SRI LANKA STANDARD 311 : 1975
UDC 546.815 : 543

METHOD FOR THE DETERMINATION OF LEAD

BUREAU OF CEYLON STANDARDS

METHOD FOR THE DETERMINATION OF LEAD

SLS 311 : 1975

(Attached AMD 411)

Gr.4

BUREAU OF CEYLON STANDARDS
53,Dharmapala Mawatha,
Colombo 3,
Sri Lanka.

AMD 411

AMENDMENT NO: 01 TO SLS 311 : 1975
METHOD FOR THE DETERMINATION OF LEAD

SRI LANKA STANDARDS INSTITUTION

AMD 411

Amendment No: 01 approved on 2010-10-15 to SLS 311 : 1975

AMENDMENT NO: 01 TO SLS 311 : 1975
METHOD FOR THE DETERMINATION OF LEAD

FOREWORD

Insert the following under 4th paragraph of **FOREWORD**.

"Introduction of the atomic absorption spectrophotometric method for the determination of Lead is given in Appendix **B**."

Insert the following at the end of Appendix **A**.

" APPENDIX B
ATOMIC ABSORPTION SPECTROPHOTOMETRIC METHOD

The atomic absorption spectrophotometric method is to be adopted if and when it could be used as a routine method."

…….

SRI LANKA STANDARD

METHOD FOR THE DETERMINATION OF LEAD

FOREWORD

This Sri Lanka Standard was prepared by the Drafting Committee on Chemical Test Methods. It was approved by the Agricultural and Chemicals Divisional Committee of the Bureau of Ceylon Standards and was authorised for adoption and publication by the Council of the Bureau on 1975-06-04.

Assistance derived from the following publications in the preparation of this standard is acknowledged.

Official standards and Recommended Methods of Analysis, Analytical Methods Committee, Society for Analytical Chemistry, London 1967.

1 SCOPE

This standard prescribes a method for the determination of lead.

2 METHODS

2.1 Precautions against contamination

a) Apparatus made of borosilicate glass or silica should be used.

b) Atmospheric dust normally contains substantial amounts of lead, often to the extent of several thousand mg/kg. Particular attention must therefore be paid to the possibility of dust contamination during all stages of a determination.

c) All water shall be glass distilled or de-ionised and free from lead.

2.2 Principle of method

After removal of interfering substances, lead is extracted with dithizone at pH 9 to pH 9.5 and determined absorptiometrically.

For the preliminary separation of lead, two methods are given. In Method A, lead is extracted with dithizone from an alkaline citrate and hexametaphosphate solution.

Method B requires additional manipulative work and should be used only when Method A will not suffice, i.e. for samples that have so high a content of calcium, magnesium and phsophate that sodium hexametaphosphate and ammonium citrate in the stated amounts will not allow the quantitative extraction of lead with dithizone under the alkaline conditions of Method A; a preliminary extraction of lead from acid solution with a solution of diethyl ammonium diethyl dithiocarbamate in chloroform is therefore substituted for the hexametaphosphate procedure.

2.3 Range

The range is for lead contents up to 5 mg/kg, but it can be extended by using a suitable amount of sample. The calibration graph, based on the use of an absorptiometer and 10 mm cells, covers the range 0 µg to 40 µg of lead (approximately) in 10 ml of solution.

2.4 Applicability

The method is of wide applicability, although bismuth is liable to interfere. An optical density measurement at 490 nm as well as at 520 nm may be useful in deciding whether bismuth interference is considerable. It has been found that with a solution of pure lead dithizonate, the optical density at 490 nm is approximately 0.84 nm times that at 520 nm; with a solution of pure bismuth dithizonate, the optical density at 490 nm is approximately 1.20 times that at 520 nm. When considerable bismuth interference is indicated, the modified procedure given under "Interference by Bismuth" should be used.

2.5 Apparatus

Lead-free borosilicate glass or silica should be used throughout.

