Determination of Airborne Particulate Lead by the Ring Oven Technique

1. INTRODUCTION

Airborne particulates containing lead, will generally consist of the metal oxide, chlorides, bromides or chlorobromides. The major source of airborne lead in urban areas is the combustion of leaded gasoline. However, other sources such as manufacturing operations involving lead, use of pesticides, combustion of coal, incineration of refuse, etc., are also significant. The average ambient concentration of the metal in U.S. in 1964-65 was reported as $0.79\mu g/m^3$ with the maximum concentration found to be $8.60\mu g/m^3$ (9.1). Atomic absorption spectroscopy must be considered the method of choice in critical studies for the determination of lead 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 is recommended for use where circumstances dictate against the use of the 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 stand-by equipment and personnel are not available.

2. SCOPE AND FIELD OF APPLICATION

The ring oven method for determining traces of lead 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 same filter paper. The lead in the dust sample is solubilized by treatment with ammonium acetate. The lead acetate pseudo salt formed is washed to the

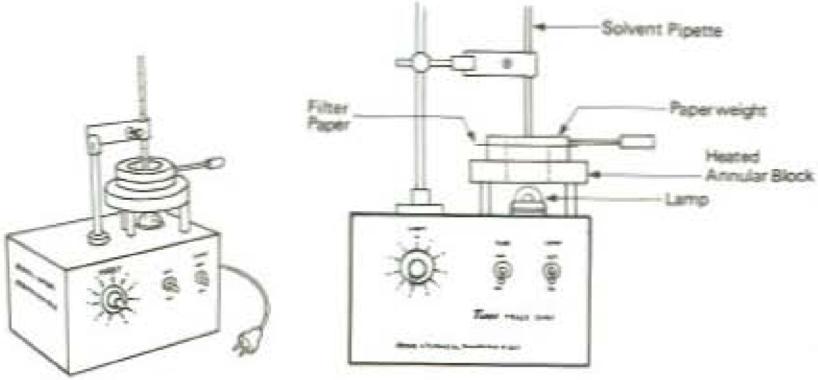

Figure 1. Ring Oven
(Arthur H. Thomas Co., Philadelphia, No. 9430-E10
"Trace Oven")

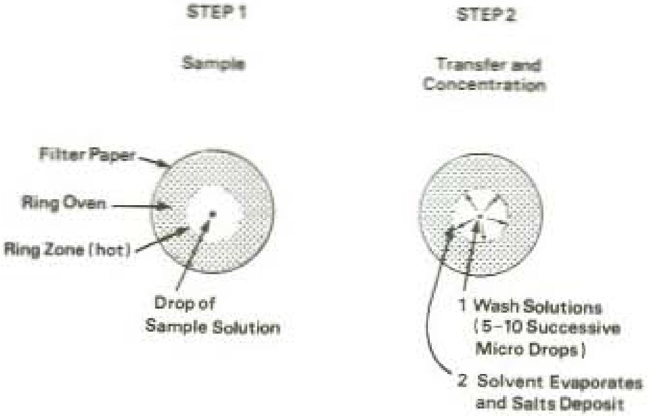

Figure 2.

heated ring zone 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 potassium cyanide. The determination of the lead present is performed colorimetrically by spraying dithizone which forms a brick-red colored complex. The excess reagent and other soluble species, are washed off with a wash solution containing cyanide and ammonia. The color so developed is compared against standards prepared in a similar manner.

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 lead solution*

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

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.

4.4 *Potassium cyanide*

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

4.5 *Sodium thiosulfate*

Dissolve 5g of reagent grade sodium thiosulfate in 100ml of distilled water.

4.6 *Cyanide wash solution*

Dissolve 0.2g of potassium cyanide in distilled water, add 2ml of concentrated ammonium hydroxide and dilute to 100ml with distilled 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 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 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 30μl sodium thiosulfate (5%). 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 Remove tape from the ring oven and spray ring zone with dithizone (0.005% in carbon tetrachloride).

7.4 Remove excess dithizone by dipping tape in cyanide wash solution for 1 minute. Finally, wash tape in running tap water, press between filter papers to remove excess water. Air dry and compare with standards. Limit of detection: 0.05μg. Range: 0.1-1.0μg.

