SRI LANKA STANDARD 345 : 1975
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STANDARD METHOD FOR THE DETERMINATION OF MERCURY

BUREAU OF CEYLON STANDARDS

METHOD FOR THE DETERMINATION OF MERCURY

SLS 345:1975

(Attached AMD 413)

Gr. 4

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Sri Lanka Standards are subject to periodical revision in order to accommodate the progress made by industry. Suggestions for improvement will be recorded and brought to the notice of the Committees to which the revisions are entrusted.

This Standard does not purport to include all the necessary provisions of a contract.

AMD 413

AMENDMENT NO: 01 TO SLS 345 : 1975
METHOD FOR THE DETERMINATION OF MERCURY

SRI LANKA STANDARDS INSTITUTION

AMD 413

Amendment No: 01 approved on 2010-10-15 to SLS 345 : 1975

AMENDMENT NO: 01 TO SLS 345 : 1975
METHOD FOR THE DETERMINATION OF MERCURY

FOREWORD

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

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

Insert the following at the end of Clause **2.5.7**.

"**APPENDIX A**
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 MERCURY

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 1975-04-02.

The assistance obtained from the following publication in the preparation of this document is acknowledged. Official Standardised and Recommended Methods of Analysis. Analytical Methods Committee, Society for Analytical Chemistry, London. 1967.

1 SCOPE

This Sri Lanka Standard prescribes a method for the determination of mercury.

2 PRINCIPLE OF METHOD

After destruction of the organic matter by wet oxidation with nitric and sulphuric acids, in the apparatus shown in Fig. 1, dilution of the resulting solution to give an acid concentration of approximately N, and reduction with hydroxy ammonium chloride to destroy oxides of nitrogen, the mercury is separated by extraction with an excess of a solution of dithizone in carbon tetrachloride.

The mercury is removed from this extract and returned to the aqueous phase by oxidation with sodium nitrite in 0.1N hydrochloric acid solution. Excess of nitrite is destroyed with hydroxy ammonium chloride, and any reamaining oxides of nitrogen are removed by treating the solution with urea. After the addition of EDTA, which hinders the reaction of copper with dithizone, mercury is extracted titratively with a solution of dithizone in carbon tetrachloride. The combined extracts are diluted to a standard volume of 4.0 ml by adding carbon tetrachloride, and the content of mercury in the sample is determined by measuring the optical density of this solution against a reagent blank in 10-mm cells at a wavelength of 485 nm and reference to a calibration graph.

In the presence of more than 60 µg of copper (in the final 4 ml of carbon tetrachloride solution), it is recommended that the final colorimetric determination should be made with a solution of dithizone in chloroform instead of in carbon tetrachloride. In this instance, the combined extract is diluted to 4.0 ml with chloroform and measurement is made at a wavelength of 492 nm. In other respects the procedure is identical with that described below.

2.1 Range

For mercury contents not less than 0.5 µg (Hg) in the sample taken. (A suitable sample is generally about 2 g).

2.2 Applicability

The method is suitable for the analysis of most types of organic materials. The method is specific for mercury in all ordinary circumstances. 60 µg of copper can be present when carbon tetrachloride is used, and 600 µg of copper can be present when chloroform is used in the final colorimetric determination, without

interference. The possibility of interference from the noble metals such as gold, palladium and platinum, has not been investigated.

2.3 Apparatus

a) *Digestion apparatus* - See Destruction of organic matter (see 2.5.2).

b) *Separating funnels,* 150-ml, 500-ml and 1000-ml capacity - Pear shaped separating funnels with well fitting glass stopcocks and stoppers.

NOTE - *All glassware should be of borosilicate glass and must be thoroughly cleaned with nitric and sulphuric acids, and then washed with distilled water, immediately before use.*

2.4 Reagents

All water shall be glass distilled or de-mineralised and free from mercury or other impurities that react with dithizone.

The acids supplied as 'low in lead' or 'for foodstuffs analysis' are suitable for the determination of mercury without further treatment.

