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Hardmetals — Determination of lead and cadmium content

Métaux-durs — Dosage du plomb et du cadmium

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Foreword

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 26482 was prepared by Technical Committee ISO/TC 119, *Powder metallurgy*, Subcommittee SC 4, *Sampling and testing methods for hardmetals*.

Hardmetals — Determination of lead and cadmium content

1 Scope

This International Standard specifies a flame atomic absorption spectrometric and inductively coupled plasma spectrometric method for the determination of the lead and cadmium contents in hardmetals.

The method is applicable to products having lead and cadmium contents between 0,000 1 % (mass fraction) and 0,1 % (mass fraction).

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.

ISO 385, *Laboratory glassware — Burettes*

ISO 648, *Laboratory glassware — Single-volume pipettes*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

3 Principle

The sample is placed in a platinum dish or polytetrafluoroethylene (PTFE) breaker. After dissociation by hydrofluoric acid, dissolve precipitated tungstic acid with sodium hydroxide solution. Mask residual cobalt with potassium cyanide and selectively separate lead and cadmium with dithizone. Then perform dilution. Perform quantitative analysis by inductively coupled plasma atomic emission spectrometry (ICP-AES) and atomic absorption spectrometry (AAS).

4 Reagents

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

4.1 Perchloric acid, $\rho = 1,67$ g/ml.

4.2 Nitric acid (HNO_3), $\rho = 1,40$ g/ml, 69 % to 71 % diluted 1 + 1 with water.

4.3 Hydrofluoric acid, 40 % (mass fraction), $\rho = 1,14$ g/ml or 50 % (mass fraction), $\rho = 1,17$ g/ml.

4.4 Ammonium citrate, 250 g/l solution.

4.5 Sodium hydroxide, 250 g/l solution.

4.6 Potassium cyanide, 100 g/l.

4.7 Ammonia solution.

4.8 Dithizone, in chloroform, 0,02 %.

Dissolve 0,2 g of dithizone in 1 000 ml of chloroform. Prepare fresh, or store in a brown bottle.

4.9 Dithizone, in chloroform, 0,005 %.

Dissolve 0,05 g of dithizone in 1 000 ml of chloroform. Prepare fresh, or store in a brown bottle.

4.10 Standard lead stock solution, $\rho_{\text{Pb(II)}} = 1$ mg/ml.

Weigh to the nearest 0,000 1 g, 0,5 g of high-purity lead [min. 99,95 % (mass fraction)] and dissolve in 30 ml of nitric acid (1 + 1) (4.2). Cool and transfer the solution quantitatively to a calibrated 500 ml one-mark volumetric flask. Keep the flask at the same temperature as the flask was calibrated at. Dilute to the mark with water and mix. The purchase and use of certified stock solutions is possible.

4.11 Standard cadmium stock solution, $\rho_{\text{Cd(II)}} = 1$ mg/ml.

Weigh to the nearest 0,000 1 g, 0,5 g of high-purity cadmium [min. 99,95 % (mass fraction)] and dissolve in 30 ml of nitric acid (1 + 1) (4.2). Cool and transfer the solution quantitatively to a calibrated 500 ml one-mark volumetric flask. Keep the flask at the same temperature as the flask was calibrated at. Dilute to the mark with water and mix.

4.12 Mixed analyte standard solution, $\rho_{\text{Pb(II)}}$ 100 µg/ml; $\rho_{\text{Cd(II)}}$ 100 µg/ml.

To a 250 ml one-mark volumetric flask containing 30 ml of concentrated nitric acid, add 25 ml each of 1 000 mg/l stock standard solutions (4.10 and 4.11) of Pb and Cd, using a burette accurately. Make up to the mark with water and mix.

5 Apparatus

Usual laboratory apparatus and in particular the following.

5.1 Inductively coupled plasma atomic emission spectrometry (ICP-AES).

The ICP-AES used will be satisfactory after optimizing according to the manufacturer's instructions.

