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Fertilizers and soil conditioners — Determination of arsenic, cadmium, chromium, lead and mercury contents

Matières fertilisantes — Détermination de l'arsenic, du cadmium, du plomb, du chrome et du mercure dans les engrais

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT), see the following URL: Foreword — Supplementary information.

The committee responsible for this document is ISO/TC 134, *Fertilizers and soil conditioners.*

Fertilizers and soil conditioners — Determination of arsenic, cadmium, chromium, lead and mercury contents

1 Scope

This International Standard specifies the test methods for determination of metals soluble in nitric acid: arsenic, cadmium, chromium, lead, and mercury contents in fertilizers.

This International Standard is applicable to the analysis of arsenic, cadmium, chromium, lead, and mercury contents in fertilizers. Special attention should be given when analysing some micro-nutrients fertilizers.

2 Normative references

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

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

3 Principle

Arsenic, cadmium, chromium, lead, and mercury in the test portion are extracted by means of nitric acid digestion in a microwave digestion system. The digested solution will be measured by inductively coupled plasma – optical emission spectroscopy (ICP-OES). Indium will be used as internal standard substance when chromium or lead is determined.

NOTE An internal standard is recommended for metals to correct for solution matrix differences between the calibration standards and the fertilizer digests, any other internal standard materials with equal effect could be utilized, provided none of these are contained in the fertilizer samples.

4 Reagents

WARNING — Nitric acid is corrosive and oxidizer. The related operations shall be performed in fume hood. This standard does not point out all possible safety problems, and the user shall bear the responsibility to take proper safety and health measures, and ensure the operations compliant with the conditions stipulated by the related laws and regulations of the state.

Use only reagents of recognized analytical grade, and water conforming to grade 3 of ISO 3696:1987.

4.1 Nitric acid, *d* = 1,40 g/ml, recommend to use trace element grade nitric acid.

4.2 Nitric acid solution, add 1 volume of nitric acid to 9 volume of water.

4.3 Standard stock solution of arsenic, cadmium, chromium, lead, mercury, 1 000 mg/l certificated substance.

4.4 Indium standard stock solution, 1 000 mg/l.

Weigh $In(NO_3)_3 \times H_2O$ [containing 0,262 0 g $In(NO_3)_3$] to a 100 ml beaker, dissolved by nitric acid solution (4.2), then transfer to a 100 ml volumetric flask, fill to the mark with nitric acid solution (4.2), and mix.

4.5 Indium standard solution, 5 mg/l.

Dilute 1 000 mg/l Indium standard stock solution with nitric acid solution (4.2) to 5 mg/l.

4.6 High-purity argon, content ≥ 99,999 %.

5 Apparatus and materials

Ordinary laboratory apparatus and the following:

5.1 Microwave digestion system.

5.2 Inductively coupled plasma — optical emission spectroscopy (ICP-OES), with a mixing device to add an internal standard.

5.3 Sieve, with the aperture size of 0,50 mm.

6 Procedure

6.1 Sample preparation

Take a representative fertilizer subsample of 100 g. Grind it until it passes through a sieve of aperture size 0,5 mm, mix thoroughly for reasons of homogeneity, place in a clean, and dry bottle with lid.

6.2 Preparation of the test solution

The replicate experiments shall be done for the determination.

Weigh 1 g sample (accurate to 0,1 mg, for fertilizer containing liming material or organic matrixes, reduce the weight properly) and transfer into a digestion vessel, keep the sample from adhering to sides of vessel. Place the digestion vessel into a fume hood, and add 10 ml of nitric acid (4.1). Predigest at room temperature until vigorous foaming subsides. Then seal the vessel and put into the microwave digestion system.

The ramped temperature program should be set under the instruction of the instrument manual. Ramping temperature from ambient to 160 °C slowly in 10 min, and then hold at 160 °C for another 10 min. Cool vessels to room temperature, vent, and transfer digests to a 100 ml volumetric flask, fill to the mark with water, and mix. Then the solution should be filtered through a dry, folded filter paper. Discard the first few millilitres portions of filter solution.

