# INTERNATIONAL STANDARD

# ISO 20702

First edition
2017-12

# Fertilizers and soil conditioners — Determination of microamounts of inorganic anions in fertilizers by ion chromatography

*Engrais et amendements — Détermination des microquantités d'anions inorganiques dans les fertilisants par chromatographie d'échange d'ions*

Reference number
ISO 20702:2017(E)

ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

# Contents

Page

# Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 134, *Fertilizers and soil conditioners.*

# Introduction

Microamounts of inorganic anions such as fluoride, chloride, bromide, iodide, nitrite and thiocyanate are usually contained in fertilizers. Excessive amounts of such inorganic anions can not only impede the growth of crops, but can also cause harmful effects on the arable land and the environment. Current standards around the world mostly focus on a few specific anions. This method, which uses ion chromatography, provides a high-throughput screening and rapid determination pathway targeting microamounts of six anions as an alternative to traditional chemical analysis.

# Fertilizers and soil conditioners — Determination of microamounts of inorganic anions in fertilizers by ion chromatography

## 1 Scope

This document specifies the ion chromatography method for the determination of microamounts of water soluble inorganic anions, such as fluoride ($F^-$), chloride ($Cl^-$), bromide ($Br^-$), iodide ($I^-$), nitrite ($NO_2^-$) and thiocyanate ($SCN^-$), in fertilizers.

## 2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 8157, *Fertilizers and soil conditioners — Vocabulary*

## 3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 8157 apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at http://www.electropedia.org/

— ISO Online browsing platform: available at https://www.iso.org/obp

## 4 Principle

Water soluble inorganic anions are extracted by sonication, centrifugation and purification using a C18 column and a Ba-ion column (where applicable). During pre-treatment, the anions are filtered by a 0,22 µm aqueous filter. They are determined by ion chromatography. Anions are separated based on their affinity for the exchange sites on the analytical column. The suppressor device reduces the background conductivity of the eluent to a low level by replacing the cations with the hydrogen ions, thereby converting the anions in the fertilizer sample to their corresponding acids with higher conductivity. The separated anions (in their acid forms) are measured by an electrical-conductivity detector. Anions are identified based on their retention times compared to known standards. Quantitation is accomplished by measuring the peak height or area compared to a calibration curve generated from known standards.

## 5 Reagents

**WARNING — Acetone and methanol are flammable and toxic. Refer to the applicable safety data sheet (SDS). The related operations shall be performed in the fume hood. This document does not point out all possible safety problems; therefore, the user shall bear the responsibility to take proper safety and health measures.**

Analytical grade reagent (A.R.) chemicals shall be used in all tests, unless otherwise indicated. The purity of water used throughout shall be understood to mean reagent water with electrical resistivity ≥18,2 MΩ·cm. In the list below, G.R. refers to guarantee reagent.

**5.1 Ultrapure water**, HPLC grade water with electrical resistivity ≥18,2 MΩ·cm.

**5.2 Potassium hydroxide (G.R.)**.

**5.3 Sodium carbonate (G.R.)**.

**5.4 Sodium bicarbonate (G.R.)**.

**5.5 Acetone, HPLC grade**.

**5.6 Methanol, HPLC grade**.

NOTE Methanol is be used for the activation of SPE-C18 column (6.8).

**5.7 Potassium hydroxide eluent**. Dissolve 5,611 g potassium hydroxide (0,1 mol, 5.2) in water (5.1). Dilute this solution to 1 l with water (5.1) and mix thoroughly. The potassium hydroxide solution can also be prepared by automated eluent generation system (OH- type). The potassium hydroxide eluent is used for gradient chromatography conditions.

**5.8 Carbonate eluent**. Dissolve 0,530 g sodium carbonate (5,0 mmol) (5.3) and 0,168 g sodium bicarbonate (2,0 mmol) (5.4) in water (5.1), and add 40 ml of acetone (5.5) to the aqueous solution. Dilute to 1 l with water (5.1) and mix thoroughly by ultrasonic treatment for 10 min. The carbonate eluent is used for isocratic chromatography conditions.

### 5.9 Stock solutions

#### 5.9.1 Fluoride stock solution (1 000 mg/l).

Dissolve 2,210 0 g NaF (sodium fluoride, A.R., pre-treated at 105 °C for 2 h) into water (5.1). Transfer the aqueous solution into a 1 000 ml volumetric flask, dilute it to 1 l with water (5.1) and mix thoroughly. Keep the fluoride stock solution in a polyethylene bottle for storage.