5.2 Flame atomic absorption spectrometer (FAAS).

The FAAS used will be satisfactory after optimizing according to the manufacturer's instructions.

5.3 Burette, of capacity 50 ml, according to ISO 385, class A.

5.4 Pipette, of capacities 1 ml, 3 ml, 5 ml, 25 ml, according to ISO 648, class A.

5.5 One-mark volumetric flasks, of capacities 100 ml, 250 ml, 500 ml, according to ISO 1042, class A.

5.6 Beaker, of capacities 250 ml, 1 000 ml, made of silica or borosilicate glass.

5.7 Platinum dish, of capacities 50 ml, 100 ml.

5.8 PTFE beaker, of capacities 50 ml, 100 ml.

6 Procedure

6.1 Test portion

Weigh, to the nearest 0,000 1 g, 1 g of the test sample and transfer it to a platinum dish. Rinse the sample into the bottom of the dish by wetting the rim of the dish using a wash bottle containing distilled water.

6.2 Attack and extraction

Add 15 ml of nitric acid (4.2) and 5 ml of hydrofluoric acid solution (4.3) and shake until exhaustion of NO_x gas (red-brown color). Heat to complete dissociation. Control the heating temperature to prevent boiling of the solution. After dissociation of the sample, add 10 ml of perchloric acid (4.1) and keep heating until generation of a white gas of perchloric acid and until the final volume of sample is 5 ml to 10 ml.

Cool the platinum dish with the sample to room temperature, add 20 ml of nitric acid (1 + 1), cover with watch glass and heat. Add 20 ml of ammonium citrate solution (25 %) (4.4) and heat again. In the warm platinum dish, stirring with a PTFE rod, put (little by little) 40 ml of sodium hydroxide (25 %)[1)] to the time of colour change (yellow to pink)[2)].

Transfer the sample solution to a 250 ml glass beaker and cool it to room temperature.

Add 3 ml of potassium cyanide (10 %) (4.6) and adjust the pH of the solution to 9,2 ± 0,2 with ammonium hydroxide (1 + 1) (4.7) or nitric acid (1 + 1) solution. Transfer the adjusted solution into a separation funnel by washing the beaker wall with distilled water. In case the pH of the solution that dissolves the sample is over 8, add 10 % potassium cyanide.

Put 20 ml of dithizone (0,02 %) (4.8) in the separation funnel and stir fully for 5 min.

Stand until separation of the dithizone layer and water layer occurs. Transfer the lower layer of dithizone to a new beaker. Add 20 ml of dithizone (0,02 %) again and stir it fully for 5 min.

Add 10 ml of dithizone (0,005 %) to the water layer of the separation funnel and wash by stirring fully for 5 min. Leave to stand to allow separation of the layers. Add the dithizone layer to the preceding dithizone layer.

Heat the solution at 60 °C to 80 °C in a warm bath until complete evaporation of chloroform occurs.

Add 10 ml of nitric acid and 5 ml of perchloric acid to the dried glass beaker and insert a glass rod into the beaker. Cover with a watch glass and heat until generation of a white gas of perchloric acid. After the generation of a white gas of perchloric acid, dry and thicken it. After cooling it at normal temperature, transfer it to a 100 ml volumetric flask, dilute it with water and mix it.

6.3 Blank test

Carry out blank tests in parallel with the determination, following the same procedure and using the same quantities of all the reagents, but omitting the test portion.

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1) Add to dissolve precipitated yellow tungstate to a pink colour.

2) In removing the watch glass from the platinum dish to add the reagent, the inner side should be washed with distilled water.

7 Analytical parameters

7.1 Atomic absorption spectrometer (AAS) wavelength

7.1.1 The spectral lines specified in Table 1 should be used in the analysis.

Table 1 — Spectral lines

Wavelength Pb nm	**Wavelength Cd** nm
283,3	228,8

7.1.2 A fuel-lean air/acetylene flame shall be used.

7.2 Inductively coupled plasma (ICP) wavelength

The spectral lines specified in Table 2 should be used in the analysis.