2.6 Reagents

All reagents including water, must be lead-free, either as purchased or by special preparation (see Appendix A).

a) Hydrochloric acid, 5 M.

b) Nitric acid, dilute. (One volume of nitric acid, sp. gr. 1.42, diluted to 100 volumes with water.)

c) Ammonium hydroxide, sp. gr. 0.880 and 5 M.

d) Ammonium citrate solution : A 25 per cent $\frac{m}{v}$ solution in water.

e) Sodium hexametaphosphate solution. A 10 per cent $\frac{m}{v}$ solution in water.

f) Potassium cyanide solution. A 10 per cent $\frac{m}{v}$ solution in water. This solution should be at least 2 days old, so that traces of sulphide may become oxidised.

g) Hydroxyammonium chloride solution. A 20 per cent $\frac{m}{v}$ solution in water.

h) Chloroform. Shake 250 ml of chloroform with 25 ml of water containing 1 ml of 10 per cent $\frac{m}{v}$ potassium cyanide solution and about 20 drops of 5M ammonium hydroxide, separate and reject the aqueous layer, wash the chloroform with water, and filter.

j) Dithizone, stock solution. 0.1 per cent $\frac{m}{v}$ solution of diphenylthio carbazone (dithizone) in chloroform. Filter, and store in a refrigerator.

k) Dithizone, working solution. Shake 6 ml of the dithizone stock solution with 9 ml of water and 1 ml of 5M ammonium hydroxide. Separate and reject the lower layer and spin the aqueous layer in a centrifuge until clear. Prepare this solution freshly on the day of use.

l) Ammoniacal sulphite-cyanide solution. Mix 340 ml of ammonium hydroxide, sp. gr. 0.880, 75 ml of 2 per cent $\frac{m}{v}$ sodium sulphite, solution, 30 ml of 10 per cent $\frac{m}{v}$ potassium cyanide solution and 605 ml of water. (The concentration of these reagents are critical.)

m) Standard lead solution.

1) Dissolve 1.60 g of lead nitrate in water, add 10 ml of concentrated nitric acid, and dilute to 1 litre.

2) Dilute 1 volume of i) to 100 volumes with water. Prepare solution ii) freshly as required.

1 ml = 10 µg of lead.

n) Thymol blue indicator solution, 0.04 per cent $\frac{m}{v}$ - Warm 0.1 g of thymol blue with 4.3 ml of 0.05 N sodium hydroxide and 5 ml of 90 per cent ethanol; when dissolution is complete, add sufficient 20 per cent ethanol to produce 250 ml of solution.

o) The following additional reagents are required when *Method B* is to be used.

1) *Sulphuric acid*, diluted (1 + 1).

2) *Perchloric acid*, sp. gr. 1.54.

3) *Sodium iodide solution*. A 20 per cent $\frac{m}{v}$ solution in water.

4) *Sodium metabisulphite solution*. A 1.25 per cent $\frac{m}{v}$ solution in water. Prepare this solution freshly as required, and filter before use.

5) *Diethylammonium diethyldithiocarbamate solution*, 1 per cent (carbamate reagent) - Dissolve 1 g of the pure crystalline reagent in 100 ml of redistilled chloroform, and store in an amber coloured bottle. This solution is not stable and should be discarded after 1 week.

6) *Methyl red indicator solution*, 0.01 per cent $\frac{m}{v}$ - Warm 25 mg of methyl red with 0.95 ml of 0.05 N sodium hydroxide and 5 ml of 90 per cent ethanol; when dissolution is complete, add sufficient 50 per cent ethanol to produce 250 ml of solution.

p) The following additional reagents are required for extraction of bismuth -

1) Hydrochloric acid, sp. gr. 1.18.

2) Diethylammonium diethyl dithicarbamate solution, 1 per cent $\frac{m}{v}$ (carbamate reagent) - prepared as described above.

2.7 Procedure

2.7.1 *Reagent blank*

Carry out a blank test by the procedure on all the reagents, ommitting only the sample.

2.7.2 *Destruction of organic matter (Refer SLS 242*)*

Destroy the organic matter in a measured amount of sample (containing not more than 40 µg of lead) by a suitable procedure (refer SLS 242*)

It should be noted, for example, that the use of sulphuric acid is to be avoided when appreciable amounts of calcium are present, and dry ashing should be avoided in the presence of large amounts of chloride.

