

Determination of Airborne Particulate Copper by the Ring Oven Technique

1. INTRODUCTION

Airborne particulates containing copper will generally consist of the metal oxide but occasionally other copper salts may be present depending on the sources. Manufacturing operations involving copper, serve as the principal sources of particulate copper in ambient air. Incineration of copper-bearing materials can also be an emission source. The average concentration of the metal in ambient atmospheres was given as $0.09\mu\text{g}/\text{m}^3$ in the U.S. in 1964-1965 and the maximum concentration reported during the same period was $10\mu\text{g}/\text{m}^3$ (9.1). Atomic absorption spectroscopy must be considered the method of choice in critical studies for the determination of copper in airborne particulates. Other methods such as neutron activation, emission spectroscopy, polarography and spectrophotometry may also be used, depending on the availability of facilities and equipment and the sophistication of the technical staff. The ring oven technique serves admirably where field methods are required or where circumstances dictate against the use of the more sophisticated techniques.

2. SCOPE AND FIELD OF APPLICATION

The ring oven method for determining traces of copper 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 field surveys and spot checks. It is not recommended for routine monitoring because of the tedium involved in processing large numbers of samples.

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 potassium cyanide which dissolves copper as the cyano complex. The complex is washed to the heated ring zone where it is deposited as a sharply defined ring. Possible interferences due to other pollutants that may be present are masked by cyanide and malonic acid which is present in the reagent itself. The

determination of the amount of copper present is performed by adding a saturated solution of dithiooxamide in ethanol containing 20% malonic acid which reacts specifically with copper to produce a dark greenish-black ring. The intensity of the sample ring is compared against a set of 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 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 copper solution*

Dissolve 1.000g of electrolytically pure copper metal in minimum amount of nitric acid and evaporate to dryness. Dissolve the residue in distilled water and dilute to 100ml. This gives a copper concentration of 10mg/ml. Suitable dilutions are made from this stock solution to obtain a copper concentration of 100 μ g/ml (or 0.1 μ g/ μ l).

4.2 *Dithiooxamide reagent*

Make a saturated solution of dithiooxamide in absolute ethanol and add enough malonic acid so that the final solution will have 20% w/v of malonic acid. All chemicals used should be reagent grade.

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.

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 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 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%). Wash to the ring zone with distilled water, remove from ring zone and let it dry at room temperature.

7.3 Spray ring zone with reagent (saturated solution of dithiooxamide in 20% malonic acid in ethanol). Dry in a jet of cold air. Compare against standards. Limit of identification: 0.08μg. Optimum range: 0.1-1.8μg.

8. CALIBRATION AND EXPRESSION OF RESULTS

A set of standard rings, containing 0.1, 0.3, 0.7, 0.9 and 1.0μg of copper is prepared by adding appropriate amounts of a standard copper solution

containing $100\mu\text{g/ml}$ (or $0.1\mu\text{g}/\mu\text{l}$) of copper 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 $\mu\text{g}/\text{m}^3$ of copper 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:

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

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 analysed as above for the copper content and a mean value of $\mu\text{g}/\text{m}^3$ should be calculated. The error for the determination varies between 10 to 20%.

9. REFERENCES

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