

Determination of Beryllium in Ambient Air Particulates

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A method is described for the determination of beryllium in airborne particulates retained on MF Millipore filters. After wet digestion of the filters and extraction of the beryllium as the trifluoroacetyl acetate, a G.L.C. method is used enabling 1×10^{-12} grammes of beryllium to be detected. The detection limit in air is 0.0001 microgramme per cubic metre but this could be lowered considerably using alternative sampling techniques. Recovery of added beryllium is satisfactory and the results from several hundred analyses range from <0.0001 to 0.0015 microgrammes per cubic metre of air.

Beryllium is a highly toxic element with a Threshold Limit Value in air of 2 microgrammes per cubic metre¹, whilst there is a Short Term Exposure limit of 25 microgrammes per cubic metre. It is known that very small amounts inhaled over long periods can cause severe respiratory damage.² Although work has been carried out in the U.S.A. to determine the levels of beryllium in air where amounts ranging from 0.000027 to 0.00049 microgrammes per cubic metre have been found,^{4,5} there are few figures available for these levels in the United Kingdom. The U.K. West Midlands area is highly industrialised and contains several factories which use or process beryllium. Consequently, it was decided in 1976 to commence a general survey of the level at which the metal is present in the air of Birmingham, particularly in the vicinity of a large non-ferrous metal extraction and fabrication complex on the north side of the city, to supplement data already obtained over many years for six heavy metals (Cd, Zn, Pb, Cr, Cu, Ni).

The determination used is the extremely sensitive G.L.C. method adopted by other workers,^{3,4,5} but with modifications detailed below. The principle of the method involves the wet destruction of the Millipore filter on which the particulate matter is collected, followed by extraction of the chelate formed by beryllium with trifluoroacetylacetone in solution in toluene and subsequent injection of this chelate onto a G.L.C. column.

Experimental

APPARATUS

McCartney bijou bottles $\frac{1}{4}$ oz (7 ml). These are readily available and of low cost. The aluminium caps are replaced with subseal silicone stoppers (size no. 30) and the bottles are silanized before use.

Shaker. Variable speed model (A Gallenkamp & Co. Ltd.).

Clamp for holding McCartney bottles. Designed to hold eight bottles, it is

constructed from two pieces of wood $\frac{1}{2}$ inch $\times$ $\frac{1}{2}$ inch $\times$ 6 inch ($13 \times 13 \times 152$ mm) screwed and sealed together to form an inverted letter T. The vertical shaft is used for clamping in the shaker and along the horizontal portion are screwed $\frac{5}{8}$ inch (16 mm) Terry clips, four on each side. The whole clamp including the clips is painted with a polyurethane varnish for protection.

5–50 microlitre Finnpiquette or similar microlitre pipette.

0.2 ml micropipette, 1 ml safety pipette, Pasteur pipettes with rubber teats.

50 ml Kjeldahl flasks.

Distillation apparatus.

GAS-LIQUID CHROMATOGRAPHY

Pye Unicam G.C.V. chromatograph fitted with an electron capture detector and connected to a Philips PM 8220 recorder.

Column: glass (1.5 metres $\times$ 4.0 mm i.d.) packed with 3 per cent. SE30 on 100–120 mesh Diatomite CQ.

Operating conditions: column temperature = 130°C ;

injection port temperature = 150°C ;

detector temperature = 200°C .

Carrier gas flow rate: 70 ml of nitrogen per minute.

Detector current: 4×10^{-10} amperes.

Attenuation range: 128 or 256.

REAGENTS

Use Analytical Reagents and glass distilled water throughout. All glassware should be thoroughly rinsed with 3N sulphuric acid followed by distilled water before use.

1. *Nitric acid*, S.G. 1.42.
2. *Sulphuric acid solutions*, 50 per cent. v/v and 3N.
3. *Perchloric acid*, S.G. 1.54.
4. *Sodium hydroxide solutions*, 50 per cent. w/v and 3N.
5. *Alkaline wash solution*. Dilute 2 ml of 3N sodium hydroxide solution to 50 ml, add 5 g of anhydrous sodium sulphate, shake to dissolve, and make up to 100 ml with water.
6. *Toluene*.
7. *Methyl red indicator solution*.
8. *Beryllium standard solutions*. (a) 1,000 microgrammes per ml. Dissolve 1.967 grammes of beryllium sulphate tetrahydrate in water, add 10 ml of 3N sulphuric acid solution and make up to 100 ml with water in a volumetric flask. (b) 10 microgrammes per ml. Pipette 1.00 ml of standard beryllium solution (1,000 microgrammes per ml) into a 100 ml volumetric flask, add 10 ml of 3N sulphuric acid solution and make up to the mark with water. This solution is stable if stored in a polythene bottle.
9. *Buffer solution*. Dissolve 5.15 grammes of disodium-EDTA-dihydrate and 85 grammes of sodium acetate trihydrate in 400 ml of water. Add 5 ml of glacial acetic acid, mix and adjust the pH of the solution to 5.7 ± 0.1

at 20°C by the dropwise addition of glacial acetic acid or 50 per cent. sodium hydroxide solution. Finally, make up to 500 ml with water, mix and check the pH.

