micrograms per cubic metre. The same sensitivity applies if the air sample is taken on cellulose. For the same test sample, the use of the flameless mode increases the sensitivity almost two orders of magnitude, to 0.00005 micrograms per cubic metre.

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 is measured by making use of its property of absorbing light of its 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 *Nitrous oxide, compressed*

In pressure cylinders.

5.4 *Glass filters*

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

5.5 *Cellulose filters*

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

5.6 *Water*

Distilled at least twice from glass or quartz.

5.7 *Hydrofluoric acid*

49%. Reagent grade, in polyethylene containers.

5.8 *Nitric acid*

71%. Reagent grade.

5.9 *Standard solution of beryllium*

Dissolve 22.757g of beryllium nitrate tetrahydrate in water and make up to 1 litre. One ml of this stock solution contains 1,000 micrograms of beryllium, Be.

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 in free depth.

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 (5.5) may be used without further treatment. Glass fibre filters (5.4) 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 filters 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 (5.7). 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 (5.8), and continue to heat gently until a few drops of nitric acid are left. Add about 10ml of water, bring nearly 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 procedure applies to the digestion of glass fibre filters. Cellulose filters may be digested or extracted with 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 beryllium by dilution of standard solution (5.9) to cover the range of 1.0 to 4.0 micrograms of beryllium per ml. Install in the spectrophotometer and align, if necessary, the hollow cathode source for beryllium. Set the wavelength of the monochromator at 234.8nm. Using a nitrous oxide acetylene flame, aspirate an unmeasured portion of each dilute standard beryllium solution for 30 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 beryllium, in micrograms per ml. Such a representative calibration curve is given in Figure 1 (Page 87).

8.3.2 Calibration curves, furnace

By means of an automatic pipette with polyethylene tip, place identical microlitre volumes of the dilute standard beryllium 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 of 0.2 to 1.0 nanograms of beryllium in steps of 0.2 nanograms (0.01 to 0.05 micrograms per ml for a 20 microlitre sample). Prepare a calibration curve of response, in arbitrary units, against concentration of beryllium in micrograms per ml. Such a representative calibration curve is given in Figure 2 (Page 87).

8.4 *Determination*

8.4.1 Determination, flame

Set the wavelength of the monochromator at 234.8nm. 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 response for each unknown. Aspirate distilled water into the flame between each unknown test portion to prevent cross contamination. Measure the beryllium in all the unknown test samples which can be accommodated to the wavelength of 234.8nm 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 beryllium present in the test sample by referring to the appropriate calibration curve, such as, for example, Figure 2 (Page 87).

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 beryllium and express blanks in micrograms of beryllium 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 beryllium the glass fibre filter blank can vary from 0.01 to 0.05 micrograms per ml using the flame mode, and from 0.001 to 0.009 micrograms per ml using the flameless mode. It should be noted that part of the filter blank value is due to interferences from elements present in large amounts in the filter, such as Na, Ba, Si, Ca, Zn, K and Al; these interferences are usually larger for the flame mode. For any one batch of filters, the blank has been found to be relatively uniform, $\pm 10\%$, and hence causes no difficulty. A considerable number of filters in each batch should be checked, however, to ensure uniformity of the blank.

9.2 *Instrumental precision*

This is defined as the standard deviation of a number of replicate determinations, expressed in micrograms per ml. For ten repeat measurements on standard samples, the following has been found: $3.00 \pm 0.02 \mu\text{g/ml}$ for the flame mode and $0.040 \pm 0.0011 \mu\text{g/ml}$ for the flameless 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 for the flame mode and $0.0002 \mu\text{g}$ per ml for the flameless mode.

9.3.2 Concentration in air

This is based on a sample volume of 2,000 cubic metres and two aliquot discs 36mm in diameter. For the flame mode this minimum measurable concentration is 0.0025 micrograms of beryllium per cubic metre, regardless of whether glass or cellulose filters were used. For the flameless mode, the greatly increased sensitivity reduces this to 0.00005 micrograms per cubic metre (for the case that the blank is small (9.2)).

9.4 Calculations

The beryllium 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 correct concentration of beryllium in the test sample. Multiplication by the dilution factor, usually 25, gives the total quantity of beryllium 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	=	2,036mm 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
Beryllium 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.

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 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 beryllium 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 and cadmium measured on high volume filters (12.2, 12.3, 12.4). 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 (12.5).

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 (12.6).

10.8 *Operating conditions, flame*

The optimum operating conditions are as given:

Wavelength	=	234.8nm
Spectral band width	=	0.7nm
Source	=	Hollow cathode
Source current	=	As recommended
Oxidant	=	Nitrous oxide
Fuel	=	Acetylene
Flame	=	Reducing, rich, red
Sensitivity	=	0.035 μ g/ml for 1% absorption

Change acetylene container before cylinder pressure drops below 50 psig.

10.9 *Graphite furnace*

The calibration curve for the flame mode obeys Beer's Law up to and beyond 4.0 micrograms of beryllium per ml of test sample as illustrated by Figure 1. A representative curve for beryllium measured by the graphite furnace, is given in Figure 2, which shows greatly increased sensitivity over the flame. Furnace operating conditions:

Wavelength	=	234.8nm
Sample size	=	20 microlitres
Purging gas	=	Argon or nitrogen

Thermal decomposition = drying (20sec, 100°C)
= charring (20sec, 1,100°C)
= atomizing (20sec, 2,400°C)

The use of a deuterium lamp background compensator is recommended.

11. SCHEMATIC REPRESENTATIVE 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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