Determination of Airborne Particulate Beryllium by the Ring Oven Technique

1. INTRODUCTION

Airborne particulates containing beryllium, will generally consist of the metal oxides, fluorides, chlorides, sulfates, and the metal fumes itself. Beryllium is commonly encountered as an atmospheric pollutant within the confines and in the proximity of industrial plants producing or using beryllium substances. The major sources of beryllium in the atmosphere are the industrial processing plants engaged in the extraction, refining, machining and alloying of the metal. The combustion of coals containing small quantities of beryllium and the proposed use of beryllium as an additive in rocket fuels, are also possible sources. The average ambient concentration of the metal in U.S. in 1964-65 was reported as less than $0.0005\mu g/m^3$ with the maximum concentration found to be $0.010\mu g/m^3$ (9.1). The determination of beryllium in airborne particulates is best made by using atomic absorption spectroscopy. Other methods such as fluorimetry, spectrophotometry, emission spectroscopy and neutron activation may be used depending upon the availability of facilities and trained personnel. The ring oven method is recommended for use where circumstances dictate against the use of more sophisticated techniques. The ring oven technique serves admirably where field methods are required and it is also useful where only occasional samples are to be run and standby equipment and personnel are not available.

2. SCOPE AND FIELD OF APPLICATION

The ring oven method for determining traces of beryllium is well suited for the analysis of airborne particulate samples. It may be applied for determining the quality of the ambient air and it is particularly well suited for use in field surveys and spot checks. Where large numbers of samples must be processed the method becomes tedious, and this imposes some restrictions on its use for routine studies.

3. PRINCIPLE

The method is based on the application of the ring oven technique to samples collected on filter media such as filter paper tapes. All processing of

the collected sample and the determination itself is performed on the filter paper. The dust sample is processed by treatment with ammonium acetate which dissolves beryllium compounds by the formation of polynuclear acetate complexes. The complex is washed to the heated ring zone with deionized water, where it is deposited in a sharply defined ring. Possible interferences due to other pollutants that may be present are masked by the addition of EDTA solution. The determination of beryllium present is performed by applying morin reagent to the ring zone and washing it in a bath containing ammonia and methanol. Beryllium reacts with morin to form a yellow-green fluorescent product, the intensity of which can be compared against those of standard under a UV lamp.

The ring oven technique was introduced in 1954, as a means for conducting separations and sample concentrations on filter paper (9.2). The technique was a preliminary step for spot test analysis and was used also as a means to provide a complete qualitative scheme of separations and analysis for samples as small as a single drop of unknown (9.3). Recent work has demonstrated the effectiveness of the method for quantitative analyses. In this regard, it is particularly attractive as a means of determining significant metallic species present in samples of airborne particulates (9.4).

Preferably, these samples are collected on filter paper tape, using sequential tape samplers. Alternatively, samples can be collected by means of high volume samplers and then a suitable areal aliquot of the sample is placed on filter paper and processed according to appropriate procedures. The ring oven methods are usually selective or even specific. The methods are very sensitive, applying generally to the microgram to nanogram range and accuracies are comparable with those of other standard trace analytical procedures. The general construction and appearance of a ring oven is shown in Figure 1. The steps involved in the preparation and analysis of an airborne particulate sample is summarized in Figure 2. It is often possible to perform four or even more separate determinations on one sample by simply cutting as many sectors of the ring as there are determinations to be performed (Figures 1 and 2, Page 124).

4. REAGENTS

4.1 *Standard beryllium solution*

Dissolve 10.4g of $Be(NO_3)_2 \cdot 3H_2O$ in deionized water, acidify with 1ml of nitric acid and dilute to 50ml. This gives a solution containing 10mg/ml of beryllium. Suitable dilutions are made from this stock solution to obtain beryllium concentration of 10μg/ml (or 0.01μg/μl).

4.2 *Morin reagent crayon*

Melt a mixture of 1.5g of paraffin wax and 3.5g of glycerylstearate in a test tube. Slowly add 50mg of morin (3,5,7,2,4-pentahydroxyflavone) into the

hot melt, with constant agitation until the morin dissolves in the melt and becomes homogenous and transparent. Pour the melt into a plastic straw. After the wax is cooled and solidified, it is exposed as needed, by peeling off the protective plastic, and used by rubbing its tip on the deposit in the ring.

4.3 *Ammonium acetate*

Dissolve 15g of reagent grade ammonium acetate in distilled water and dilute to 100ml.

4.4 *Potassium cyanide*

Dissolve 0.5g of reagent grade potassium cyanide in distilled water and dilute to 100ml.

4.5 *Ethylenediaminetetraacetic acid (EDTA)*

Dissolve 3g of reagent grade EDTA in 100ml of distilled water (0.1M).

4.6 *Ammonia – Methanol wash solution*

Mix 50ml of concentrated ammonium hydroxide (approximately 58%) and 50ml of methanol and stir well.

5. APPARATUS

5.1 *Ring oven*

Preferably with a 33mm ring and an adapter with 22mm ring size for use with 1in and ½in dust spot respectively.

5.2 Sequential tape sampler or high volume sampler.

5.3 Whatman 41 or Munktells 00 filter tapes and filter papers, lambda pipettes and capillary tubes.

6. SAMPLING

Sequential tape samplers are preferred for sample collection. Collect 0.5 to $2m^3$ of sample (depending on the level of the dust burden) on sample tape. Center dust spot on the ring oven.

In case of samples collected using a high volume sampler, areal samples of suitable sizes are punched out, and placed on the ring oven.

7. PROCEDURE

7.1 Add 30μl of ammonium acetate (15%) and wash to the ring zone with distilled water.

7.2 Add 30μl ammonium acetate (15%) and 30μl potassium cyanide (0.5%) and wash to the ring zone with distilled water.

7.3 Add 30μl of EDTA (0.1M) and wash to the ring zone with distilled water and dry it.

7.4 Place the dried paper on the oven surface and carefully apply a thin coating of the reagent crayon to the ring.

7.5 Soak the sector in the ammonia-methanol bath for about 5 minutes. Dry the sector in a current of warm air. Examine the intensity of fluorescence under a UV lamp and compare against standards prepared in a similar way. Limit of identification: 0.01μg. Range: 0.03-0.2μg.

8. CALIBRATION AND EXPRESSION OF RESULTS

A set of standard rings, containing 0.03, 0.05, 0.07, 0.09, 0.1 and 0.3μg of beryllium is prepared by adding appropriate amounts of a standard beryllium solution containing 10μg/ml (or 0.01μg/μl) of beryllium and following the above procedure 7. The estimation of an unknown is made by visual comparison of the fluorescent intensities of the unknown ring to the standard rings, under a UV lamp.

In the case of the tape samples, the $\mu g/m^3$ of beryllium is directly obtained by dividing the estimated microgram value by the volume of air sampled. For the high volume samples, it is given by the following relation:

$$\mu g/m^3 \text{ of beryllium} = \text{Estimated } \mu g \times \frac{\text{Total area of high volume sample filter}}{\text{Area of disc}} \times \frac{1}{\text{Volume of air}}$$

assuming uniform deposition of the pollutants on the filter. Very often this is not the case. Therefore, a suitable number of discs should be punched out of the large filter at random, each disc analyzed as above for the beryllium content and a mean value of $\mu g/m^3$ should be calculated. The error for the determination varies between 10 to 20%.