SLOVENSKI STANDARD
SIST EN 12938:2002

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Metode kemijske analize okrasne kositrove zlitine (pewter) - Določanje zlitinskih elementov in nečistoč z atomsko spektrometrijo

Methods for the analysis of pewter - Determination of alloying and impurity element contents by atomic spectrometry

Analyse von Zinnlegierungen - Bestimmung des Gehaltes an Legierungs- und Verunreinigungselementen durch Atomspektrometrie

Méthodes d'analyse de l'étain pour la fabrication d'objets - Détermination de la teneur en alliages et en impuretés par spectrométrie atomique

Ta slovenski standard je istoveten z: **EN 12938:1999**

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77.040.30	Kemijska analiza kovin	Chemical analysis of metals
77.120.60	Svinec, cink, kositer in njihove zlitine	Lead, zinc, tin and their alloys

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English version

Methods for the analysis of pewter - Determination of alloying and impurity element contents by atomic spectrometry

Méthodes d'analyse de l'étain pour la fabrication d'objets - Détermination de la teneur en alliages et en impuretés par spectrométrie atomique

Analyse von Zinnlegierungen - Bestimmung des Gehaltes an Legierungs- und Verunreinigungselementen durch Atomspektrometrie

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EUROPEAN COMMITTEE FOR STANDARDIZATION
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Contents

Foreword

This European Standard has been prepared by Technical Committee CEN/TC 220 "Tin and tin alloys", the secretariat of which is held by BSI.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by May 2000, and conflicting national standards shall be withdrawn at the latest by May 2000.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

Within its programme of work, Technical Committee CEN/TC 220 requested CEN/TC 220/WG1, "Methods of analysis for tin and tin alloys", to prepare the following standard:

EN 12938 *Methods for the analysis of pewter — Determination of alloying and impurity element contents by atomic spectrometry.*

The annexes A and B are normative.

1 Scope

This European Standard specifies atomic spectroscopic methods (either AAS or AES) for the analysis of pewter alloy defined in EN 611-1.

NOTE This method is also suitable for inductively-coupled plasma emission spectrometry (ICP). It is written for use by experienced analysts familiar with atomic spectrometric techniques.

2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

EN 611-1 *Tin and tin alloys — Pewter and pewterware — Part 1: Pewter*

3 Principle

The test sample is dissolved in hydrochloric acid plus nitric acid and tartaric or citric acid, and the concentration of the element sought is measured using atomic absorption spectrometry (AAS) or atomic emission spectrometry (AES). Interference is minimised by matching sample and standard materials and by the choice of instrument parameters.

For alloying amounts of silver dissolution of the sample in dilute nitric acid, followed by measurement as above.

4 Reagents

4.1 *General*

During the analysis, unless otherwise stated, use only reagents of recognised analytical grade and only distilled water or water of equivalent purity.

4.2 *Hydrochloric acid, concentrated ($\rho \approx 1{,}18$ g/ml).*

4.3 *Dilute hydrochloric acid (1 + 1). Dilute 100 ml hydrochloric acid (4.2) with 100 ml water.*

NOTE For safety reasons, the acid should be added to the water.

4.4 *Dilute hydrochloric acid (1 + 19).* Dilute 10 ml hydrochloric acid (4.2) with 190 ml water.

NOTE For safety reasons, the acid should be added to the water.

4.5 *Nitric acid*, ($\rho \approx 1{,}42$ g/ml).

4.6 *Sulphuric acid*, ($\rho \approx 1{,}84$ g/ml).

4.7 *Tartaric acid or citric acid.*

4.8 *Acid mixture.* Add 250 ml hydrochloric acid (4.2) to 250 ml water. Cool. Add 250 ml nitric acid (4.5) and 50 g tartaric (or citric) acid (4.7). Dilute to 1 l with water.

4.9 *Dilute nitric acid (1 + 1).* Add 100 ml nitric acid (4.5) to 100 ml water.

4.10 *Dilute nitric acid (1 + 4).* Add 50 ml nitric acid (4.5) to 200 ml water.

4.11 *Dilute nitric acid (1 + 9).* Add 25 ml nitric acid (4.5) to 225 ml water.