Other reagents used should be of analytical reagent quality. Certain of the reagent solutions used may be purified in order to reduce blank values and so increase the accuracy of the method at low levels of mercury. The purifications of hydroxy ammonium chloride solution is described.

a) *Hydroxy ammonium chloride solution*

Prepare a 20 per cent *m/v* solution in water and purify it as follows:

Transfer the solution to a separating funnel. Add a few millilitres of dithizone stock solution, shake for

2 minutes, and allow the layers to separate. Reject the organic layer. Repeat the extraction with dithizone until the organic layer has the colour of pure dithizone solution. Finally extract the solution with successive small amounts of chloroform until the extracts are colourless, and discard the extracts.

b) *Dithizone stock solution*

Prepare a 0.05 per cent m/v solution in chloroform. This solution should be stored in a dark glass bottle in a refrigerator.

NOTE - *Commercially available analytical reagent grade dithizone can usually be used without purification. If however, purification of the reagent is considered desirable, the reagent solution may be prepared as follows:*

Dissolve 0.1 g of dithizone in 150 ml of chloroform in a separating funnel and shake for 10 minutes. Filter the solution through an ashless filter paper into a second separating funnel, add sbout 100 ml of approximately 0.1 N ammonia solution and shake vigorously for one minute. Allow the layers to separate and run the organic layer back into the first separating funnel and shake it for one minute with a further 100-ml portion of approximately 0.1 N ammonia solution. Discard the organic phase and combine the ammonical solutions in a large separating funnel. Wash the solution with three successive 5-ml portions of chloroform and discard the washings. Add 200 ml of chloroform, neutralize with approximately N sulphuric acid and add 10 ml of the acid in excess. Extract the dithizone into the chloroform by shaking vigorously for 2 minutes, allow to separate and run the organic layer through a dry ashless filter paper into a dark glass bottle. Store the solution in a refrigerator.

c) *Dilute dithizone solution in carbon tetrachloride*

Dilute 2 ml of the stock solution to 100 ml with carbon tetrachloride.

d) *Dilute dithizone solution in chloroform*

Dilute 2 ml of the stock solution to 100 ml with chloroform.

NOTE - *Dilute dithizone solutions should be freshly prepared.*

e) *Hydrochloric acid solution,* 0.1 N*.

f) *Sodium nitrate solution,* 5 per cent *m/v* aqueous*.

g) *Urea solution,* 10 per cent *m/v* aqueous*.

h) *EDTA solution**

Dissolve 2.5 g of EDTA (disodium salt dihydrate) in 100 ml of water.

j) *Acetic acid solution,* approximately 4 N*.

k) *Carbon tetrachloride.*

l) *Chloroform.*

m) *Standard mercury stock solution*

Dissolve 0.1354 g of mercuric chloride in 1 litre of 0.1 N hydrochloric acid.

1 ml of solution = 100 μg of mercury (Hg).

These solutions can be purified as described for hydroxy ammonium chloride solution.

n) *Dilute standard mercury solution*

Dilute 10 ml of the stock solution to 1 litre with 0.1 N hydrochloric acid.

1 ml of solution = 1 µg of mercury (Hg).

This solution should be prepared freshly as required.

o) *Sulphuric acid*, sp.gr. 1.84.

p) *Nitric acid*, sp.gr. 1.42.

2.5 Procedure

2.5.1 Reagent blank value

Carry out a blank test by the entire procedure; use the precise amounts of the reagents used in the test and omit only the sample.

2.5.2 Destruction of organic matter

The apparatus shown in Figure 1 should be used for the wet digestion of the sample. The method described below is suitable for the oxidation of most materials. Sample masses of up to about 10 g of dry solid can be oxidised by this procedure with 50 ml of nitric acid. Care should be taken in applying the method of wet oxidation to samples containing fats since, although this method has been applied to several such substances, some workers who have possibly used other conditions have experienced explosiye reactions.

