INTERNATIONAL STANDARD

ISO 17318

First edition
2015-06-01

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

Reference number
ISO 17318:2015(E)

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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.

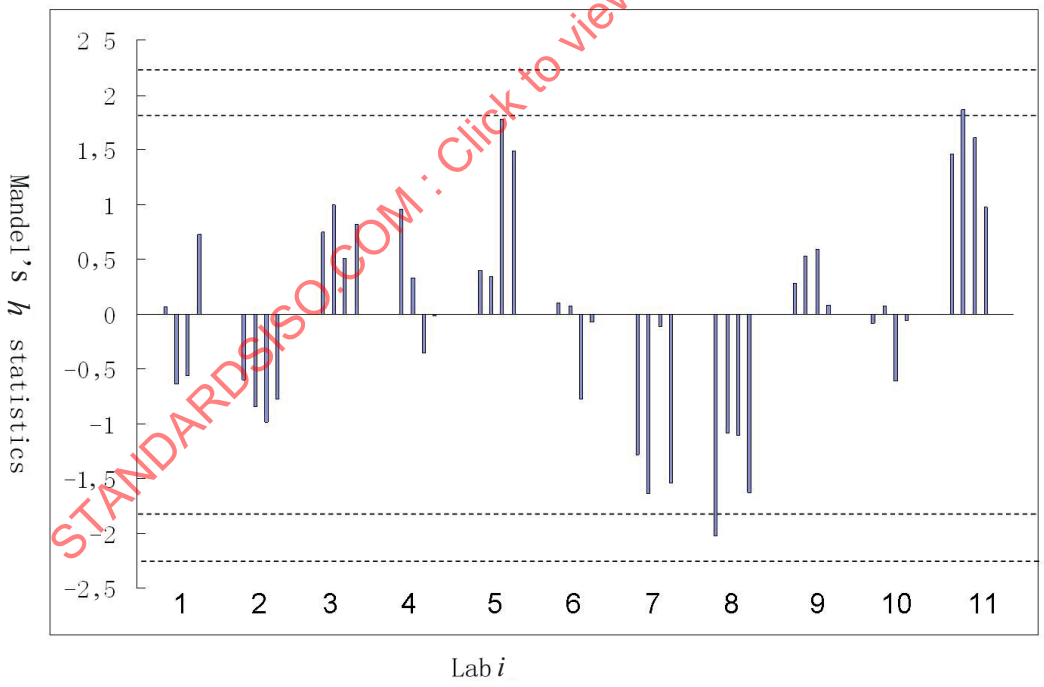

Figure 1 — Mandel's between-laboratory consistency statistic, *h*, grouped by laboratories

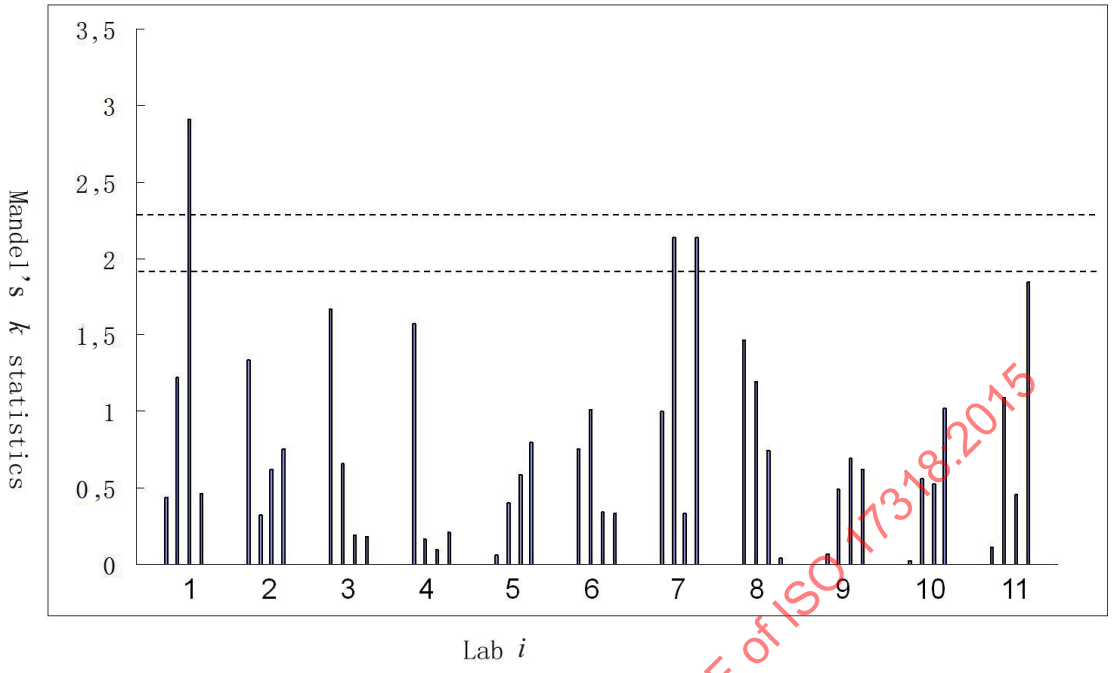

Figure 2 — Mandel's within-laboratory consistency statistic, *k*, grouped by laboratories

Horizontal dotted lines in figures above represent 1 % and 5 % critical values of Mandel's *h* and *k* statistics, respectively.

The *h* graph has shown that laboratory 8 had a straggler on level A, and laboratory 11 had a straggler on level B, while no outlier has been founded herein.

The *k* graph has exhibited rather large variability between replicate test results for laboratory 7 on levels B and D, as well as laboratory 1 on level C.

Cochran's test

Application of Cochran's test led to the values of the test statistic *C* given in Table A.4.

Table A.4 — Values of Cochran test statistic, *C*

Level *j*	A	B	C	D	Type of test
C	0,254	0,415	0,769	0,414	Cochran's test statistics
Stragglers (P = 11)	0,570	0,570	0,570	0,570	Cochran's critical values
Outliers (P = 11)	0,684	0,684	0,684	0,684	

If the test statistic is greater than its 5 % critical value and less than or equal to its 1 % critical value, the item tested is regarded as a straggler;

If the test statistic is greater than its 1 % critical value, the item tested is regarded as an outlier.