6.3 Preparation of the blank test solution

The experiment steps are the same as the preparation of the test solution, with the exception of adding the sample.

6.4 Preparation of the working standard solution

Pipet appropriate amount of element standard stock solution (4.3), dilute with nitric acid solution (4.2) into volumetric flasks according to Table 1, prepare blended multi-element standard solution series.

Table 1 — Typical concentrations of blended multi-element standard solutions (mg/l)

Element standard	As	Cd	Cr	Pb	Hg
No. 0	0	0	0	0	0

Table 1 *(continued)*

Element standard	As	Cd	Cr	Pb	Hg
No. 1	0,02	0,02	0,02	0,02	0,02
No. 2	0,1	0,1	0,1	0,1	0,1
No. 3	0,5	0,5	0,5	0,5	0,5
No. 4	2,0	2,0	2,0	2,0	2,0
No. 5	5,0	5,0	5,0	5,0	5,0

NOTE Useful concentrations for standardization can be quite different for different instrument types.

6.5 Determination of arsenic, cadmium, chromium, lead and mercury contents by inductively coupled plasma–optical emission spectroscopy (ICP-OES)

Before the determination, refer to the instrument operation manual. Select the best operation conditions in accordance with the elements properties. The recommended operating conditions of ICP are listed in Table 2. Other conditions which can achieve the same results can also be used.

Table 2 — Recommended operating conditions of ICP

Wavelength	As 189,042 nm, Cd 228,802 nm, Pb 220,353 nm, Cr 283,563 nm, Hg 184,950 nm, In 230,606 nm.
Maximum integration time	Low wavelength scale: 10 s, High wavelength scale: 10 s
Flush velocity of sample pump	50 r/min
Analysis velocity of sample pump	50 r/min
Sample pump stable time	5 s
Light source	Radiofrequency, power of 1 150 W
Flow rate of auxiliary gas	0,5 l/min
Flow rate of gas within the nebulizer	0,5 l/min

NOTE Special attention should be given on the wavelength resolution of ICP instrument, the use of a second or third wavelength for confirmation purposes may be recommended, if appropriate.

Determine the working standard solutions (6.4), the blank test solution (6.3), and the test solutions (6.2) in order. When the concentration of Cr or Pb are determined, use the 5mg/l indium standard solution (4.5) as the internal standard substance, mix the internal standard substance solution and test solution (1:5 *V*/*V*) by a mixing device. If the concentration of the element in the test solution exceeds the concentration range of the standard curve, dilute the test solution to a certain ratio with nitric acid solution (4.2) for re-determination.

6.6 Calculation and expression of the results

The determination results of elements (mg/kg) are calculated as follows:

$$X = \frac{(c - c_0) \times 100 \times D}{m} \quad (1)$$

where

C is the concentration in mg/l, of the determined element in the test solution;

c_0 is the concentration in mg/l, of the determined element in the blank test solution;

100 is the total volume in ml, of the test solution;

D is the dilution ratio of the test solution when required, otherwise D is removed or assigned a value of 1;

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

The determination result is the arithmetic average of the parallel determination results.

7 Precision

7.1 Ring test

Details of Ring test on the precision of the method are summarized in Annex A.

7.2 Repeatability

Element	As	Cd	Cr	Pb	Hg
Repeatability limit, r, mg/kg	$0{,}227x^{0{,}621}$	$0{,}173x^{0{,}586\,2}$	$0{,}145x^{0{,}755\,2}$	$0{,}100x^{0{,}849\,9}$	$0{,}252x^{0{,}582\,4}$

7.3 Reproducibility

Element	As	Cd	Cr	Pb	Hg
Reproducibility limit, R, mg/kg	$0{,}316x^{0{,}809}$	$0{,}048x^{1{,}116\,7}$	$1{,}017x^{0{,}521\,9}$	$0{,}499x^{0{,}643\,2}$	$0{,}374x^{0{,}771\,5}$

8 Test report

The test report shall contain at least the following information:

a) all information necessary for the complete identification of the sample;

b) test method used with reference to this International Standard (i.e. ISO 17318);

c) test results obtained;

d) date of sampling and sampling procedure (if known);

e) date when the analysis was finished;

f) whether the requirement of the repeatability limit has been fulfilled.