10. *1:1:1 Trifluoroacetylacetone (T.F.A.)*. Obtainable from B.D.H. Ltd., Poole, Dorset. This is usually impure as received but purification is achieved during the following distillation procedure.
11. *T.F.A. chelating solution 0.04 M*. A simple distillation apparatus, without thermometer, is required using, for 40 ml quantities, a 100 ml Quickfit flask. Into the flask place 50 ml of toluene and a few anti-bumping granules. Using the 0.2 ml micropipette add 0.2 ml T.F.A. to the toluene and mix. Distil exactly 40 ml into a graduated stoppered cylinder, using a hotplate and transfer the well mixed distillate to a polythene bottle. This solution is stable for at least one month if stored in a refrigerator.

PROCEDURE

(A) Digestion

The digestion of the filters can be carried out using perchloric or sulphuric acid.

Insert the exposed Millipore filter (see Discussion) carefully down the neck of the Kjeldahl flask. Add 2 ml of perchloric acid and 5 ml of nitric acid, boil down to white fumes of perchloric acid and maintain at this temperature for about 5 minutes. Allow to cool. To ensure absence of nitrous fumes add 10 ml water and again boil down to fuming. The digestion with sulphuric acid is similar but substituting 1 ml of 50 per cent. v/v sulphuric acid for the 2 ml of perchloric acid and completing the wet digestion with the addition of a few drops of nitric acid in the usual way. Whichever digestion is used, after removal of nitrous fumes, cool the residue, wash into a calibrated 25 ml flask, make up to volume with water, mix and filter through a 7 cm Whatman no. 41 filter paper if necessary.

(B) Determination

Pipette 1 ml of digest into a McCartney bottle, add one drop of methyl red indicator followed by 3N sodium hydroxide solution until one drop changes the colour of the indicator. Add 1 ml of buffer solution, mix and, using the 1-ml safety pipette, add 1 ml of chelating solution.

Insert the stopper, ensuring that the neck of the bottle is dry, and place the bottle in the clamp. Shake vigorously for 1 hour and then allow to separate. The solutions are stable and can be left at this stage if necessary, but the following steps should be carried out just prior to injection.

Remove the stopper and, with a Pasteur pipette fitted with a rubber teat, carefully remove all the lower aqueous layer and discard. Add 2 ml of alkaline wash solution, re-stopper and shake vigorously by hand for exactly 30 seconds. Allow 1 minute for the upper organic layer (which should be clear and colourless) to separate, then remove all the alkaline wash solution with a second Pasteur pipette and discard. Add 0.2 grammes of anhydrous sodium sulphate and inject 1 microlitre onto the G.L.C. column. Perform all injections in

duplicate. The chelate is stable for at least 30 minutes after which a slow decomposition occurs. While a sample is eluting from the chromatograph, perform the alkaline wash step on the next sample to be analysed and inject this after the chromium of the previous sample has eluted.

(C) Calibration

Prepare a blank digest by taking one unexposed Millipore filter through the relevant digestion procedure. Into each of four McCartney bottles pipette 1 ml of blank digest, and, with the Finn timer, add 5, 10 and 15 microlitres of 10 microgrammes per ml beryllium standard solution to three bottles, respectively. Carry out the determination part of the procedure (B) from the addition of indicator and subtract the blank peak height from that given by each of the standards. The resulting figures should have a linear relationship. Once this has been established, it is only necessary to include a blank and one standard determination with each batch of samples tested. Calculate the amount of beryllium present by subtracting the blank peak height from that of the sample and comparing this figure with the corrected peak heights given by the standards.

Discussion

High volume air sampling equipment is installed at six selected sites in the Birmingham area and air drawn through Millipore filters pore size 0.8 micrometers (37 mm diameter) for weekly sampling periods at a rate to give a total air flow of about 200 cubic metres. This gives a detection limit of 0.0001 microgrammes of beryllium per cubic metre by the above method but this could be lowered if necessary by using larger filters and larger air flows. The detection limit for beryllium itself, obtained from numerous determinations by both digestion procedures is 1×10^{-12} g with the given instrument conditions but this could be lowered to 1×10^{-13} g by injecting larger volumes at decreased attenuation settings. This is possible since the major part of the blank value normally arises from the T.F.A. but, in the method described, it is reduced to a low level by the toluene distillation.