Cochran's test here shown that the test statistic reached 0,769, calculated by the cell absolute difference (3,53) from laboratory 1 on level C.

The Cochran's critical value at the 1 % significance level was 0,684, therefore the test results from laboratory 1 on level C is a outlier, which should be discarded here.

Cochran's test was repeated on the remaining tests values from the 10 laboratories on level C, the test statistic obtained this time was 0,221, which is less than the Cochran's critical value at the 5 % significance level (0,602, P = 10). So we have confirmed that no straggler exist this time (and of course no outlier, either).

Grubbs' test

Application of Grubbs' test to cell means led to the values of the test statistic G shown in Table A.5.

Table A.5 — Application of Grubbs' test to cell means

Level j;P	Single low	Single high	Double low	Double high	Type of test
A;11	2,027	1,465	0,301 5	0,629 9	Grubbs' test statistics
B;11	1,641	1,866	0,529 2	0,461 8	
C;10	1,121	1,666	1,966 5	0,301 1	
D;11	1,630	1,492	0,386 7	0,615 7	
Stragglers					Grubbs' critical values
P = 10	2,290	2,290	0,186 4	0,186 4	
P = 11	2,355	2,355	0,221 3	0,221 3	
Outliers					
P = 10	2,482	2,482	0,115 0	0,115 0	
P = 11	2,564	2,564	0,144 8	0,144 8	

For the Grubbs' test for one outlying observation, outliers and stragglers give rise to values which are larger than its 1 % and 5 % critical values respectively.

For the Grubbs' test for two outlying observation, outliers and stragglers give rise to values which are smaller than its 1 % and 5 % critical values respectively.

Application of Grubbs' test to our cell means here confirms no stragglers (and of course no outlier, either).

A.2.5 Calculation of the general mean and standard deviations

Calculation of the general mean, s_r, s_R of arsenic contents in each sample has led to Table A.6, with the unit of mg/kg.

Table A.6 — Calculation results of the general mean, s_r, s_R of arsenic contents

Sample/Level	C	D	A	B
Number of Laboratories	11	11	11	11
Outliers	1	0	0	0
General mean, x	14,92	57,38	75,26	98,20
Repeatability standard deviation, s_r	0,433	0,931	1,429	1,261
Reproducibility standard deviation, s_R	0,975	3,419	3,554	4,373

A.2.6 Dependence of precision on general mean, x

From Table A.6 it seems clear that the standard deviations tend to increase with higher values of x, so it is likely that it might be permissible to establish some form of functional relationship.

The actual fitting calculation has shown well linear correlation between $\log_{sr}$, $\log_{SR}$ with $\log_x$, respectively, the formulae were shown as follows:

$\log_{sr} = 0{,}621 \log_x - 1{,}090\ 7 \quad R^2 = 0{,}941$

$\log_{SR} = 0{,}809 \log_x - 0{,}947 \quad R^2 = 0{,}982\ 8$

A.2.7 Final Values of precision

The precision of the as-contents measurement method should be quoted as follows:

— repeatability standard deviation: $s_r = 0{,}081\ 2x^{0{,}621}$

— reproducibility standard deviation: $s_R = 0{,}113x^{0{,}809}$

The conclusion above were determined from a uniform-level experiment involving 11 laboratories, in which one test value from a laboratory on level C has been discarded as an outlier.

(Based on the formulae above, for fertilizer sample with As content at 20 mg/kg, the repeatability standard deviation should be 0,522 mg/kg, the reproducibility standard deviation should be 1,275 mg/kg; the repeatability limit should be 1,46 mg/kg, the reproducibility limit should be 3,57 mg/kg)

A.3 Statistical analysis of the test results of cadmium contents

A.3.1 Original test results

There are 14 laboratories has participated in the determination of cadmium contents in fertilizers. The test results were listed in Table A.7, with the unit of mg/kg.

Table A.7 — Original test results of the determination of cadmium contents

Laboratory *i*	Level *j*							
	A		B		C		D	
1	49,83	50,77	86,36	88,12	19,70	19,87	69,09	67,71
2	48,48	50,78	92,47	94,71	18,86	20,02	69,55	72,06
3	47,41	47,36	90,51	91,04	19,15	19,05	71,28	71,45
4	47,53	49,40	92,78	92,53	19,69	19,77	72,44	72,77
5	46,35	46,22	88,70	88,99	18,63	18,94	70,30	70,51
6	49,78	49,38	94,13	94,08	19,11	19,05	71,36	70,73
7	48,91	47,83	90,83	91,49	19,14	18,40	69,69	70,01
8	51,13	50,95	97,52	97,85	19,33	19,23	74,61	72,21
9	47,42	47,19	90,84	92,05	18,88	18,97	68,34	67,80
10	49,16	49,24	95,02	95,12	19,98	19,16	72,11	72,10
11	48,68	48,83	93,56	93,51	18,93	18,95	71,94	71,77
12	48,43	48,22	91,44	90,79	18,87	19,16	70,93	69,54
13	49,16	48,90	94,69	95,76	20,14	20,26	70,61	73,44
14	48,97	48,30	96,06	97,31	19,07	18,66	68,82	68,89

A.3.2 Cell means

The cell means of the determination of cadmium contents were listed in Table A.8, with the unit of mg/kg.

Table A.8 — Cell means of the determination of cadmium contents

Laboratory *i*	Level *j*			
	A	B	C	D
1	50,300	87,240	19,785	68,400
2	49,630	93,590	19,440	70,805
3	47,385	90,775	19,100	71,365
4	48,465	92,655	19,730	72,605
5	46,285	88,845	18,785	70,405
6	49,580	94,105	19,080	71,045
7	48,370	91,160	18,770	69,850
8	51,040	97,685	19,280	73,410
9	47,305	91,445	18,925	68,070
10	49,200	95,070	19,570	72,105
11	48,755	93,535	18,940	71,855
12	48,325	91,115	19,015	70,235
13	49,030	95,225	20,200	72,025
14	48,635	96,685	18,865	68,855

A.3.3 Cell absolute differences

The cell absolute differences of the determination of cadmium contents were listed in Table A.9, with the unit of mg/kg.