#### 5.9.2 Chloride stock solution (1 000 mg/l).

Dissolve 1,648 0 g NaCl (sodium chloride, A.R., pre-treated at 105 °C for 2 h) in water (5.1). Transfer the aqueous solution into a 1 000 ml volumetric flask, dilute it to 1 l with water (5.1) and mix thoroughly.

#### 5.9.3 Bromide stock solution (1 000 mg/l).

Dissolve 1,490 0 g KBr (potassium bromide, A.R., pre-treated at 105 °C for 2 h) in water (5.1). Transfer the aqueous solution into a 1 000 ml volumetric flask, dilute it to 1 l with water (5.1) and mix thoroughly. Keep the bromide stock solution in an amber glass bottle for storage.

#### 5.9.4 Iodide stock solution (1 000 mg/l).

Dissolve 1,308 0 g KI (potassium iodide, A.R., pre-treated at 105°C for 2 h) in water (5.1). Transfer the aqueous solution into a 1 000 ml volumetric flask, dilute it to 1 l with water (5.1) and mix thoroughly. Keep the iodide stock solution in an amber glass bottle for storage.

#### 5.9.5 Nitrite stock solution (1 000 mg/l).

Dissolve 1,489 0 g $NaNO_2$ (sodium nitrite, A.R., pre-dried in a desiccator for approximately 24 h) in water (5.1). Transfer the aqueous solution into a 1 000 ml volumetric flask, dilute it to 1 l with water (5.1) and mix thoroughly.

Nitrite is easily oxidized, especially in the presence of moisture, thus only fresh reagents are to be used. Place approximately 2 g of $NaNO_2$ in a 100 ml beaker and dry to constant weight (approximately 24 h) in a desiccator. Preservation by refrigeration at 4 °C is required for nitrite.

### 5.9.6 Thiocyanate stock solution (1 000 mg/l).

Dissolve 1,673 0 g KSCN (potassium thiocyanate, pre-treated at 105 °C for 2 h) into water (5.1). Transfer the aqueous solution into a 1 000 ml volumetric flask, dilute to 1 l with water (5.1) and mix thoroughly.

### 5.10 Anion standard working solutions.

Prepare anion standard working solutions (including $F^-$, $Cl^-$, $Br^-$, $I^-$, $NO_2^-$ and $SCN^-$) in volumetric flasks according to the concentration ranges listed in Table 1. Alternatively, certificated standard solutions of single or mixed anions may also be used for the preparation of anion working solutions.

The concentration ranges for standard working solutions may be adjusted according to the levels expected in the samples.

Preservation by refrigeration at 4 °C is required for solutions containing nitrite.

**Table 1 — Preparation of anion standard working solutions**

| Working solution | $F^-$<br>mg/l | $Cl^-$<br>mg/l | $Br^-$<br>mg/l | $I^-$<br>mg/l | $NO_2^-$<br>mg/l | $SCN^-$<br>mg/l |
|---|---|---|---|---|---|---|
| Blank | 0 | 0 | 0 | 0 | 0 | 0 |
| Standard 1 | 0,2 | 0,2 | 0,2 | 0,2 | 0,2 | 0,2 |
| Standard 2 | 0,5 | 0,5 | 0,5 | 0,5 | 0,5 | 0,5 |
| Standard 3 | 1,0 | 1,0 | 1,0 | 1,0 | 1,0 | 1,0 |
| Standard 4 | 5,0 | 5,0 | 5,0 | 5,0 | 5,0 | 5,0 |
| Standard 5 | 20,0 | 20,0 | 20,0 | 20,0 | 20,0 | 20,0 |

## 6 Apparatus and materials

**6.1 Ion chromatograph**, with electrical-conductivity detector.

**6.2 Ultrasonic cleaner**.

**6.3 Centrifuge**, with a rotational speed of 4 000 r/min.

NOTE Relative centrifugal force can be calculated as 0,000 001 18 times the rotational radius (in mm) times the square of the revolutions per minute (r/min).

**6.4 High speed pulverizer**.

**6.5 Analytical balance**, with a sensitivity of 0,1 mg.

**6.6 Syringe-driven filter**, with an aqueous filter membrane with 0,22 µm pores.

**6.7 Ba-ion filter column**, 1 ml.

NOTE The Ba-ion filter column (for example, a Ba-Polystyrene resin column) is used to eliminate excess amounts of sulfate and phosphate from the sample which can serve as potential interference.