Table 2 — Spectral lines

Wavelength Pb nm	**Wavelength Cd** nm
220,3	228,8

8 Preparation of calibration curve

8.1 Using burettes or pipettes, transfer 0 ml, 1 ml, 3 ml and 5 ml of lead and cadmium standard solution (100 mg/l, see 4.12) to 100 ml volumetric flasks. Add 15 ml of nitric acid, dilute to the mark by adding distilled water and mix well.

8.2 Spray the solutions into an inductively coupled argon plasma or atomic absorption spectrometer serially and plot calibration curves by measuring the emission strength at the wavelengths noted in 7.1 and 7.2.

8.3 After plotting the calibration curve, measure each element in the test solution and blank solution.

9 Calculation

The Pb or Cd content, expressed in milligrams per kilogram (mg/kg), in the sample, is given by Equations (1) and (2):

$$w_{\mathrm{Pb}} = \frac{(\rho_1 - \rho_2)V}{m} \tag{1}$$

$$w_{\mathrm{Cd}} = \frac{(\rho_1 - \rho_2)V}{m} \tag{2}$$

where

w_{Pb} is the Pb content in the sample, in milligrams per kilograms (mg/kg);

w_{Cd} is the Cd content in the sample, in milligrams per kilograms (mg/kg);

ρ_1 is the mass concentration of the element in the test solution, in milligrams per litre (mg/l);

ρ_2 is the mass concentration of the reagent blank solution, in milligrams per litre (mg/l);

V is the dilution volume of the test solution, in millilitres (ml);

m is the mass of sample, in grams (g).

10 Test report

The test report shall include at least the following information:

a) all information necessary for the identification of the sample, the laboratory and the date of analysis;

b) the method used by reference to this International Standard;

c) the results and the form in which they are expressed;

d) the analytical line used;

e) any unusual features noted during the determination;

f) any operation not specified in this International Standard, or any optional operation which may have influenced the results.

Annex A
(informative)

Hardmetals — Determination of lead and cadmium content

A.1 Introduction

There is a significant matrix effect from the primary ingredient of a coexisting element in the analysis of trace elements in an ultra-hard metal sample by AAS or ICP, so direct measurement from a sample solution cannot provide good precision. A reproducibility test of the solvent extraction method that separates and concentrates Pb and Cd from the primary ingredient to examine the optimum analysis method and the reproducibility has been conducted.

A.2 Repeatability results of hardmetals — Test samples

Due to a lack of certified reference materials (CRM) of ultra-hard metal that ensure concentrations of Pb and Cd, a composition of test samples of tungsten (W) metal equal to that of the common sample given in Table A.1 has been made. Also Pb oxide and Cd oxide were added to high-purity tungsten carbon (WC) and cobalt (Co) powders for levels of Pb and Cd.

The results for the test samples are summarized in Table A.1. The result of reviewing the uniformity on these reference materials and testing repeatability is given in Table A.2.

Table A.1 — Chemical composition of test samples

Sample	WC % (mass fraction)	Co % (mass fraction)	Pb content mg/kg	Cd content mg/kg
HM 1	94	6	200	100
HM 2	94	6	400	200

Table A.2 — Repeatability results ($n = 6$)

ICP and AAS data		Pb content		Cd content	
		mg/kg		mg/kg	
		Sample HM 2	Sample HM 1	Sample HM 2	Sample HM 1
ICP	Average level	395,3	199	195,1	98,1
	Relative standard deviation (RSD) (%)	7,91	6,43	1,81	0,84
	Precision (%)	98	96,8	98,2	99,1
	Reproducibility (%)	98,8	99,5	97,6	98,1
AAS	Average level	381,6	196	212,5	108,3
	Relative standard deviation (RSD) (%)	5,39	5	1,7	1,62
	Precision (%)	98,6	97,5	99,2	98,5
	Reproducibility (%)	95,4	98	106,2	108,3

A.3 Round-robin test

The result of a round-robin test of the test samples are noted in Tables A.3, A.4, A.5 and A.6.