Table A.9 — Cell absolute differences of the determination of cadmium contents

Laboratory *i*	Level *j*			
	A	B	C	D
1	0,94	1,76	0,17	1,38
2	2,30	2,24	1,16	2,51
3	0,05	0,53	0,10	0,17
4	1,87	0,25	0,08	0,33
5	0,13	0,29	0,31	0,21
6	0,40	0,05	0,06	0,63
7	1,08	0,66	0,74	0,32
8	0,18	0,33	0,10	2,40
9	0,23	1,21	0,09	0,54
10	0,08	0,10	0,82	0,01
11	0,15	0,05	0,02	0,17
12	0,21	0,65	0,29	1,39
13	0,26	1,07	0,12	2,83
14	0,67	1,25	0,41	0,07

A.3.4 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.

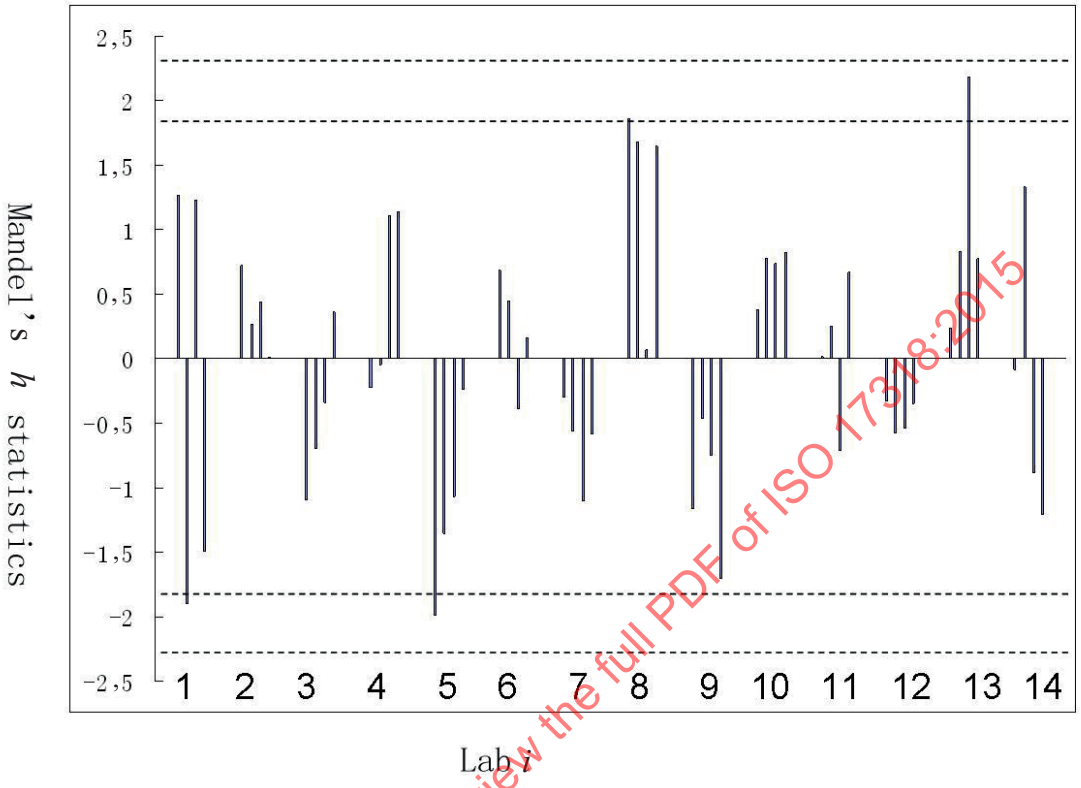

Figure 3 — Mandel's between-laboratory consistency statistic, *h*, grouped by laboratories

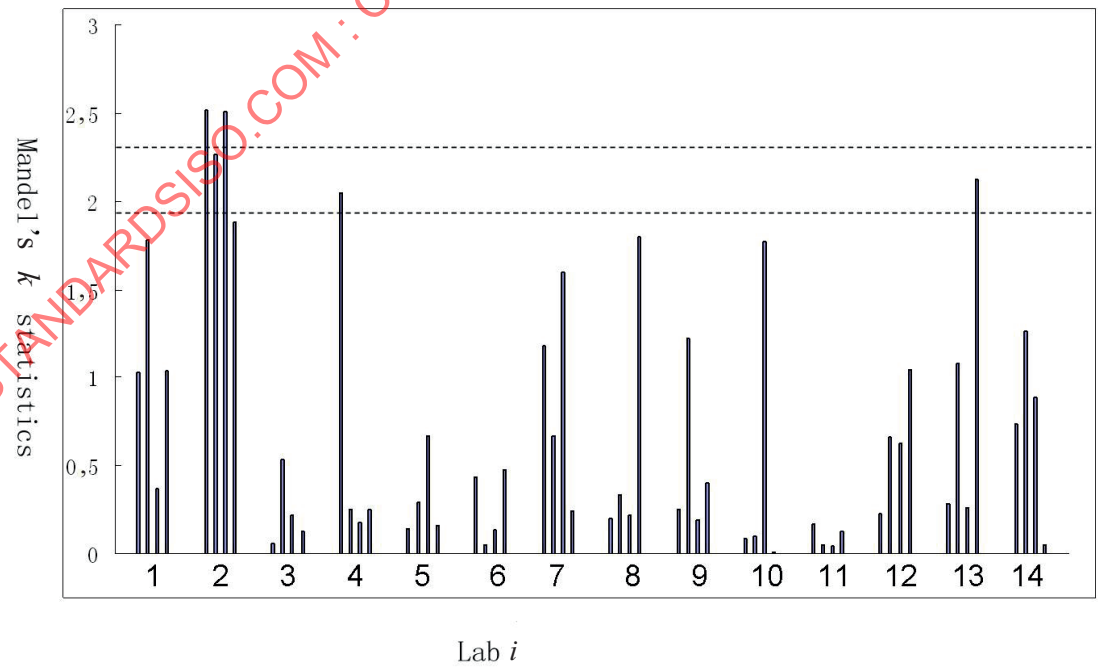

Figure 4 — Mandel's within-laboratory consistency statistic, *k*, grouped by laboratories

Horizontal dotted lines in figures above represent 1 % and 5 % critical values of Mandel's *h* and *k* statistics, respectively.