### 6.8 **SPE-C18 column**, 1 ml.

NOTE The SPE-C18 column is used to eliminate interfering amounts of organic compounds from the sample which can serve as potential interference.

### 6.9 **Ag/H filter column**, 1 ml.

NOTE Since chloride and nitrite elute very closely together, they are potential interferences for each other. The Ag/H filter column is used to eliminate excess amounts of chloride to more accurately measure nitrite.

## 7 Test procedure

### 7.1 General

Two replicate experiments shall be done for the determination.

### 7.2 Preparation of test sample

Prepare a test portion by reducing the fertilizer sample to 100 g. Grind the sample until it passes through a sieve of aperture size 0,5 mm and mix until homogenous. Place in a clean and dry bottle with a lid.

### 7.3 Activation of the filter columns

#### 7.3.1 Activation of the Ba-ion filter column

Flush the Ba-ion filter column with 10 ml water (5.1) before use, keeping the water outflow velocity less than 3 ml/min. The column shall be kept in stand-by mode after activation.

#### 7.3.2 Activation of the SPE-C18 column

First, flush the SPE-C18 column with 5 ml methanol, keeping the methanol outflow velocity less than 3 ml/min. Then, flush the column with 15 ml water (5.1), keeping the water outflow velocity less than 3 ml/min. Keep the column flat for 20 min while it activates. The column shall be kept in stand-by mode after activation.

#### 7.3.3 Activation of the Ag/H filter column

Flush the Ag/H filter column with 10 ml water (5.1) before use; keep the water outflow velocity less than 3 ml/min. The column shall be kept on stand-by after activation.

### 7.4 Preparation of the test solution

Accurately weigh to 0,000 2 g an appropriate amount (1 g to 2 g) of the ground test portion into a 100 ml volumetric flask and add water (5.1) to near 100 ml mark.

Choose a sample weight that ensures the concentrations of ions of interest lie within the following ranges: $F^-$ (10 mg/kg to 2 000 mg/kg), $Cl^-$ (10 mg/kg to 20 000 mg/kg), $Br^-$ (20 mg/kg to 2 000 mg/kg), $I^-$ (20 mg/kg to 2 000 mg/kg), $NO_2^-$ (10 mg/kg to 2 000 mg/kg), $SCN^-$ (40 mg/kg to 2 000 mg/kg).

Dissolve using an ultrasonic bath for 30 min, and then allow the contents of the volumetric flask to reach the room temperature.

Dilute to volume with water (5.1), and mix thoroughly by shaking.

Centrifuge a 10 ml portion of the solution at a rotational speed of 4 000 r/min for 5 min to 10 min.

Remove 5 ml of supernatant from the centrifuge tube and filter with syringe-driven filter (6.6).

Filter the solution with tandem filter columns of SPE-C18 column (activated), Ba-ion filter column (activated) and Ag/H filter column (activated) respectively, keeping the solution outflow velocity less than 3 ml/min.

Discard the first 3 ml of filtrate and keep the remaining 1 ml to 2 ml solution for testing.

NOTE The SPE-C18 column is used to eliminate organic compounds as interferences in the test solution. The Ba-ion filter column is used to eliminate excess amounts of sulfate and phosphate in the test solution. The Ag/H filter column is used to eliminate excess chloride to accurately measure nitrite. The use of these filter columns is dependent upon the sample being tested.

## 7.5 Ion chromatography condition A (Gradient chromatography condition)

**7.5.1** Chromatographic column: hydroxide selective, gradient elution compatible, high capacity anion exchange column.

**7.5.2** Column temperature: 30 °C.

**7.5.3** Suppressor device: membrane-based self-regenerating anion suppressor device. An equivalent suppressor device may be used provided that comparable method detection limits can also be achieved and that adequate baseline stability is attained.

**7.5.4** Detector: electrical-conductivity detector with cell temperature held at 35 °C.

**7.5.5** Eluent: potassium hydroxide eluent (5.6); gradient elution schedule listed in Table 2.

**Table 2 — Gradient elution schedule**

| **Time**<br>min | **$OH^-$ concentration**<br>($mmol \cdot l^{-1}$) |
|---|---|
| 0,00 | 12 |
| 13,00 | 12 |
| 14,00 | 80 |
| 46,00 | 80 |
| 47,00 | 12 |
| 54,00 | 12 |

**7.5.6** Eluent flow rate: 1,0 ml/min.

**7.5.7** Injection volume: 25 µl. The injection volume can be adjusted according to the concentrations of ions of interest in the test solution.