4.12 *Dilute nitric acid (1%).* Dilute 5 ml nitric acid (4.5) up to 500 ml.

4.13 *Standard solutions of metals.* Freshly purchased standard metal solutions may be used or standard metal solutions should be made up as follows (4.13.1 to 4.13.7).

4.13.1 Standard antimony solution (1 ml contains 1 mg Sb). *Place 0,10 g Sb in 5 ml sulphuric acid (4.6) and heat to complete dissolution. Cool. Carefully add approximately 10 ml water and cool again. Transfer to a 100 ml volumetric flask with dilute hydrochloric acid (1 + 1) (4.3).*

4.13.2 Standard copper solution (1 ml contains 1 mg Cu). *Dissolve 0,10 g Cu in 10 ml dilute nitric acid (1 + 4) (4.10) and transfer to a 100 ml volumetric flask. Make up to volume with water. Mix well.*

4.13.3 Standard copper solution (1 ml contains 10 mg Cu). *Dissolve 30 g Cu in 10 ml nitric acid (1 + 4) (4.10) and transfer to a 100 ml volumetric flask. Make up to volume with water. Mix well.*

4.13.4 Standard lead solution (1 ml contains 1 mg Pb). *Dissolve 0,10 g Pb in 10 ml dilute nitric acid (1 + 4) (4.10) and transfer to a 100 ml volumetric flask. Make up to volume with water. Mix well.*

4.13.5 Standard bismuth solution (1 ml contains 1 mg Bi). *Dissolve 0,10 g Bi in 10 ml dilute nitric acid (1 + 1) (4.9) and transfer to a 100 ml volumetric flask. Make up to volume with water. Mix well.*

4.13.6 Standard cadmium solution (1 ml contains 1 mg Cd). *Dissolve 0,10 g Cd in 10 ml dilute nitric acid (1 + 4) (4.10) and transfer to 100 ml volumetric flask. Make up to volume with water. Mix well.*

4.13.7 Standard silver solution (1 ml contains 1 mg Ag). *Dissolve 0,787 g silver nitrate in 50 ml water. Transfer to a 500 ml volumetric flask and make up to the volume with nitric acid (1 %) (4.12). Mix well.*

4.13.8 Standard silver solution (1 ml contains 0,1 mg Ag)

Transfer 10 ml silver solution (**4.13.7**) to a 100 ml volumetric flask. Make up to volume with water. Mix well.

4.14 *Tin, min. purity 99,99 % (mass fraction).*

5 Apparatus

5.1 *Ordinary laboratory apparatus.* Use grade A glassware.

5.2 *Burette, of capacity 5 ml,* graduated in 0,02 ml.

5.3 *Atomic absorption or atomic emission spectrometer*, conforming to the performance requirements in normative annexes A and B.

NOTE Plasma inductively-coupled emission spectrometer is also suitable.

5.4 *Hollow cathode lamps or electrodeless discharge lamps for antimony, bismuth, cadmium, copper, lead and silver.*

NOTE The presence of other elements may also need to be ascertained.

5.5 *Analytical balance,* with an accuracy of 0,1 mg.

6 Sampling

The sample for analysis shall be obtained as described in EN 611-1.

7 Procedure

7.1 *Preparation of the solution of the sample under test for the determination of antimony, copper, lead, bismuth, cadmium and silver up to 0,01 %.*

7.1.1 *Weigh accurately about 0,5 g of the sample and transfer to a 150 ml beaker. Add 20 ml of the acid mixture (**4.8**), heat to complete dissolution and cool. Transfer to a 100 ml volumetric flask and make up to the mark with dilute hydrochloric acid (1 + 19) (**4.4**). Mix well.*

7.1.2 *For the determination of antimony in all alloys and for copper in alloys nos. 1, 2, 3 and 6 (see EN 611-1), introduce 10 ml of the solution (**7.1.1**) into a 100 ml volumetric flask and make up to the mark with dilute hydrochloric acid (1 + 19) (4.4). Mix well.*

7.1.3 *Prepare a blank solution following the procedure described in **7.1.1**, but using 0,5 g of high purity tin (**4.14**) instead of the sample.*

7.2 *Preparation of the sample for the determination of silver from 0,01 % to 5 % (mass fraction).*

Weigh accurately 0,5 g ± 0,1 g of the sample into a 250 ml beaker. Add 20 ml dilute nitric acid (1 + 1) (**4.9**), warm to dissolve, add antibumping granules or similar and boil vigorously to expel brown fumes. Cool and transfer the solution and the precipitate to a 250 ml volumetric flask with dilute nitric acid (1 + 9) (**4.11**). Mix well and allow to stand until the precipitate has settled.

