

Determination of Traces of Lead and Cadmium in Water

1. SCOPE

The methods are suitable for samples containing up to 10 micrograms per litre of dissolved cadmium or 100 micrograms per litre of dissolved lead.

2. PRINCIPLE OF METHOD

Lead and cadmium are selectively complexed by chelation with ammonium pyrrolidine dithiocarbamate, extracted into 4-methylpentan-2-one and estimated by direct aspiration of the organic phase in an atomic absorption spectrometer (8.1).

3. REAGENTS

Deionised water; Nitric acid, concentrated; Standard cadmium solutions, 0.5 to 10 micrograms per litre; Standard lead solutions, 5 to 100 micrograms per litre; Hydrochloric acid 1N or 6N; Ammonium pyrrolidine dithiocarbamate solutions, 4% w/v; 4-Methylpentan-2-one.

4. APPARATUS

Atomic absorption spectrophotometer; Burner suitable for air-acetylene flame; Centrifuge, Separating funnels, 250ml.

5. SAMPLING PRECAUTION

Samples should be examined as soon as possible after being taken. Steps must be taken to ensure that traces of lead or cadmium are not lost by absorption on the surface of sampling vessels (2). Soft glass or polyvinyl chloride vessels should not be used.

6. PROCEDURE

Adjust the pH of 200ml of sample to 2.2-2.8 with hydrochloric acid. Add 1ml ammonium pyrrolidine dithiocarbamate solution, mix and add 5ml

4-methylpentan-2-one and shake for 2min. If an emulsion forms at the interface of the two layers, centrifuge for 10min. Repeat the extraction with a second 5ml 4-methylpentan-2-one and combine the two extracts. If a precipitate forms in the solvent phase during the first extraction, add an additional 5ml 4-methylpentan-2-one and repeat the extraction with a second 10ml. Since the extra solvent reduces the concentration factor and sensitivity of the method, do not apply unless necessary. Determine the metal in the organic phase by comparison with standards that have similarly been extracted. Aspirate the organic phase into the flame, reducing the fuel-to-air ratio as necessary, using the 283.3nm line for lead and the 228.8nm line for cadmium.

7. EXPRESSION OF RESULTS

Results should be expressed as micrograms of cadmium (Cd) or lead (Pb) per litre and should indicate whether filtered or unfiltered samples have been used.

8. REFERENCES

8.1 Standard Methods for the Examination of Water and Wastewater, 13th Edn, pp. 211-215, American Public Health Association, 1971.

Determination of Total Lead and Cadmium in Biological Media

1. SCOPE

The method is applicable to homogenised samples. The method of sample digestion may depend on the exact nature of the sample: the validity of the procedure used should be checked by recovery experiments on similar samples.

2. PRINCIPLE OF METHOD

The sample is ashed or wet oxidised under controlled conditions, taking care to avoid losses of trace metal by volatilisation or absorption (6). Lead and cadmium are removed from interfering matter as dithiocarbamate complexes and estimated by atomic absorption spectrophotometry.

3. REAGENTS

3.1 *For wet oxidation*

Nitric acid, concentrated; sulphuric acid, concentrated.

3.2 *For ashing*

Hydrochloric acid solution, 5N.

3.3 *For end method*

Ammonium pyrrolidine dithiocarbamate solution, 2% w/v 4-methylpentan-2-one.

4. APPARATUS

4.1 *For wet oxidation*

Silica digestion (Kjeldahl) flasks; volumetric flasks, 50ml.

4.2 *For ashing*

Platinum dishes; infra-red drying lamps; muffle furnace; volumetric flasks, 50ml.

4.3 *For end method*

Separating funnels, 100ml; filter papers, siliconised; atomic absorption spectrophotometer with air-acetylene burner.

5. SAMPLES AND SAMPLING

The sample is thoroughly mixed by shaking, kneading, mashing or passing through a mincer with non-metallic implements. Subsamples for digestion should be 15-20g for most solid materials (5-10g for fatty materials), 50ml for liquids.