Use the same size of sample loop for all standards, samples, and fortified samples. If removal of the background matrix is not around 100 %, increasing the sample loop size will increase the overall mass loading to the guard and the analytical columns, potentially saturating a column's exchange capacity and shifting retention times for the unknowns.

## 7.6 Ion chromatography condition B (Isocratic chromatography condition)

**7.6.1** Chromatographic column: carbonate selective, high capacity anion exchange column.

**7.6.2** Column temperature: 40 °C.

**7.6.3** Suppressor device: self-regenerating anion suppressor device. An equivalent suppressor device may be used provided that comparable method detection limits can also be achieved and that adequate baseline stability is attained.

**7.6.4** Detector: electrical-conductivity detector with cell temperature held at 35 °C.

**7.6.5** Eluent: carbonate eluent (5.7), isocratic elution.

**7.6.6** Eluent flow rate: 0,7 ml/min.

**7.6.7** Injection volume: 20 µl. The injection volume can be adjusted according to the concentrations of ions of interest in the test solution.

## 7.7 Determination of standard working solutions and sample test solutions

### 7.7.1 Determination of standard working solutions

Use $F^-$, $Cl^-$, $Br^-$, $I^-$, $NO_2^-$ and $SCN^-$ standard solutions (5.10) to prepare the mixed-anion standard working solutions given in Table 1. Plot the standard curves using the concentration of inorganic anions, corresponding to the peak heights/areas obtained in the test.

Filter the mixed-anion standard working solutions with syringe-driven filter and tandem filter columns of SPE-C18 column (activated) and Ba-ion filter column (activated), if necessary.

It is recommended to run a minimum of two standard curves for each set of unknowns, preferably at the beginning and end of each set of unknowns. Additional standard curves are recommended for large (>20) sets of unknowns.

### 7.7.2 Determination of sample test solutions

Test a blank solution and the sample test solutions under the same conditions as the standards. Use the retention times to identify the inorganic anions, and derive the concentrations of inorganic anions in the test solutions from the standard curves. Typical ion chromatograms are shown in Annex B (for gradient chromatography conditions) and Annex C (for isocratic chromatography conditions).

The blank solution is prepared in the same manner as the test solutions, except for adding any test samples.

If the response value (peak height/area) of any anion in a test solution exceeds the linear calibration range of a standard solution, appropriate dilutions should be prepared.

For the determination of anions in liquid fertilizer, the instrumental detection limit (IDL, D.3) should be verified before the analysis of the sample. For the determination of anions in liquid fertilizer containing $NO_3^-$, the proposed method (7.5 and 7.6) shall be carried on very carefully, and anions standard working solutions (5.10) shall be injected to identify the retention time of $Br^-$.

# 8 Calculation and expression of results

## 8.1 General

The mass fraction of fluoride ($F^-$), chloride ($Cl^-$), bromide ($Br^-$), iodide ($I^-$), nitrite ($NO_2^-$) and thiocyanate ($SCN^-$), $w$, in the unit of mg/kg, is calculated using Formula (1):

$$w = \frac{(\rho - \rho_0) \times V \times f}{m} \tag{1}$$

where

$\rho$ is the mass concentration of fluoride ($F^-$), chloride ($Cl^-$), bromide ($Br^-$), iodide ($I^-$), nitrite ($NO_2^-$) and thiocyanate ($SCN^-$), expressed in milligrams per litre (mg/l)of the test solutions;

$\rho_0$ is the mass concentration of fluoride ($F^-$), chloride ($Cl^-$), bromide ($Br^-$), iodide ($I^-$), nitrite ($NO_2^-$) and thiocyanate ($SCN^-$), expressed in milligrams per litre (mg/l) of the blank solution;

$V$ is the volume of the test/blank solutions, expressed in millilitres (ml);

$f$ is the dilution factor of the test solutions;

$m$ is the mass of the test portion, expresses in grams (g).

The determination result is the arithmetic average of two parallel determination results, and shall be rounded off to three significant figures.

