

Determination of Airborne Particulate Nickel by Ring Oven Technique

1. INTRODUCTION

Airborne nickel particulates consist usually of the oxide or sulfide. Sources of nickel in the atmosphere include metallurgical operations, exhausts from engines burning nickel containing fuels, burning oil and coal and the incineration of various nickel containing products. Nickel concentrations in urban air in the United States was reported to average $0.032\mu\text{g}/\text{m}^3$ in 1964. The maximum concentration reported was $0.690\mu\text{g}/\text{m}^3$ (9.1). Atomic absorption spectroscopy must be considered the method of choice for critical studies of airborne particulates for nickel content. Other methods such as neutron activation, emission spectroscopy, polarography, and spectrophotometry may be used depending on the availability of facilities and equipment and the sophistication of the technical staff. The ring oven technique is recommended for use where circumstances dictate against the use of the more sophisticated techniques. The ring oven method compares favorably with other methods in regard to reliability and accuracy. It is more sensitive than most methods, it is far cheaper than other available methods, it is easy to apply and may be used for field studies. It is particularly effective for use where only occasional samples are to be run and stand-by equipment and personnel are not available.

2. SCOPE AND FIELD OF APPLICATION

The ring oven method for determining traces of nickel in samples of airborne particulates is suitable for determining ambient air quality for spot checks and field surveys. It is not recommended for routine monitoring because of the tedium involved in processing large numbers of samples. Reliable results can be obtained over the range of 0.1 to $1.0\mu\text{g}$ of nickel. Errors for the method should run no more than 10 to 20% and the method can be considered specific for nickel.

3. PRINCIPLE

The method is based on the use of the ring oven which serves as a means for completely processing the sample as collected, on a filter medium such as filter paper tape. The nickel in the dust species is made soluble by treatment

with cyanide. The resultant nickel complex is washed to the heated ring zone where it is deposited as a sharply defined ring. The nickel complex is treated with formaldehyde which releases (demasks) the nickel which is then determined colorimetrically by the addition of dimethylglyoxime and exposure to ammonia fumes.

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 nickel solution*

Dissolve 1.00g of reagent grade nickel metal in minimum amount of nitric acid and evaporate to dryness. Dissolve the residue in distilled water and dilute to 100ml. This gives a nickel concentration of 10mg/ml. Suitable dilutions are made from this stock solution to obtain a nickel concentration of 100 μ g/ml (or 0.1 μ g/ μ l).

4.2 *Dimethylglyoxime*

Dissolve 1g of reagent grade dimethylglyoxime in 100ml of absolute ethanol.

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 *Formaldehyde solution*

Use a reagent grade chemical of approximately 37%.

4.6 *Ammonium hydroxide*

Use a reagent grade concentrated solution of approximately 58%.

5. APPARATUS

5.1 *Ring oven*

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

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, 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%), wash to ring zone with distilled water.

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

- 7.3 Expose ring zone to formaldehyde fumes for two minutes.
- 7.4 Add or spray dimethylglyoxime (1% in ethanol) to the test ring.
- 7.5 Expose to ammonia fumes. A brilliant red ring develops. Compare against standards.

8. CALIBRATION AND EXPRESSION OF RESULTS

A set of standard rings, containing 0.1, 0.3, 0.5, 0.7, 0.9, and 1.0 μg of nickel is prepared by adding appropriate amounts of a standard nickel solution containing 100 $\mu\text{g}/\text{ml}$ (or 0.1 $\mu\text{g}/\mu\text{l}$) of nickel, and following the above procedure 7. The estimation of an unknown is done 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 nickel 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:

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

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 nickel content and a mean value of $\mu\text{g}/\text{m}^3$ should be reported. The error for the determination varies between 10 and 20%.

9. REFERENCES

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