If Method B is used, an ashing aid in the form of a 10 per cent solution of magnesium nitrate Mg $(NO_3)_2.6H_2O$, may be used for dry ashing.

2.7.3 *Preliminary treatment of sample*

a) If the organic matter has been destroyed by wet decomposition

Allow the contents of the Kjeldahl flask to cool, and add 5 ml of water.

If the solution is free from insoluble matter, transfer it to a 100-ml conical flask, rinsing with two 1-ml portions of water. Place 10 ml of 5M hydrochloric acid in the Kjeldahl flask, boil gently for 5 minutes, swirl vigorously to wash the sides of the flask, and drain the acid into the conical flask. Finally, wash out the Kjeldahl flask with two 1-ml portions of water.

If the contents of the Kjeldahl flask contain insoluble deposit or suspended matter, however small in amount, filter the solution and washings through a 70 mm Whatman No. 1 filter paper. If possible, retain any deposit in the Kjeldahl flask until it has been boiled with 5M hydrochloric acid, and pass the hot acid also through the filter.

**SLS 242 Methods of destruction of organic matter.*

If the organic matter has been destroyed by an appropriate method, the amount of insoluble matter remaining should not be so great as to cause significant loss of lead through absorption or occlusion. Any such difficulty is also minimised by restricting the amount of the sample.

b) If the organic matter has been destroyed by dry ashing

Add 5 ml of water and 10 ml of 5M hydrochloric acid to the ash in the silica or platinum basin, and boil gently for 5 minutes. Transfer the solution to a 100 ml conical flask, and filter if insoluble matter is present, as described in (a) above.

2.7.4 *Separation of lead*

2.7.4.1 Method A (For samples in which the concentrations of calcium, magnesium and phosphate are not high)

Cool the solution, and add 5 ml of ammonium citrate solution and 10 ml of sodium hexametaphosphate solution. (For certain samples, for example: Cheese, interference by high calcium and phosphate concentrations may be prevented by the addition of 10 ml of ammonium citrate solution, otherwise Method B must be used).

Add a few drops of thymol blue indicator solution and sufficient ammonium hydroxide to give the blue-green colour indicating pH 9.0 to 9.5. Cool, add 1 ml of potassium cyanide solution, and, if much iron is present, add 1 ml of hydroxylamine hydrochloride solution. Transfer the solution to a 100-ml separating funnel containing 10 ml of chloroform, and rinse with a few millilitres of water. The volume of the aqueous layer at this stage should be approximately 50 ml. Add 0.5 ml of dithizone working solution, shake vigorously for 1 minute, and allow to separate. If the lower layer is red, add dithizone working solution until, after shaking, a purple, blue or green colour is obtained. Run the

chloroform layer into a second separating funnel, and wash through with 1 ml or 2 ml of chloroform. Add to the liquid in the first separating funnel 3 ml of chloroform and 0.2 ml of dithizone working solution. Shake vigorously for 30 seconds, allow the chloroform layer to separate, and add it to the main chloroform extract. This last chloroform extract should be green. If it is not, further extraction with chloroform and dithizone must be made until the green colour of the final extract indicates that all the lead has been extracted. Reject the aqueous layer. Add 10 ml of dilute nitric acid to the combined chloroform extracts, and shake vigorously for 1 minute. Allow to separate, and reject the chloroform layer as completely as possible.

2.7.4.2 Method B (For sample with a high content of calcium, magnesium and phosphate)

To the solution obtained by one of the methods described under "Preliminary treatment of the Sample" add 2 drops of methyl red indicator solution and make just alkaline with ammonium hydroxide, sp. gr. 0.880. Make the solution just acid with 5 M hydrochloric acid, and add a further 10 ml. Warm the solution to 50 °C to 70 °C, add 2 ml of sodium iodide soltuion, and reduce any liberated iodine with 2 ml of sodium metabisulphate solution. Cool the solution, transfer it to a separating funnel, and adjust the volume to 50 ml to 75 ml in order to bring the acid concentration to N with respect to hydrochloric acid. Add 10 ml of carbamate reagent by pipette, and shake the funnel vigorously for 30 seconds. Allow the layers to separate, and transfer the chloroform layer to a 100-ml flask. Wash the aqueous layer twice with small amounts of chloroform without mixing, and add these washings to the flask. Repeat the extraction with 10 ml of carbamate reagent, and add the second extract to the main extract. Reject the aqueous layer.