## 8.2 Precision

### 8.2.1 Ring test

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

### 8.2.2 Repeatability, *r*

| Anions | $F^-$ | $Cl^-$ | $Br^-$ | $I^-$ | $NO_2^-$ | $SCN^-$ |
|---|---|---|---|---|---|---|
| Repeatability limit, *r*, mg/kg | 10,424 | $0{,}015\,\overline{X} + 9{,}685$ | $0{,}011\,\overline{X} + 1{,}336$ | $0{,}050\,\overline{X} + 2{,}310$ | $0{,}339\,\overline{X}^{0{,}882}$ | $0{,}140\,\overline{X}^{0{,}802}$ |

### 8.2.3 Reproducibility, *R*

| Anions | $F^-$ | $Cl^-$ | $Br^-$ | $I^-$ | $NO_2^-$ | $SCN^-$ |
|---|---|---|---|---|---|---|
| Reproducibility limit, *R*, mg/kg | $0{,}484\,\overline{X}^{0{,}889}$ | $0{,}137\,\overline{X} + 16{,}564$ | $0{,}056\,\overline{X} + 29{,}554$ | $0{,}255\,\overline{X} + 11{,}595$ | 20,020 | $0{,}168\,\overline{X} + 11{,}155$ |

# 9 Test report

The test report contains the following information, at a minimum:

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

b) test method used with reference to this document, i.e. ISO 20702:2017;

c) test results obtained (signal-to-noise ratio plots per unknown, instrument detection limits and percent recoveries are suggested to be presented, if necessary. An explanation of these statistical indices is provided in Annex D);

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

e) date of analysis completion;

f) whether or not the requirement of the repeatability limit is fulfilled;

g) all operating details not specified in this document, 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)

# Ring test report — Report of international laboratories ring test

## A.1 Overview

The international laboratories ring test of this document has been accomplished during March 2017 to May 2017. Fifteen laboratories participated in the two parallel tests on four test samples. This international ring test was conducted by Shanghai Research Institute of Chemical Industry, Co. Ltd. and Shanghai Entry-Exit Inspection and Quarantine Bureau, P. R. China. The statistician analysis and final report was prepared by Shanghai Research Institute of Chemical Industry, Co. Ltd.

The following are the 15 laboratories that participated in the two parallel tests on four samples:

- Central Institute for Supervising and Testing in Agriculture, National Reference Laboratory, Division of NRL Brno, Czech Republic;
- CF Industries Technical Service Laboratory, USA;
- China National Supervision and Testing Centre of Fine Chemicals;
- Hunan Testing Institute of Product and Commodity Supervision, P. R. China;
- Institution of Supervision and Inspection Product Quality of Guizhou Province, P. R. China;
- Metrohm China Limited;
- Ningbo Entry-Exit Inspection and Quarantine Bureau, P. R. China;
- Office of Indiana State Chemist, USA;
- Product Quality Supervising and Inspecting Centre of Taizhou city, P. R. China;
- Shaanxi Entry-Exit Inspection and Quarantine Bureau, P. R. China;
- Shandong Institute for Product Quality Inspection, P. R. China;
- Shanghai Research Institute of Chemical Industry, Co. Ltd., P. R. China;
- Shanghai Entry-Exit Inspection and Quarantine Bureau, P. R. China;
- Thermo Fisher Scientific Inc.;
- Yunnan Chemical Product Quality Supervision & Inspection Station, P. R. China.

NOTE Participating laboratories are listed in alphabetic order, which has no relation to the sequences listed in the tables below.

The test method described in this document was adopted for the determination of fluoride, chloride, bromide, iodide, nitrite and thiocyanate contents in the fertilizer samples.

Four different types of fertilizer samples were used during the ring test, each with several mean levels. The test samples were: sample A (ammonium phosphate), sample B (nitro-compound fertilizer), sample C (complex fertilizer) and sample D (potassium sulfate). The six anion contents to be determined and involved in the statistics in the four fertilizer samples generally lie in the range of 10 mg/kg to 1 700 mg/kg, and the standard working solutions in the standard were designed to cover the range of 0 mg/kg to 2 000 mg/kg.

The precision of the test results was evaluated based on ISO 5725-2.

## A.2 Statistical analysis of the test results of fluoride ($F^-$) contents

### A.2.1 Original test results

Fourteen laboratories participated in the determination of fluoride ($F^-$) contents in fertilizer test samples. The results are listed in Table A.1. The fluoride ($F^-$) contents in fertilizer sample B was determined to have the mean value over 2 000 mg/kg, which were used as training data and was not included in the statistics and calculation.

