INTERNATIONAL STANDARD 3112

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Copper and copper alloys — Determination of lead — Extracting titration method

Cuivre et alliages de cuivre — Dosage du plomb — Méthode de titrage par extraction

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FOREWORD

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Copper and copper alloys — Determination of lead — Extracting titration method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies an extracting titration method for the determination of lead in copper and copper alloys.

The method is applicable for the determination of lead as an alloying element as well as an impurity in copper and all types of copper alloys listed in ISO Recommendations or International Standards.

2 PRINCIPLE

Determination of lead by extracting titration using a solution of dithizone in chloroform as titrant and employing a special titrating apparatus equipped with a high-speed stirrer.

3 REAGENTS

All the reagents shall be of the analytical grade. Distilled or deionized water shall be used.

3.1 Acid mixture.

Mix 1 volume of hydrochloric acid (ρ 1,19 g/ml) with 1 volume of nitric acid (ρ 1,4 g/ml) and 1 volume of water.

3.2 Hydrochloric acid, 6 N.

3.3 Ammonia solution (ρ 0,91 g/ml).

3.4 Ammonium citrate, ammoniacal solution containing 20 g of citric acid and 400 ml of ammonia (ρ 0,91 g/ml) per litre (the pH of the solution shall be 11,2).

3.5 Ammonium citrate, ammoniacal solution containing 100 g of citric acid and 500 ml of ammonia (ρ 0,91 g/ml) per litre (the pH of the solution shall be 10,9).

3.6 Citric acid, 333 g/l solution.

3.7 Hydroxylamine hydrochloride solution.

Dissolve 100 g of hydroxylamine hydrochloride in approximately 700 ml of water, bring to pH 8,8 by means of ammonia and make up to 1 l.

3.8 Potassium cyanide, 100 g/l solution, preferably stored in a polyethylene flask, equipped with a constant volume dispenser.

3.9 Dithizone stock solution.

Dissolve 0,320 g of dithizone in 1 000 ml of re-distilled chloroform and keep this solution protected from light. (Bottles of brown glass are unsuitable because they favour the decomposition of dithizone.)

3.10 Dithizone standard solution.

Mix 300 g of the dithizone stock solution (3.9) and 680 ml of chloroform (1 ml of this solution is equivalent to approximately 25 μg of lead).

For standardizing this solution proceed as follows :

Transfer 5 ml of the hydrochloric acid (3.2), 25 ml of the lead test solution (3.12) and 10 ml of the ammoniacal ammonium citrate solution (3.4) into the titrating apparatus, stir, check whether the solution is ammoniacal by adding 2 to 3 drops of the copper solution (3.13), add 5 ml of the hydroxylamine hydrochloride solution (3.7) and 5 ml of the potassium cyanide solution (3.8), and titrate. The consumption of dithizone should be 35 to 45 ml. The solution has to be standardized daily. In the case of a determination involving high lead content it is recommended to standardize the solution just before the analysis.

3.11 Lead standard solution.

Dissolve 1,000 g of lead (lead content $>$ 99,95 %) in 30 ml of nitric acid 1 + 2, boil out the nitrous oxides and dilute to 1 000 ml.

3.12 Lead test solution, containing 40 mg of lead per litre.

Mix 40,0 ml of the lead standard solution (3.11) with 20 ml of the hydrochloric acid (3.2) and make up to 1 l.

3.13 Copper solution.

Dissolve with cooling 2,0 g of lead-free copper (lead content $<$ 0,000 5 %) in 20 ml of the hydrochloric acid (3.2) and 20 ml of hydrogen peroxide (30 %), added in small portions. When the reaction has ceased, destroy the excess hydrogen peroxide by boiling, and dilute to 1 l.

3.14 Chloroform, special dithizone grade.

4 APPARATUS

4.1 Normal laboratory apparatus.

4.2 Special titrating apparatus (see figure), comprising the following parts :

a) **cylindrical titrating vessel;**

b) **high-speed stirrer;**

c) **self-filling burette.**[1]

The titrating cylinder, inside diameter 33 mm, height 120 mm, capacity approximately 100 ml, is provided with a baffle plate, made of PTFE, width 9 mm, approximately 90 mm long, 4 mm thick, held in a vertical position by means of a clamp, and a stopcock at its lower end for draining.