Table A.3 — Comparison of results obtained by different laboratories on lead of synthetic hardmetal reference materials with ICP

Sample No. and statistical data	Pb content obtained by laboratory (L)											
	L 1		L 2		L 3		L 4		L 5		L 6	
	400 mg/kg	200 mg/kg	400 mg/kg	200 mg/kg	400 mg/kg	200 mg/kg	400 mg/kg	200 mg/kg	400 mg/kg	200 mg/kg	400 mg/kg	200 mg/kg
Sample 1	362	185	371,6	195	391,4	198,8	364,9	177,7	378	195,7	371,6	195
Sample 2	360	191	367	197,2	396,4	195,5	364,4	181,4	381,3	198	370	197,2
Sample 3	358	189	365,4	195,9	392,2	195,6	369,1	180	379	192,3	374	197,9
Average level	360	188	368	196,1	393,3	196,7	366,1	179,5	379,4	195,3	371,9	196,7
Standard deviation	2	3,1	3,2	1,1	2,7	1,9	2,6	1,9	1,7	2,9	2	1,5
Precision (%)	99,44	98,4	99,1	99,4	99,3	99,1	99,3	99	99,6	98,5	99,5	99,2

Table A.4 — Comparison of results obtained by different laboratories on lead of synthetic hardmetal reference materials with AAS

Sample No. and statistical data	Pb content obtained by laboratory (L)											
	L 1		L 2		L 3		L 4		L 5		L 6	
	400 mg/kg	200 mg/kg	400 mg/kg	200 mg/kg	400 mg/kg	200 mg/kg	400 mg/kg	200 mg/kg	400 mg/kg	200 mg/kg	400 mg/kg	200 mg/kg
Sample 1	373	186	374,5	197,3	384,5	194,6	366	190	376	191,3	380	195,1
Sample 2	352	193	367	197,8	384,7	193,9	363	191	380	188,7	376,5	204,7
Sample 3	340	189	372,4	194,2	385,9	195,1	361	186	372	191,7	383,5	201,5
Average level	355	189	371,3	196,4	385	194,5	363,2	188,8	376	190,6	380	200,4
Standard deviation	16,7	3,5	3,9	2	0,7	0,6	2,6	2,6	4	1,6	3,5	4,9
Precision (%)	95,3	98,1	99	99	99,8	99,7	99,3	98,6	98,9	99,1	99,1	97,6

Table A.5 — Comparison of results obtained by different laboratories an cadmium of synthetic hardmetal with ICP

Sample No. and statistical data	Cd content obtained by laboratory (L)											
	L 1		L 2		L 3		L 4		L 5		L 6	
	200 mg/kg	100 mg/kg	200 mg/kg	100 mg/kg	200 mg/kg	100 mg/kg	200 mg/kg	100 mg/kg	200 mg/kg	100 mg/kg	200 mg/kg	100 mg/kg
Sample 1	198	106	199,6	100,1	199,1	98,2	183	92	200,7	98,6	182,9	97,3
Sample 2	209	103	199,8	100,8	198,4	99,4	183	94	202	100,5	187,6	94,5
Sample 3	210	111	197,5	99,9	194,3	97,9	185	95	202	98,3	189,8	96,8
Average level	206	107	199	100,3	197,2	98,5	184	94	201,6	99,1	186,8	96,2
Standard deviation	6,67	4,1	1,3	0,5	2,6	0,8	1,1	1,5	0,8	1,2	3,5	1,5
Precision (%)	96,77	96,2	99,4	99,5	98,7	99,2	99,4	98,4	99,6	98,8	98,1	98,5