The *h* graph has shown that laboratories 5 and 8 both had stragglers on level A, laboratory 1 had a straggler on level B, and laboratory 13 had a straggler on level C, while no outlier has been founded herein.

The *k* graph has exhibited rather large variability between replicate test results for laboratory 2 on many levels, as well as laboratory 13 on level D.

Cochran's test:

Application of Cochran's test led to the values of the test statistic *C* given in Table A.10

Table A.10 — Values of Cochran test statistic, *C*

Level *j*	A	B	C	D	Type of test
C	0,452	0,366	0,449	0,321	Cochran's test statistics
Stragglers ($P = 14$)	0,492	0,492	0,492	0,492	Cochran's critical values
Outliers ($P = 14$)	0,599	0,599	0,599	0,599	

If the test statistic is greater than its 5 % critical value and less than or equal to its 1 % critical value, the item tested is regarded as a straggler;

If the test statistic is greater than its 1 % critical value, the item tested is regarded as an outlier.

We have confirmed that no straggler exist by Cochran's test here (and of course no outlier, either).

Grubbs' test

Application of Grubbs' test to cell means led to the values of the test statistic *G* shown in Table A.11

Table A.11 — Application of Grubbs' test to cell means

Level *j*;*P*	Single low	Single high	Double low	Double high	Type of test
A	1,984	1,865	0,531	0,546	Grubbs' test statistics
B	1,902	1,674	0,513	0,590	
C	1,101	2,186	0,789	0,441	
D	1,702	1,642	0,539	0,643	
Stragglers ($P = 14$)	2,507	2,507	0,311 2	0,311 2	Grubbs' critical values
Outliers ($P = 14$)	2,755	2,755	0,228 0	0,228 0	

For the Grubbs' test for one outlying observation, outliers and stragglers give rise to values which are larger than its 1 % and 5 % critical values respectively.

For the Grubbs' test for two outlying observation, outliers and stragglers give rise to values which are smaller than its 1 % and 5 % critical values respectively.

Application of Grubbs' test to our cell means here confirms no stragglers (and of course no outlier, either).

A.3.5 Calculation of the general mean and standard deviations

Calculation of the general mean, s_r, s_R of Cd contents in each sample has led to Table A.12, with the unit of mg/kg.

Table A.12 — Calculation results of the general mean, s_r, s_R of Cd contents

Sample/Level	C	A	D	B
Number of Laboratories	14	14	14	14
Outliers	0	0	0	0
General mean, x	19,25	48,74	70,79	92,80
Repeatability standard deviation, s_r	0,327	0,646	0,943	0,699
Reproducibility standard deviation, s_R	0,470	1,317	1,730	2,962

A.3.6 Dependence of precision on general mean, x

From Table A.12 it seems clear that the standard deviations tend to increase with higher values of x, so it is likely that it might be permissible to establish some form of functional relationship.

The actual fitting calculation has shown well linear correlation between $\log_{sr}$, $\log_{SR}$ with $\log_x$, respectively, the formulae were shown as follows:

$\log_{Sr} = 0{,}586\ 2 \log_x - 1{,}209 \qquad R^2 = 0{,}81$

$\log_{SR} = 1{,}116\ 7 \log_x - 1{,}770\ 2 \qquad R^2 = 0{,}984\ 1$

A.3.7 Final Values of precision

The precision of the Cd contents measurement method should be quoted as follows:

— repeatability standard deviation: $s_r = 0{,}061\ 8x^{0{,}586\ 2}$

— reproducibility standard deviation: $s_R = 0{,}017x^{1{,}116\ 7}$

The conclusion above was determined from a uniform-level experiment involving 14 laboratories, no straggler has been reported.

(Based on the formulae above, for fertilizer sample with Cd content at 20 mg/kg, the repeatability standard deviation should be 0,358 mg/kg, the reproducibility standard deviation should be 0,482 mg/kg; the repeatability limit should be 1,00 mg/kg, the reproducibility limit should be 1,35 mg/kg)

A.4 Statistical analysis of the test results of lead contents

A.4.1 Original test results

There are 13 laboratories has participated in the determination of cadmium contents in fertilizers. The test results were listed in Table A.13, with the unit of mg/kg.

Table A.13 — Original test results of the determination of Pb contents

Laboratory i	Level j							
	A		B		C		D	
1	50,91	52,64	95,34	98,03	17,14	16,58	87,72	86,61

Table A.13 *(continued)*

Laboratory *i*	Level *j*							
	A		B		C		D	
2	52,48	50,14	97,60	102,00	19,15	20,62	90,47	92,43
3	48,70	47,92	94,20	99,18	19,95	20,92	89,32	91,57
4	50,40	51,32	103,05	101,70	18,74	19,06	92,89	93,56
5	51,12	51,08	102,75	102,22	18,51	18,49	95,34	100,15
6	53,47	51,20	97,26	97,29	18,67	18,39	88,98	90,94
7	52,57	52,13	98,19	99,41	17,89	18,71	89,87	89,15
8	48,67	49,83	97,73	96,20	18,68	18,07	96,32	92,82
9	51,46	49,72	99,99	97,55	17,62	17,98	84,40	88,76
10	51,08	51,17	96,98	98,06	17,98	18,32	91,20	90,13
11	46,95	47,06	95,57	94,98	15,45	15,35	84,76	83,77
12	52,43	52,21	100,52	99,45	18,17	18,57	91,23	87,57
13	51,89	52,34	104,43	106,20	19,47	19,81	94,79	99,01

A.4.2 Cell means

The cell means of the determination of Pb contents were listed in Table A.14, with the unit of mg/kg.