Other procedures may be found suitable for the wet oxidation of particular types of organic matter. For example, the destruction of sugars and other carbohydrates is facilitated by heating the sample under reflux with nitric acid and water for some time before cooling, adding sulphuric acid, and completing the digestion.

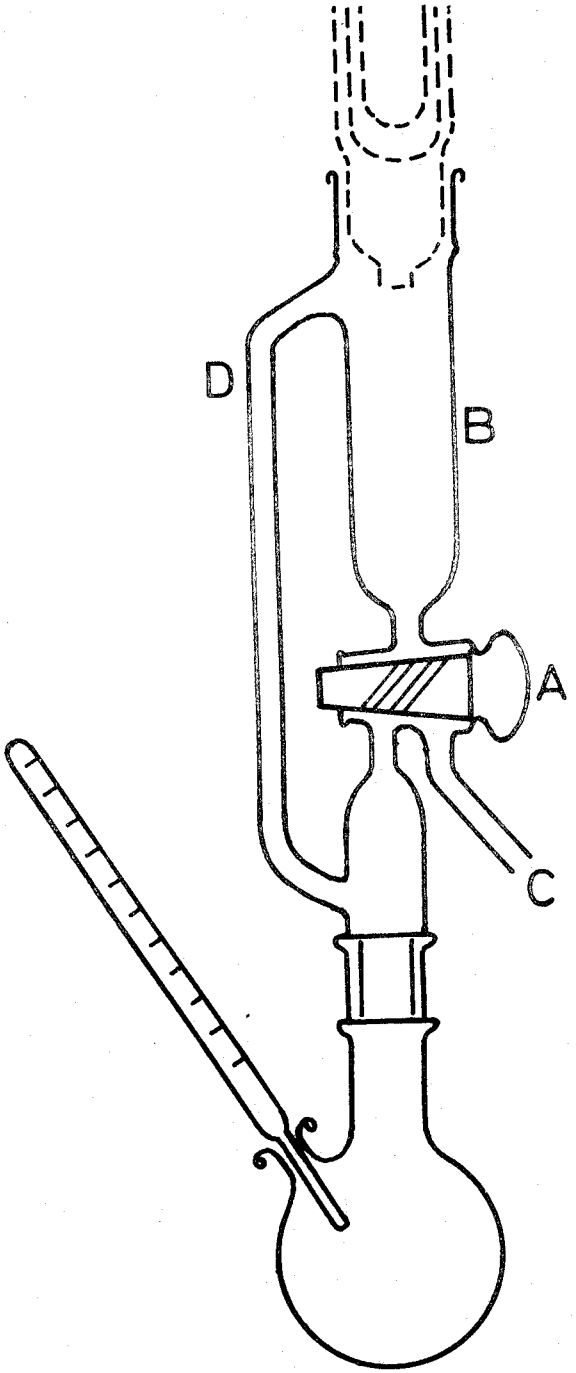

FIG. 1 - Apparatus for the wet decomposition of organic matter

2.5.3 Description of apparatus

The flask has a capacity of 250 ml and the reservoir, *B*, has a capacity of 150 ml to 200 ml. The condenser is a standard double surface or spiral surface reflux type. The thermometer is calibrated for temperatures upto 200 °C and all the connections are made through standard ground glass joints.

2.5.4 Method

Transfer a weighed amount of sample to the oxidation flask and add a cooled mixture of 20 ml of water, 5 ml of sulphuric acid and 50 ml of nitric acid. (If the sample is wet, reduce the volume of water added, and if the sample mass exceeds 10 g of dry solid add up to a further 5 ml of nitric acid for each gram of dry solid in excess). Add a few anti-bumping granules or glass beads and assemble the apparatus as illustrated. Allow any initial reaction to subside and then heat, cautiously at first, collecting the distillate in the reservoir, *B*, with tap *A* closed. When the temperature indicated by the thermometer reaches 116 °C (see Note 1), run off the contents of the reservoir through the drain tube, *C*, and collect in a measuring cylinder.