The high-speed stirrer is operated by a direct current motor, adjustable between 0 and 15 V, with a current maximum of 1,5 A. The stirrer is a three-blade propeller stirrer (diameter of the blade approximately 150 mm), connected to the motor by a stainless steel bushing of 5 mm bore, which is in turn screwed onto the shaft butt of the motor. The speed of the stirrer is preferably in the range 7 000 to 10 000 rev/min. In view of this speed, the stirrer must be centred extremely well. It is cemented into the bushing by means of a hard-setting wax, for example "Picein". The centring is done while the motor is running and before the wax cools down completely.

Any other stirring device may be used, provided it can be operated at a similar stirring speed. (The efficiency of the stirring device improves with decreasing distance between the stirring blades and the baffle.)

The self-filling burette consists of a 1 l storage jar, made of white glass and provided with a light-proof coating. The stopcocks of the burette are made of PTFE.

NOTE — The use of a special titrating apparatus according to the description above greatly facilitates the practical execution of this determination. In principle, however, other mechanical stirring equipment and even shaking by hand is feasible.

5 SAMPLING

Carry out the sampling in accordance with the requirements of ISO . . .[2]

6 PROCEDURE

6.1 For lead contents from 0,02 to 0,5 % (*m/m*)

This procedure is applicable if the alloy

- is practically free of Bi (0,01 % Bi simulates 0,015 % Pb),
- its Be content is lower than 0,01 %,
- its P content is lower than 0,2 %.

Dissolve 1,000 g of the sample in a 100 ml graduated flask with 15 ml of the acid mixture (3.1), boil briefly, cool and make up to the mark. Pipette 25 ml of this solution into the titrating apparatus, add with stirring 10 ml of the citric acid solution (3.6), 20 ml of the ammonium citrate solution (3.5), 5 ml of the hydroxylamine hydrochloride solution (3.7), 15 ml of the potassium cyanide solution (3.8) and finally 1 ml of the dithizone solution (3.10). If the chloroform phase turns red, add another 1 ml, and continue in 1 ml steps to a maximum of 10 ml. Stir for 30 s and then drain the red, Pb-containing extract into a 100 ml beaker that has been rendered lead-free by prior rinsing with dithizone solution.

Continue titrating until, after adding 1 ml of dithizone solution and stirring for 30 s, the red-coloured dithizone solution turns lilac, and record the volume of the dithizone solution required. Drain the organic extract into the beaker.

To the aqueous phase add 2 ml of the dithizone solution and 2 ml of the chloroform (3.14) and stir for 60 s. If the extract remains green, repeat the addition of 2 ml of the dithizone solution, stir again for 60 s and combine the organic phases in the beaker.

Return the combined extracts to the cleaned titrating apparatus containing 20 ml of water and 5 ml of the hydrochloric acid (3.2). Stir for 10 s, thus transferring the lead to the aqueous phase again, drain the chloroform phase and discard it. To the aqueous phase add 2 drops of the copper solution (3.13), 10 ml of the ammonium citrate ammoniacal solution (3.4), 5 ml of the hydroxylamine hydrochloride solution (3.7), 5 ml of the potassium cyanide solution (3.8), and again titrate with the dithizone solution (3.10).

Introduce in portions of not more than 10 ml the total amount less the 2 ml of dithizone solution required in the rough titration. Stir for 30 s after each addition and drain off the extract. Wash the aqueous phase by adding 2 ml of the chloroform (3.14) and stirring for approximately 2 s, drain the wash chloroform and continue titrating with the dithizone solution in 0,2 ml steps, adding each time 2 ml of chloroform. Stir for 30 s, drain the extract after each addition and wash the aqueous phase with 2 ml of chloroform as described above.

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[1] The apparatus can be supplied by H. Middendorff Nachf., 44 Münster/Westf., Alter Steinweg 17-18, Germany.

[2] In preparation.

