

**Aluminium och aluminiumlegeringar – Kemiska
analysmetoder – Induktivt kopplad plasma-
emissionsspektrometri**

**Aluminium and aluminium alloys – Chemical
analysis – Inductively coupled plasma optical
emission spectral analysis**

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Aluminium and aluminium alloys - Chemical analysis - Inductively coupled plasma optical emission spectral analysis

Aluminium et alliages d'aluminium - Analyse chimique -
Analyse par spectrométrie d'émission optique en plasma
induit

Aluminium und Aluminiumlegierungen - Chemische
Analyse - Optische Emissionspektalanalyse mit induktiv
gekoppelter Plasmaanregung

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Foreword

This document (EN 14242:2004) has been prepared by Technical Committee CEN/TC 132 "Aluminium and aluminium alloys", the secretariat of which is held by AFNOR.

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of an identical text or by endorsement, at the latest by March 2005, and conflicting national standards shall be withdrawn at the latest by March 2005.

Within its programme of work, Technical Committee CEN/TC 132 requested CEN/TC 132/WG 17 "Chemical analysis" to prepare the following standard:

EN 14242, *Aluminium and aluminium alloys — Chemical analysis — Inductively coupled plasma optical emission spectral analysis*.

This document includes a Bibliography.

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

EN 14242:2004 (E)

Introduction

This document describes detailed steps for dissolution and preparation of calibration solutions. The preferred use is for certification and referee analysis. All instrumentation, including software used in the testing laboratories, are different and subject to change. Therefore, general criteria for calibration and measurement are specified.

This method has to be used with primary reference materials whose mass of substance have a significant smaller uncertainty as required of the repeatability of the testing procedure.

1 Scope

This document specifies the inductively coupled plasma optical emission spectral analysis (ICP-OES) of aluminium and aluminium alloys. This method is applicable to the determination of silicon, iron, copper, manganese, magnesium, chromium, nickel, zinc, titanium, gallium, vanadium, beryllium, bismuth, calcium, cadmium, cobalt, lithium, sodium, lead, antimony, tin, strontium, and zirconium in aluminium and aluminium alloys.

NOTE The national safety instructions should be taken into consideration.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

prEN 12258-2:2001, *Aluminium and aluminium alloys — Terms and definitions — Part 2: Chemical analysis*.

prEN 14361, *Aluminium and aluminium alloys — Chemical analysis — Sampling from metal melts*.

EN ISO 3696, *Water for analytical laboratory use — Specification and test methods (ISO 3696:1987)*.

EN ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories (ISO/IEC 17025:1999)*.

ISO 3534-1, *Statistics — Vocabulary and symbols — Part 1: Probability and general statistical terms*.

3 Terms and definitions

For the purposes of this document, the terms and definitions given in prEN 12258-2:2001 apply.

4 Principle

A test portion is dissolved with:

- sodium hydroxide solution and acidification with a mixture of nitric acid and hydrochloric acid; or
- nitric acid and hydrofluoric acid; or
- a mixture of hydrochloric acid and nitric acid; or
- hydrochloric acid and hydrogen peroxide

according to the alloy type and the element contents to be determined. This solution is nebulized and excited in an inductively coupled plasma connected with an optical emission spectrometer. The emission signals on selected analytical lines (see Annex A) are compared with those of calibration solutions.

The ranges of application and the accuracy of the method or any alternative steps shall be validated by the laboratory. Approximate ranges of application are given in Annex A.

EN 14242:2004 (E)**5 Reagents****5.1 General**

All volumetric measurements shall be made at the temperature specified on the pipettes and volumetric flasks.

Each mixture shall be thoroughly mixed.

For the analysis, reagents of recognized analytical grade and deionized water, shall be used in accordance with EN ISO 3696.

5.2 Sodium hydroxide solution (10 M)

Dissolve 400,0 g sodium hydroxide NaOH in a plastic beaker with a lid. Transfer the solution to a 1 000 ml volumetric plastic flask and make up to volume with water.

5.3 Hydrogen peroxide, 30 % (mass fraction) solution

5.4 Nitric acid ($\rho = 1,4$ g/ml, 65 % mass fraction)

5.5 Nitric acid (1 + 1)

Carefully add 500 ml nitric acid (5.4) to 400 ml water, allow to cool, and make up the volume to 1 000 ml with water.

5.6 Nitric acid (4 M)

Carefully add 27,7 ml nitric acid (5.4) to 50 ml water, allow to cool, and make up the volume to 100 ml with water.