6. PROCEDURE

6.1 *Preparation of sample*

The sample is digested either by wet oxidation or (lead only) by ashing.

6.1.1 Wet oxidation

Transfer the sample to a silica digestion flask, disperse as necessary with added water, Add 10ml concentrated nitric acid and heat (if necessary) to initiate oxidation. Allow initial reaction to subside, heat to boiling, cool. Add 10ml concentrated sulphuric acid and heat gently until charring *just* commences: continue with stronger heating adding concentrated nitric acid carefully, dropwise as charring occurs; avoid excessive charring. When solution fails to darken on prolonged heating, cool (if not colourless when cold, further digestion is necessary), carefully add 50ml water, boil gently to fuming. Cool, add carefully 10ml water, boil gently to fuming to remove last traces of nitric acid; cool, add carefully 20ml water, cool, transfer quantitatively to 50ml volumetric flask, dilute to mark with water; mix.

6.1.2 Ashing (lead only)

Place the sample in a platinum dish and dry carefully under infra-red lamp, burning off fats as necessary. Transfer to muffle furnace, hold at 490°C for 12-15hr, cool; dampen with water and reheat in muffle furnace at 490°C, if necessary until the ash is completely white. Cool. Add 5ml water, simmer with 10ml 5N hydrochloric acid to dissolve and transfer quantitatively to 50ml standard flask, dilute to mark with water; mix.

6.2 *End method*

Transfer a suitable aliquot of the prepared digest to a 100ml separating funnel, dilute (as necessary) to 50ml, ensure that the solution is thoroughly

cool, and add 2ml 2% ammonium pyrrolidine dithiocarbamate solution. Mix thoroughly, stand for 3-5 minutes, add by pipette 5 or 10ml 4-methylpentan-2-one, stopper flask and shake for 30secs. Allow phases to separate, discard aqueous phase, filter ketone phase through siliconised paper to remove last traces of water into a small plastic bottle. Aspirate in air-acetylene flame using 283.3nm line for lead, 228.8nm line for cadmium. Prepare standard and blank solutions in the same way by extracting aqueous solutions of the same acidity as the sample solution.

7. EXPRESSION OF RESULTS

For solid and semi-solid samples, results are expressed in mg per kg, for liquid samples in mg or micrograms per litre (according to the amount present) to one, or at the most two, significant digits.

8. NOTES ON PROCEDURE

Samples should be stored in acid-washed pyrex glassware or high density polyethylene containers. A reflux system similar to that described by Smith may be used for the wet digestion procedure (10.1, 10.2).

Cadmium analyses by atomic absorption spectrophotometry at low levels can be improved by using a deuterium background detector to compensate for molecular absorption. Alternative methods for cadmium are based on polarography, spectrophotometry (10.3) or spectrofluorimetry (10.4). An alternative method for lead is the colorimetric dithizone procedure (10.5) although difficulty may be encountered due to instability of the coloured complex.

9. SCHEMATIC REPRESENTATION OF PROCEDURE

Sample preparation; ashing or wet oxidation; adjustment of volume of digest to 50ml; separation from interfering materials by extraction of dithiocarbamates with 4-methylpentan-2-one; examination for lead, cadmium by atomic absorption spectrophotometry.

10. REFERENCES

- 10.1 Gorsuch, T. T., *Analyst*, 1959, 84, 135.
- 10.2 Smith, G. F., *Anal. Chim. Acta*, 1957, 17, 175-185.

- 10.3 Ssekaslo, H., *Lab. Practice*, 1970, **19**, 720.
- 10.4 Analytical Methods Committee, *Analyst*, 1969, **94**, 1153-1158.
- 10.5 Haworth, D. T. and Boeckler, R. H., *Microchem. J.*, 1968, **13**, 158-164.
- 10.6 Analytical Methods Committee, *Analyst*, 1958, **84**, 127-134.