All operating details not specified in this standard, or regarded as optional, together with details of any incidents occurred when performing the method, which might have influenced the test results.

Annex A
(informative)

Interlaboratory testing

A.1 Overview

The International Laboratories Ring Tests of this International Standard have been accomplished from Sep. 2012 to Dec. 2012. There are 14 laboratories participating in the two parallel tests on each four samples. This international ring test was conducted by Shanghai Research Institute of Chemical Industry, P. R. China, the statistician analysis and final report was prepared by Shanghai Research Institute of Chemical Industry, P. R. China.

The following are the14 laboratories participating in the two parallel tests on each four samples.

— Shanghai Research Institute of Chemical Industry, Testing Center, China

— CF Industries Laboratory, USA

— Jiangsu Province Products Quality Supervising and Testing Institute, China

— Hunan Province Products Quality Supervising and Testing Institute, China

— Shandong Province Products Quality Supervising and Testing Institute, China

— Guizhou Province Products Quality Supervising and Testing Institute, China

— Guizhou Kailin Quality Testing Center, China

— Guangxi Zhuang Autonomous Region Products Quality Supervising and Testing Institute, China

— Heilongjiang Province Products Quality Supervising and Testing Institute, China

— Xingjiang Uygur Autonomous Region Products Quality Supervising and Testing Institute, China

— Yunnan Province Chemical Products Quality Supervising and Testing Center, China

— Shanghai Entry-Exit Inspection and Quarantine Bureau, China

— Yunnan Province Products Quality Supervising and Testing Institute, China

— Shenyang Fertilizer Quality Supervising and Testing Center, Ministry of Agriculture, China

NOTE The above sequence has nothing to do with the order of the tests in the laboratory.

The test method described in this International Standard was adopted here for determination of arsenic, cadmium, lead, chromium, and mercury contents in the fertilizer samples.

Four different kinds of fertilizer samples were used during the ring test, and constitute a gratitude of mean levels of 4. There are sample A-NPK compound fertilizer, sample B-NPK complex fertilizer, sample C-diammonium phosphate, and sample D-organic fertilizer. The arsenic, cadmium, lead, chromium and mercury contents in all of the 4 fertilizer samples lie in 8 mg/kg to 120 mg/kg.

The precision of the test results is evaluated based on ISO 5725-2:1994.

A.2 Statistical analysis of the test results of arsenic contents

A.2.1 Original test results

There are 11 laboratories has participated in the determination of arsenic contents in fertilizers. The test results were listed in Table A.1, with the unit of mg/kg.

Table A.1 — Original test results of the determination of arsenic contents

Laboratory *i*	Level *j*							
	A		B		C		D	
1	75,03	75,91	94,39	96,57	12,61	16,14	60,11	59,50
2	74,56	71,86	94,85	94,27	14,37	13,61	55,27	54,27
3	76,13	79,51	103,05	101,87	15,45	15,21	60,00	60,24
4	80,10	76,92	99,79	99,49	14,50	14,62	57,20	57,48
5	76,56	76,68	100,03	99,31	16,82	16,11	62,91	61,86
6	76,37	74,85	99,41	97,61	13,97	14,39	56,91	57,35
7	69,87	71,89	89,27	93,08	14,57	14,98	53,63	50,82
8	66,87	69,84	94,61	92,47	13,43	14,34	51,94	51,88
9	76,14	76,28	100,90	100,02	14,98	15,82	57,26	58,08
10	74,99	74,94	99,03	98,03	14,01	14,65	57,85	56,51
11	80,37	80,14	105,22	107,16	16,04	16,59	59,42	61,85

A.2.2 Cell means

The cell means of the determination of arsenic contents were listed in Table A.2, with the unit of mg/kg.