5.7 Hydrochloric acid ($\rho = 1,18$ g/ml, 37 % mass fraction)

5.8 Hydrochloric acid (1 + 1)

Carefully add 500 ml hydrochloric acid (5.7) to 400 ml water, allow to cool, and make up the volume to 1 000 ml with water.

5.9 Sodium nitrite**5.10 High-purity aluminium**

Aluminium, purity equal or better than 99,999 % mass fraction; the content of the elements to be determined shall not be higher than 10 % of the detection limits of this method or of the element content to be determined.

5.11 Hydrofluoric acid, ($\rho = 1,14$ g/ml, 40 % mass fraction)

5.12 Stock solutions

The concentrations of the stock solutions shall be traceable to international standard units mass and amount of substances i.e. kilogram (kg) and mol (mol) according to EN ISO/IEC 17025. Examples of preparation of stock solutions are described in B.3.

Stock solutions containing sulphate ions shall not be used if the determination of an element is required which forms insoluble compounds with sulphate. Stock solutions shall not to be used when the time of stability is expired.

5.13 Standard solutions

Prepare standard solutions from the stock solutions by dilution steps not more than 1 : 5 using calibrated pipettes not smaller than 10 ml and calibrated volumetric flasks not smaller than 100 ml. Standard solutions and calibration solutions with element contents equal or less than 50 mg/l can be unstable and shall be prepared just before use.

NOTE Calibration solutions can be made directly from stock solutions by means of weight measurement (see 8.4).

5.14 Reference element solutions

5.14.1 Reference element solution lanthanum, 1 g/l

Transfer 1,173 g lanthanum oxide La_2O_3 , purity equal or better than 99,99 % mass fraction, previously dried at 150 °C to constant mass, to a 400 ml beaker with a lid. Add 40 ml hydrochloric acid solution (5.8), transfer the solution into a 1 000 ml volumetric flask and make up to volume with water.

5.14.2 Reference element solution, lanthanum, 200 mg/l

Transfer 20,00 ml of reference element solution, lanthanum (5.14.1) into a 100 ml volumetric flask, add 1 ml hydrochloric acid solution (5.8) and make up to volume with water.

5.14.3 Reference element solution, scandium, 0,1 g/l

Transfer 100,0 mg scandium purity equal or better than 99,99 % mass fraction into a 400 ml beaker with a lid. Add 20 ml hydrochloric acid solution (5.8). Heat gently, if necessary, until the dissolution is complete, allow to cool, and transfer the solution into a 1 000 ml volumetric flask and make up to volume with water.

NOTE Scandium solutions can be unstable.

5.14.4 Reference element solution, scandium, 20 mg/l

Transfer 20,00 ml of reference element solution scandium (5.14.3) into a 100 ml volumetric flask, add 1 ml hydrochloric acid solution (5.8) and make up to volume with water.

5.14.5 Reference element solution, molybdenum, 1 g/l

Transfer 1,84 g ammonium molybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \times 4 \text{H}_2\text{O}$ into a 1 000 ml volumetric flask and make up to volume with water.

5.14.6 Reference element solution, molybdenum, 200 mg/l

Transfer 20,00 ml of reference element solution molybdenum (5.14.5) into a 100 ml volumetric flask, add 1 ml hydrochloric acid solution (5.8) and make up to volume with water.

6 Equipment

6.1 Optical emission spectrometer with inductively coupled argon plasma excitation and polychromator or monochromator (for analytical lines, see Annex A), for solutions containing hydrofluoric acid. The spectrometer shall be equipped with a fluoride-resistant nebulizer.

NOTE The nebulizer should be selected carefully. Many of the available fluoride-resistant nebulizers are not as stable as standard nebulizers.

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6.2 PTFE-beakers with lid, 400 ml

6.3 Platinum crucibles with a lid, 100 ml to 120 ml

6.4 Plastic measuring pipettes, 2,0 ml, 6,0 ml and 10,0 ml

NOTE The plastic equipment should be selected carefully to avoid losses and contaminations.

6.5 Plastic bottle with small neck and cap, approximately 100 ml

NOTE The plastic equipment should be selected carefully to avoid losses and contaminations.

6.6 Glass beakers with lid, 250 ml

6.7 Volumetric flasks, 100 ml and 500 ml

7 Sampling and samples

7.1 General

Sampling from aluminium melts shall be carried out in accordance with prEN 14361.

The analytical result shall indicate the average chemical composition of a test sample, a laboratory sample or an inspection lot. For an inspection lot or a laboratory sample the minimum quantity of laboratory samples or test samples, respectively shall be investigated by preliminary tests, for the determination of the average chemical composition of the inspection lot with the required accuracy.

