

Determination of Airborne Particulate Zinc by the Ring Oven Technique

1. INTRODUCTION

Zinc is mainly present in airborne particulates as the metal oxide. Metallic Zn fumes, and some common salts of Zn have also been often detected in the airborne particulate samples. The primary sources of emissions of zinc compounds into the atmosphere are zinc, lead and copper smelting operations and possibly the incineration of zinc bearing materials. Zinc is very widely used in galvanising of iron and steel and also in producing alloys of brass. The average concentration of zinc in the ambient atmospheres in the U.S. in 1964-65 has been reported as $0.67\mu\text{g}/\text{m}^3$ and the maximum concentration was found to be $58.00\mu\text{g}/\text{m}^3$ (9.1). The best accepted method for the determination of zinc in airborne particulates is atomic absorption spectroscopy. Other instrumental methods such as emission spectroscopy, spectrophotometry, polarography, X-ray fluorescence and neutron activation can also be adapted for the determination of Zn in air samples depending upon the availability of trained personnel and the equipments. The ring oven methods serve admirably where field methods are required for occasional spot checks.

2. SCOPE AND FIELD OF APPLICATION

The ring oven method is sensitive and reliable. It is well suited for the determination of zinc in airborne particulate samples. It can be applied for determining the quality of ambient air and because the equipment is portable, it is particularly well suited for use in field surveys and spot checks. It is not recommended for routine analysis, where large numbers of samples must be processed, because of the tedium involved in sample processing.

3. PRINCIPLE

The method is based on the application of the ring oven technique to airborne particulate samples collected on filter media, such as filter paper tapes. The collection, dissolution of the desired metal species, concentration and the final colorimetric determination can all be performed on the same filter paper. The zinc in the dust sample is solubilized by addition of

potassium cyanide, whereby the zinc forms the soluble tetracyanate complex. The complex is washed to the ring zone with distilled water, and when the solvent evaporates, it is deposited in a sharply defined ring. A solution of ammonium thiosulfate is also washed to the ring zone. Possible interferences that may be present along with zinc in the dust sample, are masked by the presence of cyanide and thiosulfate ions. The determination of zinc present is performed colorimetrically by spraying the ring zone with a dilute solution of dithizone in carbontetrachloride. An intense purple red ring develops, which can be compared against standards prepared in a similar manner.

The ring oven technique was introduced in 1954, as a means of 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 analysis. 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 a sequential tape sampler. Alternatively, samples can be collected by means of high volume samples and then a suitable areal aliquot of the sample is placed on a 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 zinc solution*

Dissolve 1.000g of reagent grade zinc metal in minimum amount of nitric acid and evaporate to dryness carefully. Dissolve the residue in distilled water and dilute to 100ml. This gives a zinc concentration of 10mg/ml. Suitable dilutions are made from this stock solution to obtain a zinc concentration of 100 μ g/ml.

4.2 *Dithizone*

Dissolve 0.005g of reagent grade diphenylthiocarbazone (dithizone) in 100ml of carbon tetrachloride.

4.3 *Ammonium acetate*

Dissolve 15g of reagent grade ammonium acetate in distilled water and dilute to 100ml. It has been our experience in this laboratory, that all reagent grade ammonium acetates commercially available are contaminated with traces of zinc, thereby, giving objectionably high blanks for zinc. The ammonium acetate solution can be purified by first extracting it with a 5ml aliquot of dithizone solution and then repeated extractions with only carbon tetrachloride to remove the traces of dithizone dissolved in the aqueous phase.

4.4 *Potassium cyanide*

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

4.5 *Ammonium thiosulfate*

Dissolve 5g of reagent grade ammonium thiosulfate in distilled water and dilute to 100ml. This solution should also be purified as described in 4.3.

5. APPARATUS

5.1 *Ring oven*

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

5.2 Sequential tape sampler on 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 2m³ 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 dust side down on the center of a filter paper and placed on the ring oven.

7. PROCEDURE

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

7.2 Add 30 μ l ammonium acetate (15%) and 30 μ l potassium cyanide (0.5%), and wash to the ring zone using ammonium thiosulfate (5%).

7.3 Remove tape from the ring oven and allow it to air dry. Add 30 μ l of dithizone solution allowing the reagent to diffuse to the ring zone by capillary action. Wash the reagent to the ring zone using only carbon tetrachloride. An intense purple-red ring develops. Compare against standard rings made by the same procedure. Limit of detection: 0.05 μ g. Range: 0.1-2.0 μ g.

8. CALIBRATION AND EXPRESSION OF RESULTS

A set of standard rings containing 0.1, 0.3, 0.7, 0.9, and 1.0 μ g of zinc is prepared by adding appropriate amounts of a standard zinc solution containing 100 μ g/ml (or 0.1 μ g/ μ l) of zinc and following the above procedure 7. The estimation of an unknown is made by visual comparison of the intensities of the unknown ring to the standard rings.

In the case of the tape samples, the μ g/m³ of zinc 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:

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

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 zinc content and a mean value of μ g/m³ should be calculated. The error for the determination varies between 10 to 20%.

9. REFERENCES

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