Table A.14 — Cell means of the determination of Pb contents

Laboratory *i*	Level *j*			
	A	B	C	D
1	51,775	96,685	16,860	87,165
2	51,310	99,800	19,885	91,450
3	48,310	96,690	20,435	90,445
4	50,860	102,375	18,900	93,225
5	51,100	102,485	18,500	97,745
6	52,335	97,275	18,530	89,960
7	52,350	98,800	18,300	89,510
8	49,250	96,965	18,375	94,570
9	50,590	98,770	17,800	86,580
10	51,125	97,520	18,150	90,665
11	47,005	95,275	15,400	84,265
12	52,320	99,985	18,370	89,400
13	52,115	105,315	19,640	96,900

A.4.3 Cell absolute differences

The cell absolute differences of the determination of Pb contents were listed in Table A.15, with the unit of mg/kg.

Table A.15 — Cell absolute differences of the determination of Pb contents

Laboratory *i*	Level *j*			
	A	B	C	D
1	1,73	2,69	0,56	1,11
2	2,34	4,40	1,47	1,96
3	0,78	4,98	0,97	2,25
4	0,92	1,35	0,32	0,67
5	0,04	0,53	0,02	4,81
6	2,27	0,03	0,28	1,96
7	0,44	1,22	0,82	0,72
8	1,16	1,53	0,61	3,50
9	1,74	2,44	0,36	4,36
10	0,09	1,08	0,34	1,07
11	0,11	0,59	0,10	0,99
12	0,22	1,07	0,40	3,66
13	0,45	1,77	0,34	4,22

A.4.4 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.

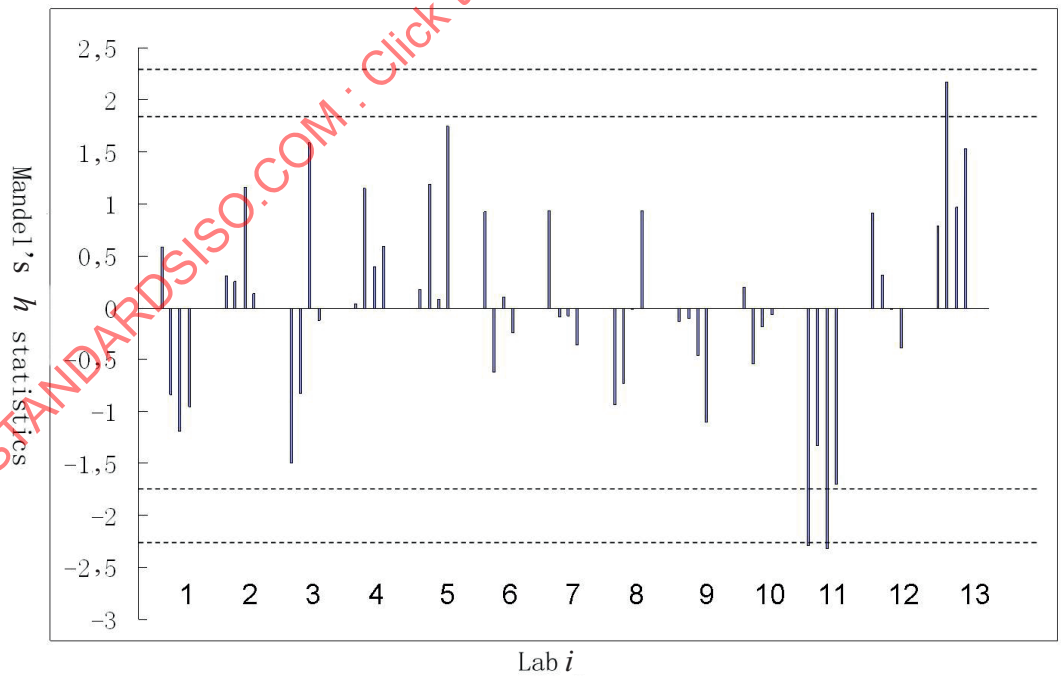

Figure 5 — Mandel's between-laboratory consistency statistic, *h*, grouped by laboratories

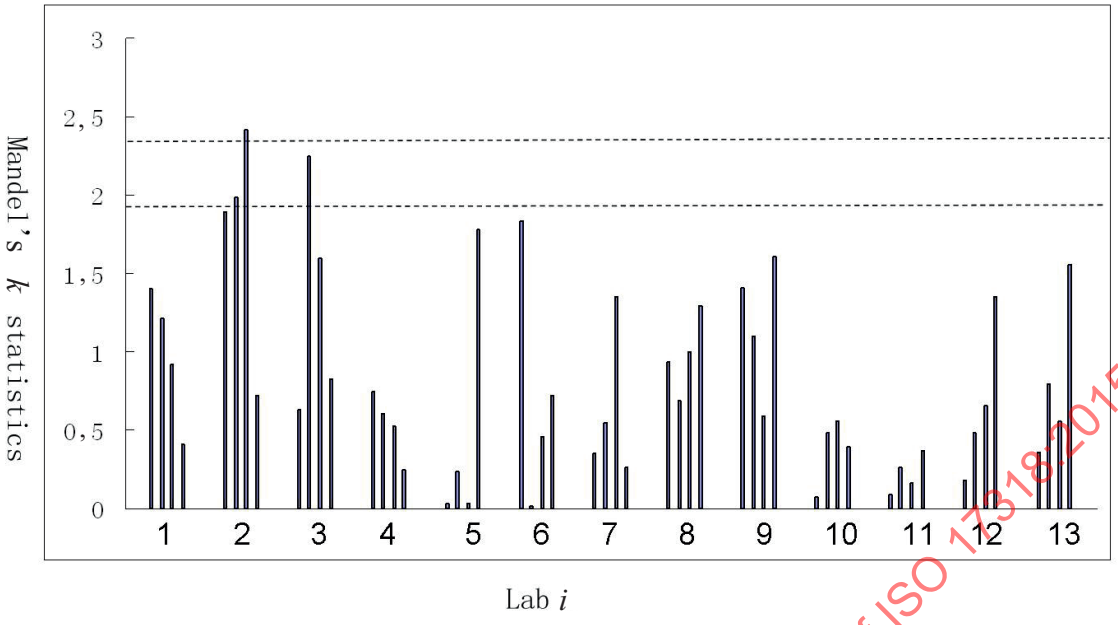

Figure 6 — Mandel's within-laboratory consistency statistic, *k*, grouped by laboratories

Horizontal dotted lines in figures above represent 1 % and 5 % critical values of Mandel's *h* and *k* statistics, respectively.