The end-point is reached when the last extract remains clear green. The titration value is then the sum of all the additions prior to that giving rise to the clear green extract (including those extracts of intermediate colours).

Determine the blank value of the reagents in the same way.

6.2 For lead contents from 0,4 to 25 % (*m*/*m*)

Two procedures, A and B, are available.

6.2.1 *Requirements for procedure A*

- The alloy must not contain any Bi (0,01 % Bi simulates 0,015 % Pb).
- The P content of the alloy must be lower than 0,5 %.
- The Be content must be lower than 0,005 %.
- The total of the Al, Co, Cr, Ti and Zr contents must not exceed the Pb content.
- The total of the Fe and Sn contents must not exceed twice the amount of the Pb content.

6.2.2 *Requirements for procedure B*

- The alloy must not contain any Bi (0,01 % Bi simulates 0,015 % Pb).
- The P content of the alloy must be lower than 0,5 %.
- The Be content must be lower than 0,03 %.

6.2.3 *Preparation of the stock solution*

Dissolve the required mass of sample in the amount of acid mixture (3.1), boil briefly, cool and make up in a graduated flask to the corresponding volume as indicated in the table.

6.2.4 *Procedure A*

Pipette 20 ml of the stock solution into the titrating apparatus containing 5 ml of the ammonium citrate solution (3.5). Add 5 ml of the hydroxylamine hydrochloride solution (3.7), stir briefly and add 5 ml of the potassium cyanide solution (3.8). In the case of Fe-containing alloys the solution will have a yellow colour.

For the rough titration of the lead content add 1 ml of the dithizone solution (3.10) and stir. If the chloroform phase turns red add another 1 ml and continue in 1 ml steps to a maximum of 10 ml. Stir for 30 s and drain the red-coloured extract. Continue titrating until, after an addition of 1 ml of the dithizone and 30 s stirring, the red dithizone solution turns reddish-lilac. Drain the extract.

The end-point is as in the case of 6.1 the production of a permanent clear green extract.

For the accurate determination add to the sample solution prepared for titration in the titrating apparatus, in portions of not more than 10 ml, the total amount less the 1 ml of dithizone solution required in the rough titration. Stir for 30 s after each addition and drain off the extract. Then wash the aqueous phase by adding 2 ml of the chloroform (3.14) and stirring for 2 s, drain the wash chloroform and continue titrating with quantities of 0,1 ml of the dithizone solution, adding each time 2 ml of chloroform. Stir for 30 s, drain the extract after each addition and wash the aqueous phase with 2 ml of chloroform as described above. Continue titrating until the last extract remains clear green. Those additions causing intermediate colours must be included (as in procedure 6.1).

Determine the blank value of the reagents in the same way.

6.2.5 *Procedure B*

Pipette 20 ml of the stock solution into the titrating apparatus, add with stirring 5 ml of the citric acid solution (3.6), 15 ml of the ammonium citrate solution (3.5), 5 ml of the hydroxylamine hydrochloride solution (3.7) and 5 ml of the potassium cyanide solution (3.8). Make a rough titration as in 6.2.4 and collect the Pb-containing extracts in a 100 ml beaker, which has been rinsed with dithizone solution to make it lead-free. Before draining the last extract whose green colour has persisted, add 2 ml of dithizone solution and stir for 60 s. Run this green extract also into the beaker.

Return the combined extracts to the cleaned titrating apparatus containing 20 ml of water and 5 ml of the hydrochloric acid (3.2). Stir for 10 s, thus transferring the lead to the aqueous phase again, and drain the chloroform phase. Add to the hydrochloric acid solution 2 drops of the

Lead contents	Mass of sample	Amount of acid mixture (3.1)	Final volume of stock solution	Approximate lead equivalent of 1 ml of dithizone
% (*m*/*m*)	g	ml	ml	%
0,5 to 1,5	2	30	500	0,03
1,0 to 3,0	1	30	500	0,06
2,5 to 6,0	0,5	30	500	0,125
5,0 to 10	1	80	2 000	0,25
9,0 to 20	0,5	80	2 000	0,50

copper solution (3.13), 10 ml of the ammonium citrate ammoniacal solution (3.4), 5 ml of the hydroxylamine hydrochloride solution (3.7), and 5 ml of the potassium cyanide solution (3.8), and titrate as described in 6.2.4 for the accurate determination above.