NOTE The aim is to determine the uncertainty contribution from the inconsistency of the chemical composition of the sample and to determine the number of samples necessary to meet the required accuracy for the result with test portions of 0,5 g.

7.2 Laboratory sample

A sufficient number of samples shall be taken to indicate the chemical composition of the inspection lot within the required uncertainty range.

Usually, the analytical result refers to the average content of one or more laboratory samples supplied. If required, uncertainties that result from differences between the test samples and the average composition of one or more laboratory samples or an inspection lot outside the laboratory shall also be taken into account.

7.3 Test sample

Make chips by milling or drilling of each laboratory sample. If the chemical composition of the laboratory sample is thought to be not uniform, e.g. in case of unwrought products, the preparation of the test sample shall follow a documented procedure to ensure the required representativity. If necessary, e.g. for the determination of low contents of alkaline or alkaline earth elements, clean with a suitable procedure (solution, temperature and time). The cleaning procedure shall be adapted to the alloy, analytes and the content to be determined. Make sure that the test sample is sufficient homogeneous for the quantity of the test portion. If not, take as many test portions as necessary to obtain an average test result within the required uncertainty range.

8 Procedure

8.1 Test portion

8.1.1 General

Weigh, to the nearest 0,001 g, about 0,5 g of the test sample.

8.1.2 Dissolution procedure I with sodium hydroxide solution

8.1.2.1 General

This procedure is applicable for the determination of silicon, iron, copper, manganese, magnesium, chromium, nickel, zinc, titanium, vanadium, beryllium, bismuth, cadmium, cobalt, lead, antimony, tin, strontium and zirconium in aluminium and aluminium alloys.

NOTE Iron constituents can cause problems with dissolution. Under that dissolution condition, bismuth losses can occur.

8.1.2.2 Transfer the test portion (8.1) into a 400 ml PTFE-beaker with a lid (6.2) or a platinum crucible with lid (6.3).

8.1.2.3 Cover the test portion with water. Add 6,0 ml sodium hydroxide solution (5.2) using the plastic pipette (6.4). After the dissolution reaction ceases, add 1 ml hydrogen peroxide (5.3). Heat gently until the dissolution is complete.

8.1.2.4 If the silicon content of the test sample is more than 0,5 % mass fraction carefully evaporate to a syrupy consistency. Allow to cool a little, carefully add 30 ml water and heat gently until the dissolution is complete. If the platinum crucible (6.3) has been used, transfer the solution quantitatively into a 400 ml PTFE-beaker, containing 25,0 ml nitric acid (5.5) and 10,0 ml hydrochloric acid (5.8).

8.1.2.5 Make up to volume of about 100 ml with water and add 25,0 ml nitric acid solution (5.5) and 25,0 ml hydrochloric acid (5.8) while stirring. Heat the content of the beaker immediately while frequently and carefully shaking to complete the dissolution. In case of precipitation of manganese (IV)-oxyhydrate (at higher contents of manganese), dissolve with a spatula tip of sodium nitrite (5.9). Allow to cool and transfer the clear solution into a 500 ml volumetric flask.

8.1.2.6 If the platinum crucible (6.3) has been used, add into the empty crucible some drops of nitric acid (5.6) and a spatula tip of sodium nitrite (5.9), cover the crucible and heat. Rinse lid and walls with water. Let the solution cool. Transfer this solution quantitatively into the 500 ml flask (8.1.2.5).

8.1.2.7 If necessary for the precision required (see clause 9), add about 10 g to the nearest 0,01 g or 10,00 ml of one of the reference element solution (5.14.1, 5.14.3 or 5.14.5).

8.1.2.8 Make up to volume with water and mix. Continue with 8.2.

8.1.3 Dissolution procedure II with nitric acid and hydrofluoric acid

8.1.3.1 General

This procedure is applicable for the determination of iron, copper, manganese, magnesium, chromium, nickel, zinc, titanium, gallium, vanadium, beryllium, bismuth, calcium, cadmium, cobalt, lithium, sodium, lead, antimony, tin, strontium and zirconium in aluminium and aluminium alloys.

8.1.3.2 Transfer the test portion (8.1) into a previously weighed 100 ml plastic bottle.

8.1.3.3 Add 10,0 ml nitric acid (5.5) and 2,0 ml hydrofluoric acid (5.11) using the plastic pipette (6.4).

8.1.3.4 Cover the bottle with the cap. Do not screw the cap.