The *h* graph has shown that laboratories 11 had significant low values (stragglers) on level A and C, which is approaching the outlier critical value, and laboratory 13 had a straggler on level B, which is higher than that value of other laboratories.

The *k* graph has exhibited rather large variability between replicate test results for laboratory 2 on many levels, as well as laboratory 3 on level B.

Cochran's test:

Application of Cochran's test led to the values of the test statistic *C* given in Table A.16

Table A.16 — Values of Cochran test statistic, *C*

Level *j*	A	B	C	D	Type of test
C	0,275	0,359	0,418	0,225	Cochran's test statistics
Stragglers (P = 13)	0,515	0,515	0,515	0,515	Cochran's critical values
Outliers (P = 13)	0,624	0,624	0,624	0,624	

If the test statistic is greater than its 5 % critical value and less than or equal to its 1 % critical value, the item tested is regarded as a straggler;

If the test statistic is greater than its 1 % critical value, the item tested is regarded as an outlier.

We have confirmed that no straggler exist by Cochran's test here (and of course no outlier, either).

Grubbs' test

Application of Grubbs' test to cell means led to the values of the test statistic *G* shown in Table A.17

Table A.17 — Application of Grubbs' test to cell means

Level j;P	Single low	Single high	Double low	Double high	Type of test
A	2,282	0,929	0,271 0	0,831 7	Grubbs' test statistics
B	1,323	2,174	0,761 5	0,402 7	
C	2,322	1,581	0,338 9	0,624 0	
D	1,698	1,745	0,598 1	0,470 4	
Stragglers (P = 13)	2,462	2,462	0,283 6	0,283 6	Grubbs' critical values
Outliers (P = 13)	2,699	2,699	0,201 6	0,201 6	

For the Grubbs' test for one outlying observation, outliers and stragglers give rise to values which are larger than its 1 % and 5 % critical values respectively.

For the Grubbs' test for two outlying observation, outliers and stragglers give rise to values which are smaller than its 1 % and 5 % critical values respectively.

Application of Grubbs' test to our cell means here, we have found the Grubbs' double low statistic on level A was a straggler, while we also noticed that the Grubbs' single low statistic on level A was within the critical value, so we decided to retain those values in level A.

A.4.5 Calculation of the general mean and standard deviations

Calculation of the general mean, s_r, s_R of Pb contents in each sample has led to Table A.18, with the unit of mg/kg.

Table A.18 — Calculation results of the general mean, s_r, s_R of Pb contents

Sample/Level	C	A	D	B
Number of Laboratories	13	13	13	13
Outliers	0	0	0	0
General mean, x	18,40	50,80	90,91	99,07
Repeatability standard deviation, s_r	0,4460	0,875	1,987	1,630
Reproducibility standard deviation, s_R	1,252	1,776	4,160	3,094

A.4.6 Dependence of precision on general mean, x

From Table A.18 it seems clear that the standard deviations tend to increase with higher values of x, so it is likely that it might be permissible to establish some form of functional relationship.

The actual fitting calculation has shown well linear correlation between $\log_{sr}$, $\log_{SR}$ with $\log_x$, respectively, the formulae were shown as follows:

$\log_{sr} = 0{,}849\ 9 \log_x - 1{,}446 \qquad R^2 = 0{,}953\ 3$

$\log_{SR} = 0{,}643\ 2 \log_x - 0{,}749\ 4 \qquad R^2 = 0{,}851\ 5$

A.4.7 Final Values of precision

The precision of the Pb contents measurement method should be quoted as follows:

— repeatability standard deviation: $s_r = 0{,}035\ 8x^{0{,}849\ 9}$

— reproducibility standard deviation: $s_R = 0{,}178\ 1x^{0{,}643\ 2}$

The conclusion above was determined from a uniform-level experiment involving 13 laboratories. For level A, we have found the Grubbs' double low statistic on level A was a straggler, while we also noticed that the Grubbs' single low statistic on level A was within the critical value, so we decided to retain those values in level A for statistics on precision.

(Based on the formulae above, for fertilizer sample with Pb content at 20 mg/kg, the repeatability standard deviation should be 0,457 mg/kg, the reproducibility standard deviation should be 1,223 mg/kg; the repeatability limit should be 1,28mg/kg, the reproducibility limit should be 3,42 mg/kg)

A.5 Statistical analysis of the test results of Cr contents

A.5.1 Original test results

There are 13 laboratories has participated in the determination of Cr contents in fertilizers. The test results were listed in Table A.19, with the unit of mg/kg.

Table A.19 — Original test results of the determination of Cr contents

Laboratory *i*	Level *j*							
	A		B		C		D	
1	67,82	69,31	107,60	110,00	25,18	25,45	112,60	112,50
2	62,13	64,49	112,10	110,40	21,33	21,63	112,80	117,70
3	68,60	67,08	111,29	114,41	22,08	24,10	115,35	113,21
4	66,32	68,01	117,36	116,76	25,23	26,21	—	—
5	64,90	66,26	111,71	111,59	—	—	109,36	109,35
6	65,97	67,76	109,90	107,72	21,53	21,74	112,53	111,92
7	68,91	68,03	108,19	109,95	21,51	22,01	109,57	110,03
8	67,98	68,77	120,09	117,31	21,24	21,49	118,65	116,48
9	65,60	63,95	106,60	104,80	22,07	21,99	100,50	106,30
10	66,51	67,59	112,66	112,77	21,98	22,49	108,16	110,15
11	61,83	61,83	103,95	103,85	27,03	27,33	107,35	109,23
12	68,76	68,42	111,25	109,76	21,47	22,13	108,97	110,85
13	58,26	61,12	101,39	107,64	23,92	25,21	104,37	108,90

A.5.2 Cell means

The cell means of the determination of Cr contents were listed in Table A.20, with the unit of mg/kg.