The use of toluene is preferred to the benzene favoured by other workers,^{3,4,5} as, not only is it less toxic, but it also enables the T.F.A. (B. pt. approx. 105°C) to be purified by direct distillation with toluene (B. pt. approx. 110°C) as required. Thus none of the commercial T.F.A., an expensive reagent, is wasted.

The alkaline wash step performs two functions, removing from the organic phase both the indicator (a carboxylic acid) and excess T.F.A., the presence of the latter causing a characteristically high and unstable base line. The beryllium chelate is not stable for long periods in the presence of alkali but the deterioration can be retarded, or sometimes prevented, by removing the wash liquid prior to injection. The addition of anhydrous sodium sulphate to the wash liquid enables a clean and rapid separation of the two phases to take place after the manual shaking has been carried out.

Nitric acid and nitrous fumes interfere with the determination and they must be removed. This is accomplished by boiling the digested residues with 10 ml of water as indicated in the text and the use of, for example, ammonium oxalate,

was found to be unnecessary. The interference is due to the nitration of toluene during the determination step (B), which gives a large peak close to the beryllium chelate peak.

The perchloric acid digestion was found to be more convenient than that with sulphuric acid since the solution can be used to determine other metals by atomic absorption spectrophotometry without interference from sulphuric acid. No problems were encountered with its use in the method as detailed, although the alternative sulphuric acid digestion involves a less hazardous material where beryllium only is to be determined.

The sensitivity of the method is such that, for greatest accuracy, the standards and samples should be extracted at the same time. The speed, time and temperature of shaking is particularly important in this respect.

To test the precision of the method a set of combined precision and recovery determinations were carried out. These were done by adding 25 microlitres of a standard solution of beryllium (10 microgrammes per ml) to each of five clean Millipore filters contained in separate Kjeldahl flasks and carrying out the sulphuric acid digestion (A) and the determination (B) steps of the procedure on each one. At the same time 1 ml of blank digest solution, and 1 ml of blank digest solution containing 10 microlitres of a standard solution of beryllium (10 microgrammes per ml) were taken through the calibration (C) step of the procedure to provide a blank and standard for measurement purposes. The nominal amount of beryllium injected from each of the five precision determinations was thus 1×10^{-11} g and Table I shows the results obtained. All injections were carried out in duplicate and average peak heights calculated.

TABLE I
RECOVERY OF BERYLLIUM ADDED TO MILLIPORE FILTERS

Determination	Nominal amount of beryllium injected, 10^{-12} g	Beryllium recovered, 10^{-12} g
1	10	9.9
2	10	8.6
3	10	9.0
4	10	10.5
5	10	9.4
Blank value = 1×10^{-12} grammes of beryllium		
Average recovery = 95 per cent.		
Relative standard deviation = 8 per cent.		

Determinations carried out at the same level with the perchloric acid digestion, and also at the 1×10^{-10} g beryllium level with both digestion procedures gave similar or better results. Thus, overall precision and recovery are good.

Several other metals chelate with the reagent and for some, e.g. aluminium and chromium, reliable quantitative methods are available for estimation of trace amounts by this technique. Both these elements give peaks well separated from beryllium and they are reduced to non-interfering levels by the use of EDTA (contained in the buffer solution) in the cold. The elution times of Be, Al and Cr peaks under the given conditions are 1.2, 3.0 and 6.0 minutes, respectively.

The results of several hundred analyses carried out so far are presented in Table II.

TABLE II
SUMMARY OF RESULTS FOR BERYLLIUM IN AIR PARTICULATES

Site no.	No. of filters analysed	Type of site	Results above detection limit	Range of results <i>Microgrammes of Be/metre³</i>	Average
5	82	Monitoring non-ferrous metal company mentioned in Introduction	26	<0.0001-0.0009	0.00026
8	86	Monitoring non-ferrous metal company mentioned in Introduction	37	<0.0001-0.0015	0.00031
9	81	Monitoring non-ferrous metal company mentioned in Introduction	26	<0.0001-0.0013	0.00031
13	86	Residential site control	20	<0.0001-0.0009	0.00029
15	70	Residential industrial area	18	<0.0001-0.0012	0.00029
16	82	Fringe of urban area close to airport	25	<0.0001-0.0006	0.00027

The sites referred to in Table II represent a variety of industrial-urban locations in the Birmingham area of which site no. 8 is situated near to, and downwind of, a beryllium processing plant. Filters from this site show the greatest number of positive results as well as the highest concentrations of beryllium recorded, though the average figure is not significantly higher than that of some other sites. The overall results demonstrate that, in relation to the Threshold Limit Value mentioned earlier, negligible amounts of beryllium occur in the atmosphere of the Birmingham region.

Conclusion

The G.C. determination of beryllium by chelation with trifluoroacetylacetone is a reliable method, with excellent sensitivity and specificity, for the estimation of trace quantities of the metal in air particulates.

References

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