

Determination of Airborne Particulate Cobalt by the Ring Oven Technique

1. INTRODUCTION

Airborne particulates containing cobalt will generally consist of the metal oxide, but occasionally the sulfides and other salts of cobalt are also encountered. The major sources of cobalt in the atmosphere are the industrial processing plants engaged in the extraction, refining and alloying of the metal. The average ambient concentration of the metal in U.S. in 1964-65 was reported at less than $0.0005\mu\text{g}/\text{m}^3$ with the maximum concentration found to be $0.06\mu\text{g}/\text{m}^3$ (9.1). The determination of cobalt is best made using atomic absorption spectroscopy. Other methods such as 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 cobalt 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 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 potassium cyanide which dissolves cobalt compounds by the formation of cyano complex. 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 disodium hydrogen phosphate. The determination of cobalt present is performed by adding 1-nitroso-2-naphthol in acetone to the ring zone.

Cobalt reacts with 1-nitroso-2-naphthol to form a brown colored product, the intensity of which can be compared against those of the standards.

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 are shown in Figure 1. The steps involved in the preparation and analysis of an airborne particulate sample are 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 cobalt solution*

Dissolve 1.000g of reagent grade cobalt metal in minimum amount of nitric acid and dilute to 100ml with deionized water. This gives a concentration of 10mg/ml of cobalt. Suitable dilutions are made from this stock solution to obtain cobalt concentrations of 100 μ g/ml (or 0.1 μ g/ μ l).

4.2 *1-Nitroso-2-naphthol*

Dissolve 0.1g of reagent grade 1-nitroso-2-naphthol in 100ml of acetone.

4.3 *Ammonium acetate*

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

4.4 *Potassium cyanide*

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

4.5 *Disodium hydrogen phosphate*

Dissolve 5.0g of reagent grade disodium hydrogen phosphate in 100ml of deionized water.

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 deionized water.

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

7.3 Expose the ring zone to ammonia fumes.

7.4 Add 30μl disodium hydrogen phosphate and wash to the ring zone with deionized water.

7.5 Add or spray with reagent (0.1% 1-nitroso-2-naphthol in acetone). Compare against standards. Limit of identification: 0.05μg. Range: 0.1-3.0μg.

8. CALIBRATION AND EXPRESSION OF RESULTS

A set of standard rings, containing 0.1, 0.3, 0.7, 0.9 and 1.0 μg cobalt is prepared by adding appropriate amounts of a standard cobalt solution containing 100 $\mu\text{g}/\text{ml}$ (or 0.1 $\mu\text{g}/\mu\text{l}$) of cobalt 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 cobalt 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:

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

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 cobalt content and 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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