Table A.20 — Cell means of the determination of Cr contents

Laboratory *i*	Level *j*			
	A	B	C	D
1	68,565	108,800	25,315	112,550
2	63,310	111,250	21,480	115,250
3	67,840	112,850	23,090	114,280
4	67,165	117,060	25,720	—
5	65,580	111,650	—	109,355
6	66,865	108,810	21,635	112,225

Table A.20 *(continued)*

Laboratory *i*	Level *j*			
	A	B	C	D
7	68,470	109,070	21,760	109,800
8	68,375	118,700	21,365	117,565
9	64,775	105,700	22,030	103,400
10	67,050	112,715	22,235	109,155
11	61,830	103,900	27,180	108,290
12	68,590	110,505	21,800	109,910
13	59,690	104,515	24,565	106,635

A.5.3 Cell absolute differences

The cell absolute differences of the determination of Cr contents were listed in Table A.21, with the unit of mg/kg.

Table A.21 — Cell absolute differences of the determination of Cr contents

Laboratory *i*	Level *j*			
	A	B	C	D
1	1,49	2,40	0,27	0,10
2	2,36	1,70	0,30	4,90
3	1,52	3,12	2,02	2,14
4	1,69	0,60	0,98	—
5	1,36	0,12	—	0,01
6	1,79	2,18	0,21	0,61
7	0,88	1,76	0,50	0,46
8	0,79	2,78	0,25	2,17
9	1,65	1,80	0,08	5,80
10	1,08	0,11	0,51	1,99
11	0,00	0,10	0,30	1,88
12	0,34	1,49	0,66	1,88
13	2,86	6,25	1,29	4,53

A.5.4 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.

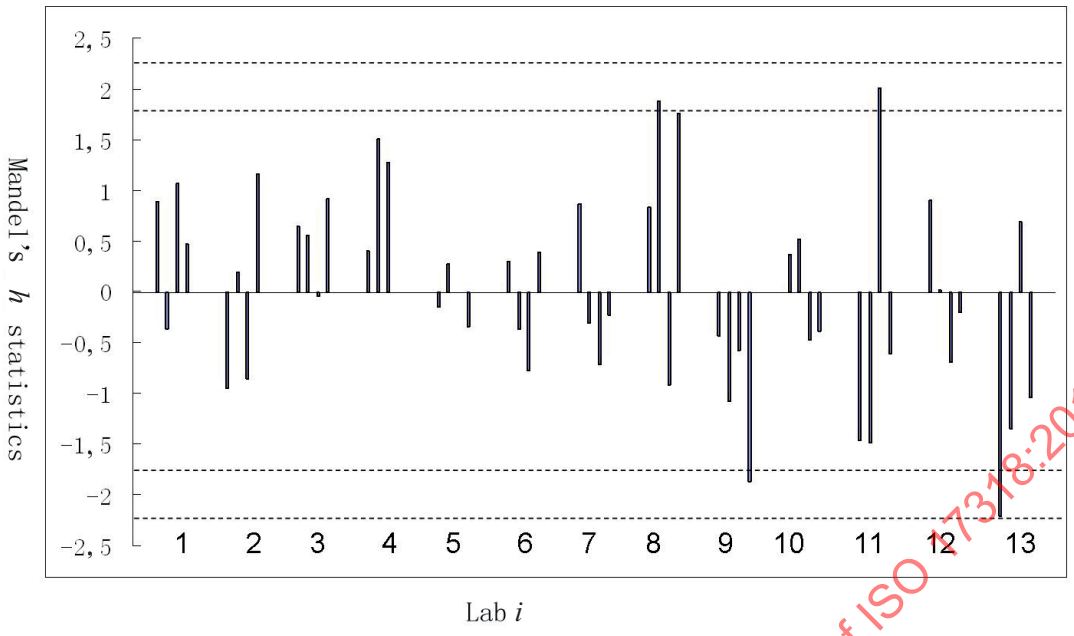

Figure 7 — Mandel's between-laboratory consistency statistic, *h*, grouped by laboratories

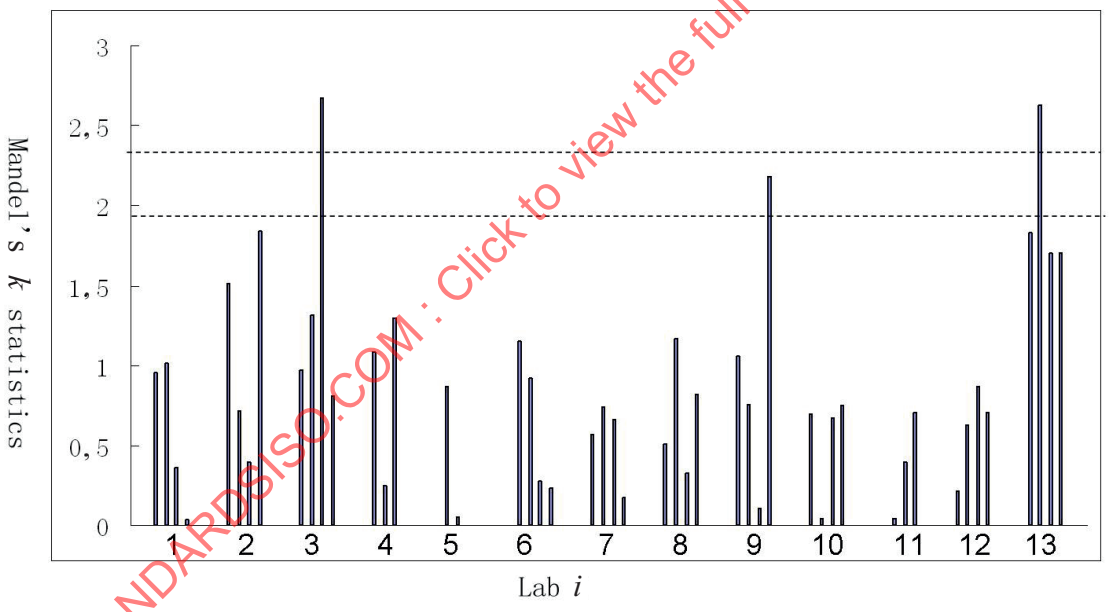

Figure 8 — Mandel's within-laboratory consistency statistic, *k*, grouped by laboratories

Horizontal dotted lines in figures above represent 1 % and 5 % critical values of Mandel's *h* and *k* statistics, respectively.