Continue collecting the distillate in the reservoir and when the oxidation mixture darkens run a little of the distillate from the reservoir to the flask. Continue this procedure, maintaining a slight excess of nitric acid in the oxidation flask, until the solution ceases to darken and fumes of sulphuric acid are evolved. Allow the mixture to cool, run the contents of the reservoir into the flask and add to first distillate in in the measuring cylinder (see Note 2).

Titrate 1 ml of this solution with standard sodium hydroxide solution to determine the normality of acid present. Dilute with water to produce a solution with a total acidity of about N (see Note 3), heat to boiling,

remove from the source of heat, and add rapidly, with mixing a volume of hydroxy ammonia chloride solution equal to one-tenth of the total bulk; then set aside for 15 minutes, and cool to room temperature.

NOTES:

1 This temperature is close to the boiling point of nitric acid.
2 The volume of the residue plus distillate is usually about 80 ml to 90 ml.
3 The volume after dilution to N is about 400 ml.

2.5.5 Separation of mercury

Transfer the solution to a separating funnel of suitable capacity and extract with carbon tetrachloride if necessary, to remove any fat. Add 10 ml of dilute dithizone solution in carbon tetrachloride, shake for one minute, allow the layers to separate and run the lower layer into a 150-ml separating funnel. Continue the extraction with successive 1 ml portions of dithizone solution until two successive extracts remain green, and combine the extracts in the second separating funnel.

Add 10 ml of 0.1 N hydrochloric acid in 1 ml of sodium nitrite solution, shake vigorously for 1 minute, allow the layers to separate and carefully discard the lower layer. Add 1 ml of hydroxy ammonium chloride solution and set aside for 15 minutes, shaking occas ionally. Add 1 ml of urea solution and 1 ml of EDTA solution.

2.5.6 Determination of mercury

Add 0.5 ml of dilute dithizone solution in carbon tetrachloride from a 10-ml burette. Shake the funnel vigorously for 10 seconds and allow the layers to separate. Run the lower layer into another separating funnel containing 5 ml of 4 N acetic acid (see Note 4) and repeat the operation until the separated layer is greenish orange; the shaking time should then be extended to

30 seconds and the increments of dithizone solution reduced to 0.2 ml. Continue the titration and separation, combining the extracts until the organic layer has a greyish mixed colour, showing that the mercury has been extracted completely and that the extract contains a slight excess of dithizone; note the volume of dithizone solution required. From another 10 ml burette add sufficient carbon tetrachloride (or chloroform) to adjust the volume of the extract to 4.0 ml.

Mix dry the stem of the funnel, and run the lower layer through a small glass wool plug, supported in a small glass funnel, into a 10-mm glass spectrophotometric cell. Measure the optical density at a wavelength of 105 nm with the blank solution as reference. Read the number of micrograms of mercury equivalent to the measured optical density from the calibration graph established as described below, and calculate the mercury content of the sample.

NOTE 4 - *Solutions of mercuric dithizonate in organic solvents are sensitive to light. Exposure to daylight causes the solutions to fade, but the original colour is slowly restored if the faded solutions are kept in the dark, and is more rapidly restored on shaking with dilute acids.*

2.5.7 Preparation of calibration graph

Transfer aliquots of dilute standard mercury solution to cover the range 0.5 µg to 10.0 µg of mercury to a series of separating funnels and dilute each to 10.0 ml if necessary, by adding 0.1 N hydrochloric acid. Transfer 10.0 ml of 0.1 N hydrochloric acid to another separating funnel to be used as a blank solution. Treat each solution as described below.

Add one ml of sodium nitrite solution and one ml of hydroxy ammonium chloride solution mix, and set aside for 15 minutes. Add one ml of urea solution and one ml of EDTA solution and complete the extraction and measurement of each extract as described under *Determination of mercury*, use the same solution of dithizone as was used in the tests.

Construct a graph relating optical density to the number of micrograms (2.5.6) of mercury. The plot should be linear and should on extrapolation, pass through the origin.

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