To the combined extracts, add 2.0 ml of diluted sulphuric acid, and evaporate the chloroform. Add 0.5 ml of

perchloric acid to the residual solution and heat until fumes are evolved and the fuming solution is clear and colourless. Cool the solution, add 10 ml of water and 5 ml of 5M hydrochloric acid, boil for 1 minute, cool, and then add 2 ml of ammonium citrate solution.

Continue as in Method A, beginning at paragraph 2, "Add a few drops of thymol blue indicator solution....."

2.7.5 *Determination of lead*

To the nitric acid layer left in the separating funnel add 30 ml of ammonical sulphite cyanide solution, exactly 10 ml of chloroform and 0.5 ml of dithizone working solution, shake vigorously for one minute, and allow to settle. Run off a little of the chloroform layer. Insert a plug of cotton-wool into the dry stem of the funnel, and, after rejecting the first runnings, fill a 10-mm spectrophotometer cell with the chloroform solution.

Measure the optical densities of the test and blank solutions against chloroform (all in 10 mm cells) with a photoelectric absorptiometer fitted with filters that possess a maximum transmission at or near 520 nm with a band width of 23 nm at 50 per cent transmission or with a spectrophotometer at 520 nm. Read the number of microgrammes of lead equivalent to the observed optical densities of the test and blank solutions from a previously prepared calibration graph, and so obtain the net measure of lead in the sample.

2.7.6 Prepare the calibration graph as follows:

Measure 0 ml, 1.0 ml, 2.0 ml, 3.0 ml and 4.0 ml of standard lead solution into separating funnels, and dilute each to 10 ml with dilute nitric acid. Proceed as described under "Determination of Lead". Measure the optical densities with chloroform in the comparison cell. Construct a graph relating the optical densities to the number of microgrammes of lead.

2.7.7 *Interference by Bismuth*

Prepare the digest from the wet decomposition or the ash in the silica or platinum basin, as described under "Preliminary treatment of sample".

If the organic matter has been destroyed by wet decomposition

Add to the contents of the flask 6.0 ml of hydrochloric acid, sp. gr. 1.18, and transfer the solution to a 50-ml graduated separating funnel. Rinse the conical flask with several 1-ml portions of water, and add the rinsings to the separating funnel. The volume of the contents of the separating funnel must not exceed 35 ml in order than the hydrochloric acid concentration may be not less than 3N (see Note).

Extract the acid solution directly in the cold first with 10 ml and then with 5 ml of carbamate reagent, shaking for 30 seconds each time; separate and discard the lower (chloroform) layer. Finally, shake the acid layer with 5 ml of chloroform for 10 s to 15 s, and discard the chloroform layer. Transfer the acid layer to a 100 ml conical flask, rinse the separating funnel with a few millilitres of water, and add the rinsings to the conical flask.

Proceed as in Method A or Method B.

If the organic matter has been destroyed by dry ashing

Add 15 ml of hydrochloric acid, sp. gr. 1.18, transfer to a 50-ml graduated separating funnel, and adjust the volume of the solution to a maximum of 35 ml in order that the hydrochloric acid concentration may be approximately 6N (see Note). Continue as described above from "Extract the acid solution....."

NOTE - After wet decomposition, the extraction solution consists of the residual sulphuric acid to which

hydrochloric acid has been added; the acidity of the solution should not be less than 3N in sulphuric acid and 3N in hydrochloric acid.

When the organic matter has been destroyed by dry ashing, the extraction solution consists of hydrochloric acid alone, and the acidity must be raised to about 6N in hydrochloric acid to effect quantitative separation of bismuth and other elements from lead.

APPENDIX A

PREPARATION OF LEAD-FREE REAGENTS

Hydrochloric, sulphuric, perchloric and nitric acids and ammonium hydroxide can be purchased lead-free to an extent that lead contamination does not exceed 0.005 mg/kg. Potassium cyanide and citric acid can be obtained with lead contents not exceeding 0.5 mg/kg.