The *h* graph has shown that laboratory 13 had a straggler on level A, laboratory 8 had a straggler on level B, laboratory 11 had a straggler on level C, and laboratory 9 had a straggler on level D, while no outlier has been founded herein.

The *k* graph has exhibited rather large variability between replicate test results for laboratory 13 on level B, laboratory 3 on level C, as well as laboratory 9 on level D.

Cochran's test:

Application of Cochran's test led to the values of the test statistic C given in Table A.22.

Table A.22 — Values of Cochran test statistic, C

Level j	A	B	C	D	Type of test
C	0,259	0,495	0,509	0,340	Cochran's test statistics
Stragglers (P = 13)	0,515	0,515	0,515	0,515	Cochran's critical values
Outliers (P = 13)	0,624	0,624	0,624	0,624	

If the test statistic is greater than its 5 % critical value and less than or equal to its 1 % critical value, the item tested is regarded as a straggler;

If the test statistic is greater than its 1 % critical value, the item tested is regarded as an outlier.

We have confirmed that no straggler exist by Cochran's test here (and of course no outlier, either).

Grubbs' test

Application of Grubbs' test to cell means led to the values of the test statistic G shown in Table A.23

Table A.23 — Application of Grubbs' test to cell means

Level j;P	Single low	Single high	Double low	Double high	Type of test
A;13	2,214	0,905	0,310 5	0,840 3	Grubbs' test statistics
B;13	1,482	1,879	0,606 6	0,429 8	
C;12	0,912	2,008	0,829 8	0,388 0	
D;12	1,870	1,758	0,506 3	0,517 9	
Stragglers					Grubbs' critical values
P = 12	2,412	2,412	0,253 7	0,253 7	
P = 13	2,462	2,462	0,283 6	0,283 6	
Outliers					
P = 12	2,636	2,636	0,173 8	0,173 8	
P = 13	2,699	2,699	0,201 6	0,201 6	

For the Grubbs' test for one outlying observation, outliers and stragglers give rise to values which are larger than its 1 % and 5 % critical values respectively.

For the Grubbs' test for two outlying observation, outliers and stragglers give rise to values which are smaller than its 1 % and 5 % critical values respectively.

Application of Grubbs' test to our cell means here confirms no stragglers (and of course no outlier, either).

A.5.5 Calculation of the general mean and standard deviations

Calculation of the general mean, s_r, s_R of Cr contents in each sample has led to Table A.24, with the unit of mg/kg.

Table A.24 — Calculation results of the general mean, s_r, s_R of Cr contents

Sample/Level	C	A	B	D
Number of Laboratories	12	13	13	12
Outliers	0	0	0	0
General mean, x	23,18	66,01	110,42	110,70

Table A.24 *(continued)*

Sample/Level	C	A	B	D
Repeatability standard deviation, s_r	0,578	1,102	1,742	2,032
Reproducibility standard deviation, s_R	1,929	2,958	4,573	4,160

A.5.6 Dependence of precision on general mean, *x*

From Table A.24 it seems clear that the standard deviations tend to increase with higher values of *x*, so it is likely that it might be permissible to establish some form of functional relationship.

The actual fitting calculation has shown well linear correlation between $\log_{sr}$, $\log_{SR}$ with $\log_x$, respectively, the formulae were shown as follows:

$\log_{sr} = 0{,}755\ 2 \log_x - 1{,}284\ 8 \qquad R^2 - 0{,}971\ 4$

$\log_{SR} = 0{,}521\ 9 \log_x - 0{,}439\ 9 \qquad R^2 - 0{,}966\ 9$

A.5.7 Final Values of precision

The precision of the Cr contents measurement method should be quoted as follows:

— repeatability standard deviation: $s_r = 0{,}051\ 9x^{0{,}755\ 2}$

— reproducibility standard deviation: $s_R = 0{,}363\ 2x^{0{,}521\ 9}$

The conclusion above was determined from a uniform-level experiment involving 13 laboratories, no straggler has been reported.

(Based on the formulae above, for fertilizer sample with Cr content at 20 mg/kg, the repeatability standard deviation should be 0,499 mg/kg, the reproducibility standard deviation should be 1,734 mg/kg; the repeatability limit should be 1,40 mg/kg, the reproducibility limit should be 4,86 mg/kg)

A.6 Statistical analysis of the test results of Hg contents

A.6.1 Original test results

There are 11 laboratories has participated in the determination of Hg contents in fertilizers. The test results were listed in Table A.25, with the unit of mg/kg.

Table A.25 — Original test results of the determination of Hg contents

Laboratory *i*	Level *j*							
	A		B		C		D	
1	8,87	9,13	—	—	69,36	72,36	44,02	45,17
2	9,13	9,58	122,29	125,00	74,83	75,82	46,21	49,52
3	7,45	7,82	104,42	108,01	65,18	65,3	39,07	39,26
4	8,30	8,19	116,09	116,96	71,00	72,38	45,11	44,73
5	9,19	9,47	123,08	122,53	71,36	70,73	42,76	42,23
6	9,17	8,95	119,51	120,91	69,78	68,86	43,85	43,35
7	8,19	8,00	122,75	122,82	—	—	45,00	43,07
8	8,43	9,58	128,10	127,30	75,37	78,10	43,24	43,50