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Sulphuric acid and oleum for industrial use — Determination of lead content — Dithizone photometric method

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FOREWORD

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International Standard ISO 2717 was drawn up by Technical Committee ISO/TC 47, *Chemistry*, and circulated to the Member Bodies in April 1972.

It has been approved by the Member Bodies of the following countries :

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This International Standard has also been approved by the International Union of Pure and Applied Chemistry (IUPAC).

No Member Body expressed disapproval of the document.

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Sulphuric acid and oleum for industrial use — Determination of lead content — Dithizone photometric method

1 SCOPE

This International Standard specifies a dithizone photometric method for the determination of the lead content of sulphuric acid and oleum for industrial use.

2 FIELD OF APPLICATION

The method is applicable to the determination of lead (Pb) contents greater than 1 mg/kg.

3 PRINCIPLE

Evaporation of a test portion, dissolution in hydrochloric acid and reduction by hydroxylammonium chloride. Formation of complexes of interfering elements with ammonium citrate and potassium cyanide. Extraction of the lead, at a pH of between 8,5 and 10, by a solution of dithizone in chloroform. Elimination of excess dithizone by an ammoniacal solution of potassium cyanide.

Photometric measurement of the lead dithizonate in chloroform solution, at a wavelength of about 520 nm.

4 REAGENTS

Distilled water, or water of equivalent purity, shall be used in the test.

4.1 Chloroform, redistilled in a borosilicate glass apparatus with ground joints, ρ 1,471 to 1,474 g/ml.

4.2 Hydrochloric acid, ρ approximately 1,19 g/ml, about 38 % (*m/m*) solution, or approximately 12 N.

4.3 Ammonium citrate $[HOCCOOH(CH_2COOHN_4)_2]$, 100 g/l solution.

Purification of the solution. To 100 ml of solution, add ammonia solution, ρ approximately 0,91 g/ml, until the pH reaches a value of between 8,5 and 10, checking with the indicator paper (4.11). Transfer the solution to a separating funnel, add 10 ml of the dithizone solution (4.7) and shake vigorously. Allow to separate and withdraw and reject the organic phase. Repeat the extraction, each time with 5 ml of the dithizone solution (4.7), until the green colour remains. Allow to separate and withdraw and reject the organic phase.

4.4 Potassium cyanide, 50 g/l solution (see in section 6) "Warning".

4.5 Hydroxylammonium chloride, 100 g/l solution.

4.6 Ammonia, approximately 5 N solution.

NOTE — A freshly prepared solution must be used in order to avoid too high a value being obtained by the blank test, due to dissolved lead. In fact, dilute ammonia dissolves lead contained in the glass more rapidly than does concentrated ammonia.

4.7 Dithizone, 0,025 g/l solution in chloroform.

If dithizone of satisfactory quality is not available, it may be purified by the method described in 4.7.1.

4.7.1 *Purification of the dithizone*

Dissolve 1 g of dithizone (biphenylthiocarbazone) in 75 ml of the chloroform (4.1). Filter the solution, collecting the filtrate in a 250 ml separating funnel. Add 100 ml of approximately 0,2 N ammonia solution and shake vigorously. Withdraw the organic phase, collecting it in another separating funnel, and repeat, a further three times, the same operation, using 100 ml of approximately 0,2 N ammonia solution each time. (The dithizone thus passes into the alkaline aqueous phase, colouring it orange, while the oxidation products remain in the organic phase, which assumes a more or less intense reddish-yellow coloration.)

Discard the organic phase, combine the orange coloured aqueous extracts, filter them and transfer them to a 1 000 ml beaker.

Precipitate the dithizone by slight acidification with a saturated solution of sulphur dioxide. Allow the precipitate to settle, filter through a sintered glass crucible and wash with water until there is no further acid reaction. Dry the precipitate in a desiccator containing a concentrated sulphuric acid solution, ρ approximately 1,84 g/ml, under vacuum and in darkness, for a period of 3 to 4 days.