8. CALIBRATION AND EXPRESSION OF RESULTS

A set of standard rings, containing 0.1, 0.3, 0.7, 0.9 and 1.0μg of lead is prepared by adding appropriate amounts of a standard lead solution containing 100μg/ml (or 0.1μg/μl) of lead 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 $\mu g/m^3$ of lead 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:

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

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 lead content and mean value of $\mu g/m^3$ should be calculated. The error for the determination varies between 10 to 20%.

9. REFERENCES

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Determination of Airborne Particulate Cadmium by the Ring Oven Technique

1. INTRODUCTION

Airborne particulates containing cadmium will generally consist of the metal oxide but occasionally cadmium sulfide or other cadmium salts may be present, depending on the sources. Manufacturing operations involving cadmium, serve as the principal pollutant sources. Cadmium is quite widely used in pigments, semi-conductors, storage batteries and in electroplating. The average concentration of the metal in ambient atmospheres was given as $0.002\mu g/m^3$ in 1964, with the maximum concentration found to be $0.350\mu g/m^3$ (9.1). The determination of cadmium in airborne particulate samples is best made using atomic absorption spectroscopy. Neutron activation, X-ray fluorescence, emission spectroscopy, polarography, and spectrophotometry may also be used depending on the availability of facilities and trained personnel. The ring oven technique serves admirably where field methods are required or where availability of facilities and technical staff imposes restrictions.

2. SCOPE AND FIELD OF APPLICATION

The ring oven method for determining traces of cadmium 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 restriction 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 the cadmium 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 the addition of sodium phosphate. The determination of the amount of cadmium present is performed by adding ferrous dipyridyl iodide which forms a highly colored addition complex. After excess reagent is washed out, the color is compared against standards prepared in a similar manner.

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 cadmium solution*

Dissolve 1.00g of reagent grade cadmium metal in minimum amount of nitric acid, evaporate to dryness, dissolve the residue in distilled water and dilute to 100ml. This gives a cadmium solution of concentration 10mg/ml. Appropriate dilutions are made from this cadmium stock solution to obtain working standard solution of concentration 100μg/ml (or 0.1μg/μl).

4.2 *Ferrous dipyridyl iodide solution*

0.25g α, α'-dipyridyl and 0.146g ferrous sulfate are dissolved in 50ml of distilled water, 10g potassium iodide is added and after shaking vigorously for 3 minutes the solution is filtered. The $[\mathrm{Fe}(\alpha, \alpha'\text{-dip})_3 \cdot I_2]$ solution contains excess iodide ions to accomplish the formation of the $[\mathrm{CdI}_4]^=$ ions essential to the cadmium test. The reagent is stable for 5 days. If it becomes turbid on long standing, it should be filtered before use.

4.3 *Ammonium acetate*

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

4.4 *Potassium cyanide*

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

4.5 *Sodium phosphate*

Dissolve 10g of reagent grade trisodium phosphate in 100ml of distilled water.

4.6 *Ammonium hydroxide*

Use concentrated ammonium hydroxide solution. Approximately 58% solution.

5. APPARATUS

5.1 *Ring oven*

Preferably with a 33mm ring and an adapter of 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 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 Add 30μl of 10% trisodium phosphate and wash it to the ring zone.

7.4 Dry the ring and expose it to ammonia fumes.

7.5 Add the reagent (ferrous dipyridyliodide) to the ring using a capillary pipet. After ten seconds, wash in a jet of distilled water for 30 seconds. Dry in a current of warm air. Compare against standards. Limit of identification: 0.08μg. Optimum range: 0.1μg-2.0μg.

8. CALIBRATION AND EXPRESSION OF RESULTS

A set of standard rings, containing 0.1, 0.3, 0.7, 0.9 and 1.0μg of cadmium is prepared by adding appropriate amounts of a standard cadmium solution containing 100μg/ml (or 0.1μg/μl) of cadmium 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 $\mu g/m^3$ of cadmium is directly obtained by dividing the estimated microgram value by the volume of air sampled. For the high volume samples, the $\mu g/m^3$ of cadmium is given by the following relation:

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

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 cadmium content and a mean value of $\mu g/m^3$ should be calculated. The error for the determination varies between 10 to 20%.

9. REFERENCES

9.1 Preliminary Air Pollution Survey of Cadmium and Its Compounds, A Literature review U.S. Dept. of HEW, Public Health Service, Consumer Protection and Environmental Health Service National Air Pollution Control Administration, Raleigh, North Carolina, 1969.

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