For the determination of silver by ICP and for up to 0,2 % by AAS use this solution. For high silver content determinations by AAS, transfer 10 ml of this solution to a 100 ml graduated flask and dilute to the mark with dilute nitric acid (1 + 9) (**4.11**).

NOTE 1 Tin and antimony will be precipitated out of the solution containing nitric acid and will not therefore be in the solution being analysed for silver content.

NOTE 2 All glassware and reagents should be chlorine free. Before use, it is recommended that all glassware is thoroughly rinsed with distilled water.

To prepare a range of standard solutions, transfer 15 ml, 20 ml, 30 ml, 40 ml, 50 ml and 60 ml silver solution (**4.13.7**) into 250 ml volumetric flasks.

Add sufficient standard copper solution (1 ml contains 10 mg Cu) (**4.13.3**) to matrix match the copper content of the alloys being analysed.

Finally dilute to the mark with dilute nitric acid (1 + 1) (**4.9**). Mix well.

7.3 *Preparation of calibration solutions*

For the determination of antimony, copper, lead, bismuth and cadmium, weigh 0,5 g ± 0,1 g tin (**4.14**) into a 400 ml beaker. Add 50 ml of the acid mixture (**4.8**) and heat to complete dissolution. Cool and transfer to a 100 ml volumetric flask and make up to the mark with dilute hydrochloric acid (1 + 19) (**4.4**). Mix well.

To each of seven 100 ml volumetric flasks, first add 10 ml of this solution and then add the amounts of the standard metal solutions shown in Table **1**.

Table 1 — Volume of standard metal solutions used in the preparation of the calibration solutions

Flask No.	Standard metal solution ml					
	Sb	Cu (4.13.2)	Pb	Bi	Cd	Ag
1	—	—	—	—	—	—
2	20	0,20	0,20	0,20	0,05	0,2
3	25	0,50	0,50	0,50	0,10	0,5
4	30	1,0	0,75	1,0	0,20	1,0
5	35	5,0	1,0	1,5	0,25	2,0
6	40	10,0	1,5	2,0	0,30	4,0
7	45	15,0	2,0	2,5	0,40	8,0
8	—	—	—	—	—	10,0

Finally, dilute all the solutions to the mark with dilute hydrochloric acid (**4.4**).

For the determination of antimony in all samples and for copper in alloy numbers 1, 2, 3 and 6 transfer 10,0 ml of the solutions to a 100 ml flask and dilute to the mark with dilute hydrochloric acid (**4.4**).

7.4 *Certified reference materials (CRM)*

Where CRM of similar matrix to the sample under test is available, treat an appropriate sample of the CRM in exactly the same way as the sample under test (**7.1**).

7.5 *Spectrometric measurements*

Set up the spectrometer (AAS or AES) using the wavelengths given in **A.3.5 or B.3.3**, as appropriate. A minimum of two runs of the sample under analysis shall be made; first the calibration solutions, then the samples under analysis, and the cycle repeated without altering the instrument parameters. For the purposes of calculating the element content in the sample, the average of readings from a minimum of two separate runs shall be used.

NOTE This also applies to ICP spectrometers.

8 Expression of results

8.1 *Determining the metal content*

By means of the calibration curves, determine the quantities of each metal corresponding to the spectrometer measurements of the test and the blank test solutions.

NOTE Calibration curves are usually prepared automatically by the instruments.

The content of each element is given, as a mass fraction in % by the formula:

$$\frac{(M_2 - M_1)}{M_0} \times 100$$

where:

M_0 is the mass of the test portion in milligrams;

M_1 is the mass of the element in the blank test solution in milligrams.

M_2 is the mass of the element in the test solution in milligrams, as indicated from the calibration curve and calculated for any dilution that may have been required.