Determine the blank value of the reagents in the same way.

7 EXPRESSION OF RESULTS

Calculate the lead content, as a percentage by mass, by the formula

$$\text{Pb \% } (m/m) = \frac{(V_1 - V_2) \times C}{10\,m}$$

where

V_1 is the volume, in millilitres, of dithizone solution used for the determination;

V_2 is the volume, in millilitres, of dithizone solution used for the blank test;

C is the lead equivalent, in micrograms of lead per millilitre, of the dithizone solution;

m is the mass, in milligrams, of the test portion.

8 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 characteristics noted during the determination;

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

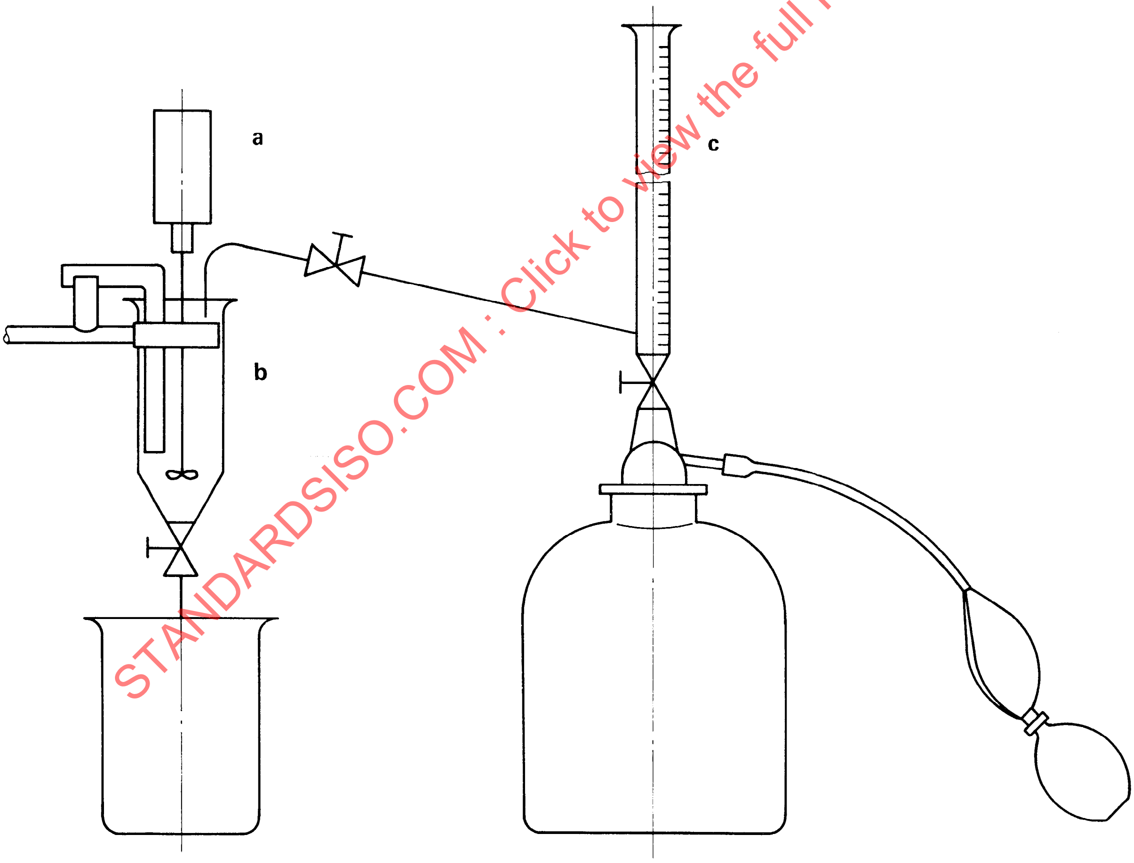

FIGURE – **Special titrating apparatus**