Table A.2 — Cell means of the determination of arsenic contents

Laboratory *i*	Level *j*			
	A	B	C	D
1	75,470	95,480	14,375	59,805
2	73,210	94,560	13,990	54,770
3	77,820	102,460	15,330	60,120
4	78,510	99,640	14,560	57,340
5	76,620	99,670	16,465	62,385
6	75,610	98,510	14,180	57,130
7	70,880	91,175	14,775	52,225
8	68,355	93,540	13,885	51,910
9	76,210	100,460	15,400	57,670
10	74,965	98,530	14,330	57,180
11	80,255	106,190	16,315	60,635

A.2.3 Cell absolute differences

The cell absolute differences of the determination of arsenic contents were listed in Table A.3, with the unit of mg/kg.

Table A.3 — Cell absolute differences of the determination of arsenic contents

Laboratory *i*	Level *j*			
	A	A	A	A
1	0,88	2,18	3,53	0,61
2	2,70	0,58	0,76	1,00
3	3,38	1,18	0,24	0,24
4	3,18	0,30	0,12	0,28
5	0,12	0,72	0,71	1,05
6	1,52	1,80	0,42	0,44
7	2,02	3,81	0,41	2,81
8	2,97	2,14	0,91	0,06
9	0,14	0,88	0,84	0,82
10	0,05	1,00	0,64	1,34
11	0,23	1,94	0,55	2,43

A.2.4 Scrutiny of results for consistency and outliers

Graphical consistency technique by Mandel's *h* and *k* statistics:

Calculate the between-laboratory consistency statistic *h*, as well as the within-laboratory consistency statistic *k*, for each level of each laboratory. Plot the *h* and *k* values for each cell in order of laboratory respectively, to get the Mandel's *h* and *k* graphs.

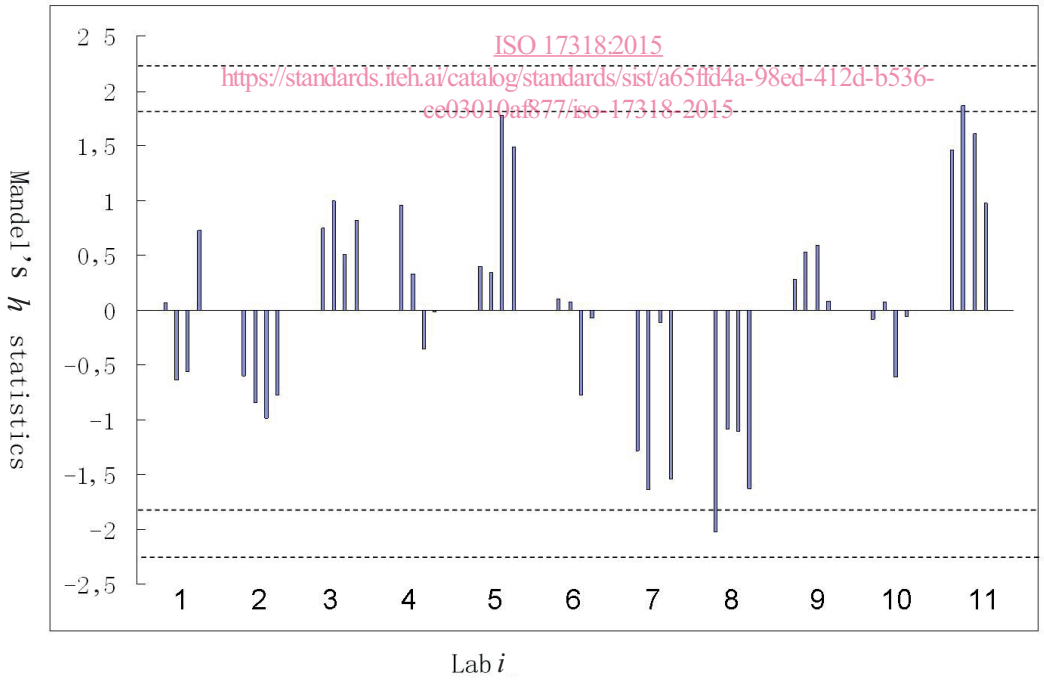

Figure 1 — Mandel's between-laboratory consistency statistic, *h*, grouped by laboratories