Grind the solid dry product quickly and transfer immediately to a small dark glass bottle. The dithizone, thus purified and stored away from direct sunlight, can be kept for at least 6 months.

4.7.2 *Preparation of the solution*

Immediately before use, weigh, to the nearest 1 mg, 25 mg of the purified dithizone (4.7.1), transfer to a 1 000 ml one-mark volumetric flask, dissolve in the chloroform (4.1), dilute to the mark with the same chloroform (4.1) and mix.

Store the solution in a dry, dark glass, air-tight bottle.

4.8 Potassium cyanide, 1 g/l ammoniacal solution (see in section 6) "Warning".

Transfer 20 ml of the potassium cyanide solution (4.4) to a 1 000 ml one-mark volumetric flask. Dilute with water, add 10 ml of ammonia solution, ρ approximately 0,88 g/ml, dilute to the mark and mix.

4.9 Standard lead solution, corresponding to 1 000 g of lead per litre.

Weigh, to the nearest 0,001 g, 1,600 g of lead nitrate [$Pb(NO_3)_2$], previously dried at 105 °C and cooled in a desiccator, and transfer to a beaker of suitable capacity. Dissolve in a little water and 1 ml of nitric acid solution, ρ approximately 1,40 g/ml. Transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 1 mg of Pb.

4.10 Standard lead solution, corresponding to 0,010 g of lead per litre.

Transfer 10,00 ml of the standard lead solution (4.9) to a 1 000 ml one-mark volumetric flask, add 1 ml of nitric acid solution, ρ approximately 1,40 g/ml, dilute to the mark and mix.

1 ml of this standard solution contains 10 μg of Pb.

Prepare this solution immediately before use.

4.11 pH indicator paper, covering the range from 8,5 to 10.

5 APPARATUS

NOTE – All glassware, including the reagent bottles, shall be of borosilicate glass or of another quality of glass free from lead, or alternatively plastics materials may be used. It shall be washed with a nitric acid solution, approximately 7 N, and rinsed with water three times.

Ordinary laboratory apparatus and

5.1 Weighing pipette, capacity about 60 ml, with ground glass stoppers.

5.2 Burette, 25 ml capacity, graduated in 0,05 ml (see ISO/R 385).

5.3 Spectrophotometer, or

5.4 Photoelectric absorptiometer fitted with filters giving maximum transmission between 500 and 540 nm.

6 PROCEDURE

WARNING – Because potassium cyanide is extremely poisonous, it must only be handled with all necessary precautions. In particular, do not add acids to solutions containing cyanides, otherwise hydrogen cyanide will be released.

6.1 Test portion

Fill the weighing pipette (5.1) with the test sample and, weighing by difference to the nearest 0,02 g, take a test portion of about 50 g. Transfer the test portion to a beaker of suitable capacity, for example 250 ml.

6.2 Blank test

Carry out, in parallel, a blank test, using the same quantities of reagents as employed for the determination, and following the same procedure for the blank test, the determination and for the preparation of the calibration curve.

6.3 Preparation of the calibration curve

6.3.1 *Preparation of the standard matching solutions*, for photometric measurements with a 1 cm cell.

Into eleven separating funnels of 100 ml capacity, fitted with ground glass stoppers, transfer 10 ml of water and add respectively the volumes, measured with the burette (5.2), of the standard lead solution (4.10) indicated in the following table.

Standard lead solution (4.10)	**Corresponding mass of Pb**
ml	μg
0*	0
1,0	10
2,0	20
3,0	30
4,0	40
5,0	50
6,0	60
7,0	70
8,0	80
9,0	90
10,0	100

* Compensation solution.

Treat each of these solutions in the following manner :

Add 1 ml of the hydroxylammonium chloride solution (4.5) and 10 ml of the ammonium citrate solution (4.3), and adjust the pH to between 8,5 and 10 by adding the

ammonia solution (4.6) drop by drop, checking with the indicator paper (4.11). Add 2 ml of the potassium cyanide solution (4.4), and shake, followed by 5 ml of the dithizone solution (4.7) and extract the lead dithizonate, shaking vigorously for 1 min. Allow to separate and draw off the organic phase, collecting it in a 50 ml one-mark volumetric flask. Continue the extraction with successive portions of 5 ml of the dithizone solution (4.7), until the last portion of the dithizone solution, after swirling, remains green. Collect the various portions of the organic phase, as drawn off, in the same 50 ml one-mark volumetric flask, including the portion that remains green. Dilute the organic phase to the mark with the chloroform (4.1) and mix.