**Table A.1 — Original test results of the determination of fluoride ($F^-$) contents**

| **Laboratory** *i* | **Column used** | **Level *j*** | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | **A** mg/kg | | **B** mg/kg | | **C** mg/kg | | **D** mg/kg | |
| 1 | AS-18 | 255,2 | 257,4 | / | / | 164,0 | 157,0 | 58,95 | 70,05 |
| 2 | AS-18 | 252,6 | 265,1 | / | / | 209,8 | 245,5 | 83,90 | 94,30 |
| 3 | Metrosep A Supp 5 | 251,7 | 253,4 | / | / | 187,3 | 190,7 | 76,55 | 77,62 |
| 4 | AS-19 | 207,9 | 208,5 | / | / | 152,8 | 155,4 | 81,20 | 81,46 |
| 5 | AS-19 | 197,7 | 195,1 | / | / | 122,4 | 127,6 | 70,08 | 74,91 |
| 6 | AS-18 | 224,0 | 233,0 | / | / | 187,0 | 194,0 | 74,00 | 74,00 |
| 7 | AS-19 | 245,3 | 245,9 | / | / | 162,2 | 165,4 | 76,00 | 69,45 |
| 8 | AS-18 | 246,0 | 249,2 | / | / | 193,1 | 190,3 | 84,32 | 83,16 |
| 9 | AS-18 | 249,5 | 249,7 | / | / | 168,2 | 168,3 | 79,92 | 79,98 |
| 10 | AS-18 | 249,2 | 249,3 | / | / | 168,1 | 168,3 | 79,99 | 79,98 |
| 11 | AS-18 | 243,9 | 245,6 | / | / | 161,7 | 163,1 | 81,68 | 85,58 |
| 12 | Metrosep A Supp 7 | 167,2 | 125,0 | / | / | 139,3 | 139,3 | 64,67 | 64,07 |
| 13 | AS-19 | 235,4 | 250,0 | / | / | 165,6 | 159,5 | 70,63 | 72,47 |
| 14 | AS-18 | / | / | / | / | 325,1 | 301,3 | 82,59 | 73,22 |

### A.2.2 Cell means by laboratory

The cell means (means of the analyses) by laboratory for the determination of fluoride ($F^-$) contents are listed in Table A.2.

**Table A.2 — Cell means of the determination of fluoride ($F^-$) contents**

| **Laboratory** *i* | **Level *j*** | | | |
|---|---|---|---|---|
| | **A** mg/kg | **B** mg/kg | **C** mg/kg | **D** mg/kg |
| 1 | 256,30 | / | 160,45 | 64,500 |
| 2 | 258,85 | / | 227,65 | 89,100 |
| 3 | 252,55 | / | 189,00 | 77,085 |
| 4 | 208,20 | / | 154,10 | 81,330 |
| 5 | 196,40 | / | 125,00 | 72,495 |
| 6 | 228,50 | / | 190,50 | 74,000 |
| 7 | 245,60 | / | 163,80 | 72,725 |
| 8 | 247,60 | / | 191,70 | 83,740 |

**Table A.2** *(continued)*

| Laboratory<br>*i* | Level *j* | | | |
|---|---|---|---|---|
| | **A**<br>mg/kg | **B**<br>mg/kg | **C**<br>mg/kg | **D**<br>mg/kg |
| 9 | 249,60 | / | 168,25 | 79,950 |
| 10 | 249,25 | / | 168,20 | 79,985 |
| 11 | 244,75 | / | 162,42 | 83,630 |
| 12 | 146,10 | / | 139,30 | 64,370 |
| 13 | 242,70 | / | 162,55 | 71,550 |
| 14 | / | / | 313,20 | 77,905 |

### A.2.3 Cell absolute differences of the analyses by laboratory

The cell absolute differences of the analyses by laboratory for the determination of fluoride ($F^-$) contents are listed in Table A.3.

**Table A.3 — Cell absolute differences of the determination of fluoride ($F^-$) contents**

| Laboratory<br>*i* | Level *j* | | | |
|---|---|---|---|---|
| | **A**<br>mg/kg | **B**<br>mg/kg | **C**<br>mg/kg | **D**<br>mg/kg |
| 1 | 2,20 | / | 7,00 | 11,10 |
| 2 | 12,50 | / | 35,70 | 10,40 |
| 3 | 1,70 | / | 3,40 | 1,07 |
| 4 | 0,60 | / | 2,60 | 0,26 |
| 5 | 2,60 | / | 5,20 | 4,83 |
| 6 | 9,00 | / | 7,00 | 0,00 |
| 7 | 0,60 | / | 3,20 | 6,55 |
| 8 | 3,20 | / | 2,80 | 1,16 |
| 9 | 0,20 | / | 0,10 | 0,06 |
| 10 | 0,10 | / | 0,20 | 0,01 |
| 11 | 1,70 | / | 1,38 | 3,90 |
| 12 | 42,20 | / | 0,00 | 0,60 |
| 13 | 14,60 | / | 6,10 | 1,84 |
| 14 | / | / | 23,80 | 9,37 |