If these are not available, ordinary laboratory reagents must be rendered lead-free as follows:

Sulphuric, nitric and hydrochloric acids

Distill from all-borosilicate glass apparatus.

Ammonium hydroxide

Distill 400 ml of ammonium hydroxide, sp. gr. 0.880, from a borosilicate-glass flask fitted with a safety trap, into 250 ml of water kept cold by means of a bath of ice, and control the pressure of the liberated ammonia gas by adjusting the rate of heating. Subsequently determine the concentration of the distillate by titration with N hydrochloric acid.

Ammonium citrate solution

Dissolve 125 g of analytical reagent grade ammonium citrate in 400 ml to 450 ml of water, make faintly alkaline to litmus paper with lead-free 5M ammonium hydroxide, and extract with chloroform and appropriate additions of the stock dithizone solution. Continue extraction until all metals have been removed and the extract is faintly green, and then make the solution just acid by adding lead-free 5M hydrochloric acid, and extract with further portions of chloroform until the final extract is colourless.

Potassium cyanide solution, 10 per cent, $\frac{m}{v}$

Dissolve 50 g of analytical - reagent potassium cyanide in water, and dilute to 100 ml. Extract this solution with chloroform add 1 or 2 drops of dithizone solution until the extract is no longer red, but has a greenish shade (Use as small an excess of dithizone as possible, because the excess is not readily removed). Extract the excess of dithizone by shaking the solution with successive portions of chloroform. Dilute the extracted cyanide solution to 500 ml with water, to remove chloroform, and then cool.

Sodium hexametaphosphate solution

Adjust to pH 9 with thymol blue indicator solution by adding lead-free ammonium hydroxide, and extract with dithizone in chloroform until free from lead. Make the solution just acid, and remove the dithizone traces by extraction with chloroform. Finally, adjust to the maximum blue colour of the indicator.

SLS CERTIFICATION MARK

The Sri Lanka Standards Institution is the owner of the registered certification mark shown below. Beneath the mark, the number of the Sri Lanka Standard relevant to the product is indicated. This mark may be used only by those who have obtained permits under the SLS certification marks scheme. The presence of this mark on or in relation to a product conveys the assurance that they have been produced to comply with the requirements of the relevant Sri Lanka Standard under a well designed system of quality control inspection and testing operated by the manufacturer and supervised by the SLSI *which includes surveillance inspection of the factory, testing of both factory and market samples.*

Further particulars of the terms and conditions of the permit may be obtained from the Sri *Lanka Standards Institution, 17, Victoria Place, Elvitigala Mawatha, Colombo 08.*

Printed at SLSI (Printing Unit)

SRI LANKA STANDARDS INSTITUTION

The Sri Lanka Standards Institution (SLSI) is the National Standards Organization of Sri Lanka established under the Sri Lanka Standards Institution Act No. 6 of 1984 which repealed and replaced the Bureau of Ceylon Standards Act No. 38 of 1964. The Institution functions under the Ministry of Science & Technology.

The principal objects of the Institution as set out in the Act are to prepare standards and promote their adoption, to provide facilities for examination and testing of products, to operate a Certification Marks Scheme, to certify the quality of products meant for local consumption or exports and to promote standardization and quality control by educational, consultancy and research activity.

The Institution is financed by Government grants, and by the income from the sale of its publications and other services offered for Industry and Business Sector. Financial and administrative control is vested in a Council appointed in accordance with the provisions of the Act.

The development and formulation of National Standards is carried out by Technical Experts and representatives of other interest groups, assisted by the permanent officers of the Institution. These Technical Committees are appointed under the purview of the Sectoral Committees which in turn are appointed by the Council. The Sectoral Committees give the final Technical approval for the Draft National Standards prior to the approval by the Council of the SLSI.

All members of the Technical and Sectoral Committees render their services in an honorary capacity. In this process the Institution endeavours to ensure adequate representation of all view points.

In the International field the Institution represents Sri Lanka in the International Organization for Standardization (ISO), and participates in such fields of standardization as are of special interest to Sri Lanka.

Printed at the Sri Lanka Standards Institution, 17, Victoria Place, Elvitigala Mawatha, Colombo 08.