In order to eliminate the excess of dithizone present in the organic phase, carry out the extraction with the minimum number of manipulations, using 5 ml portions of the ammoniacal cyanide solution (4.8) each time, until the yellow colour of the dithizone has disappeared. Then draw off the organic phase, which will have a clear pink colour, and pass it through a dry, "acid-washed" filter paper, collecting the filtrate in a dry vessel.

NOTE — Dithizonates are particularly sensitive to ultra-violet light and should, therefore, be protected from sunlight and fluorescent light.

6.3.2 *Photometric measurements*

Carry out the photometric measurements using the spectrophotometer (5.3) at the maximum of the absorption curve (wavelength of about 520 nm) or with the photoelectric absorptiometer (5.4), fitted with suitable filters; in each case adjust the instruments to zero absorbance against the compensation solution.

6.3.3 *Preparation of calibration chart*

Plot a graph having, for example, the lead (Pb) contents, expressed in micrograms per 50 ml of standard matching solution, as abscissae and the corresponding values of absorbance as ordinates.

6.4 Determination

6.4.1 *Preparation of the test solution*

Place the beaker containing the test portion (6.1) on a sand bath and evaporate cautiously to dryness in a well-ventilated fume cupboard. Cool, take up with 2 ml of the hydrochloric acid solution (4.2) and 25 ml of water, and warm moderately to complete the dissolution. Allow to cool, transfer the solution quantitatively to a one-mark volumetric flask of suitable capacity, dilute to the mark and mix.

6.4.2 *Extraction of the lead dithizonate*

According to the expected lead content, take an aliquot portion of the test solution (6.4.1) containing 10 to 100 μg of Pb and transfer it to a separating funnel of suitable capacity. Then proceed with the determination as described in 6.3.1, from the first paragraph after the table, for the preparation of the standard matching solutions.

NOTE — If the Pb content to be determined is of the order of 1 mg/kg, use the whole of the test solution, without dilution, for the extraction of the lead dithizonate.

6.4.3 *Photometric measurements*

Carry out the photometric measurements of the chloroform solution of lead dithizonate deriving from the test solution and that deriving from the blank test, according to the methods described in 6.3.2, but after having adjusted the instrument to zero absorbance against the chloroform (4.1).

7 EXPRESSION OF RESULTS

By means of the calibration curve (6.3.3), determine the quantity of lead corresponding to the values of the photometric measurements.

The lead (Pb) content is given, in milligrams per kilogram, by the formula

$$\frac{(m_1 - m_2) \times D}{m_0}$$

where

m_0 is the mass, in grams, of the test portion;

m_1 is the mass, in micrograms, of lead found in the aliquot portion of the test solution;

m_2 is the mass, in micrograms, of lead found in a corresponding aliquot portion of the blank test solution;

D is the ratio of the volume of test solution to the volume of aliquot portion taken for the extraction of the lead dithizonate.

8 NOTE ON PROCEDURE

All the chloroform used for the analysis may be recovered. For this purpose, collect the organic phase of all the tests together and remove the lead by shaking with an aqueous solution of hydrochloric acid. Then remove the dithizone by shaking with a solution of ammonia. Repeat this treatment until the chloroform becomes colourless, then wash it by shaking with water and finally distil it in a borosilicate glass apparatus, with ground glass joints, in the presence of a little phosphorus pentoxide. Boiling point 61,2 °C.

9 TEST REPORT

The test report shall include the following particulars :

a) the reference of the method used;

b) the results and the method of expression used;

c) any unusual features noted during the determination;

d) any operation not included in this International Standard, or regarded as optional.

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