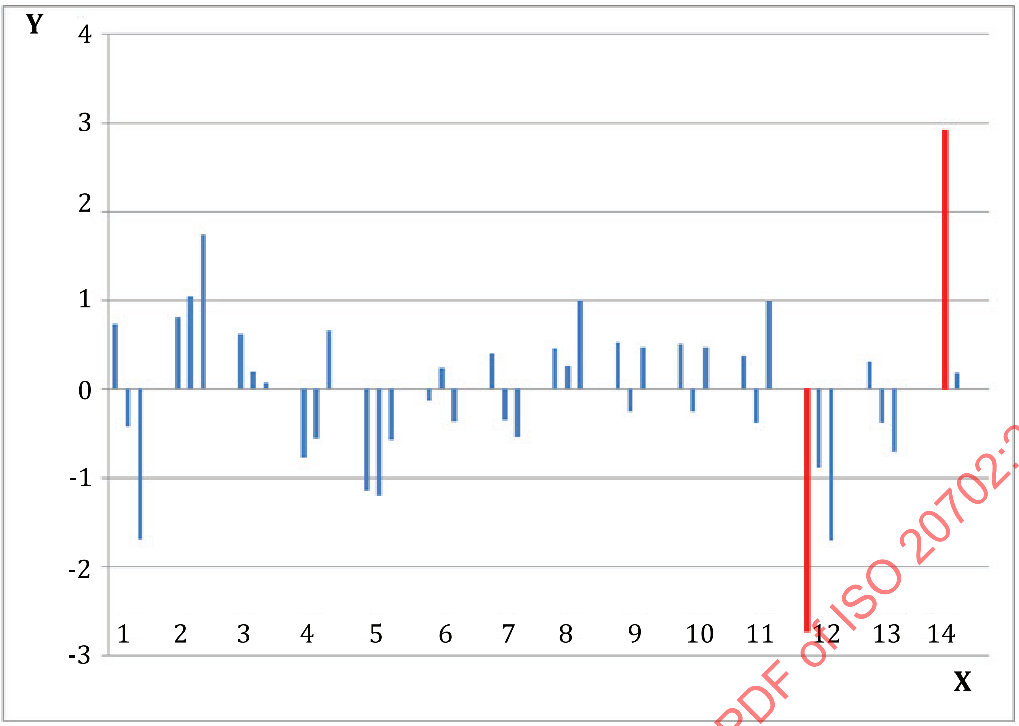
### A.2.4 Evaluation of the results for consistency and outliers

Graphical evaluations of the analytical results for consistency by Mandel's *h* and *k* statistics were studied.

The inter-laboratory consistency statistic *h* and the intra-laboratory consistency statistic *k*, for each level of each laboratory were calculated. The *h* and *k* values for each cell for the respective laboratories were plotted to obtain the Mandel's *h* and *k* graphs shown in Figures A.1 to A.12.

The Mandel's inter-laboratory consistency statistic *h* graph (Figure A.1) indicated that laboratory 12 had one outlier on level A and laboratory 14 had one outlier on level C.

The Mandel's intra-laboratory consistency statistic *k* graph (Figure A.2) exhibited rather large variability between replicate test results for laboratory 12 on level A (outlier) and laboratory 2 on level C (outlier); while laboratory 14 had one straggler on level C, and laboratory 1 and 2 both had one straggler on level D.

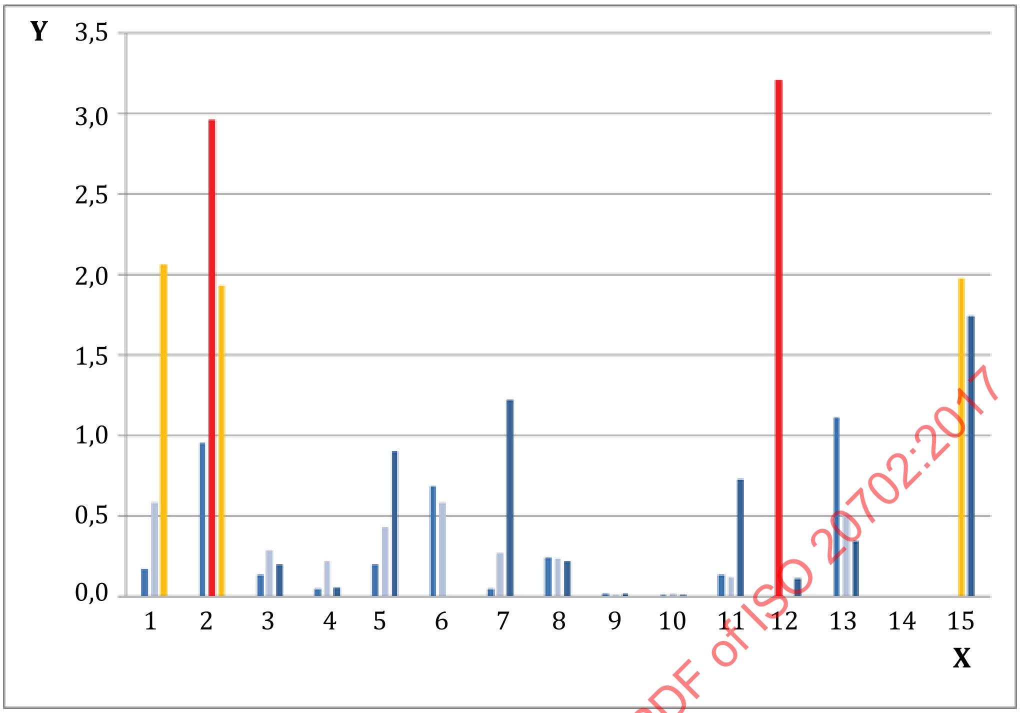


**Key**

X laboratory, *i*

Y Mandel's statistic, *h*

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



**Key**

X laboratory, *i*

Y Mandel's statistic, *k*

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

**Cochran's test**

Cochran's test is the test of the intra-laboratory variability and should be applied first, then any necessary action should be taken, and also with repeated tests if necessary.

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***<br>Before scrutiny | **A** | **B** | **C** | **D** | **Type of test** |
|---|---|---|---|---|---|
| C (Cochran) | 0,788 | / | 0,624 | 0,303 | Cochran's test statistics |
| Stragglers<br>(5 %) | 0,515 (*p* = 13, *n* = 2) | / | 0,492 (*p* = 14, *n* = 2) | 0,492 (*p* = 14, *n* = 2) | Cochran's critical values |
| Outliers<br>(1 %) | 0,624 (*p* = 13, *n* = 2) | / | 0,599 (*p* = 14, *n* = 2) | 0,599 (*p* = 14, *n* = 2) | Cochran's critical values |
| **Level *j***<br>After scrutiny | **A** | **B** | **C** | **D** | **Type of test** |
| C (Cochran) | 0,445 | / | 0,244 | 0,303 | Cochran's test statistics |
| Stragglers<br>(5 %) | 0,541 (*p* = 12, *n* = 2) | / | 0,541 (*p* = 12, *n* = 2) | 0,492 (*p* = 14, *n* = 2) | Cochran's critical values |
| Outliers<br>(1 %) | 0,653 (*p* = 12, *n* = 2) | / | 0,653 (*p* = 12, *n* = 2) | 0,599 (*p* = 14, *n* = 2) | Cochran's critical values |

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 showed that the test statistic reached 0,788, calculated by the maximum cell absolute difference (42,20) from laboratory 12 on level A.

Cochran's critical value at the 1 % significance level was 0,624, for $p$ = 13 and $n$ = 2; therefore, the test result from laboratory 12 on level A is an outlier, which should be discarded here.

Cochran's test showed that the test statistic reached 0,624, calculated by the maximum cell absolute difference (35,70) from laboratory 2 on level C.

Cochran's critical value at the 1 % significance level was 0,559, for $p$ = 14 and $n$ = 2; therefore, the test result from laboratory 2 on level C is an outlier, which should be discarded here.

Accordingly, for laboratory 12, level A was eliminated from their results, and for laboratory 2, level C was eliminated from their results.

Cochran's tests ($p$ = 12, $n$ = 2) were repeated on the remaining tests values from the 12 laboratories on level A. The test statistic obtained this time was 0,445. The values is less than Cochran's critical value at the 1 % significance level (0,653, $p$ = 12, $n$ = 2). This confirmed that no outlier existed in level A anymore.

Cochran's tests ($p$ = 13, $n$ = 2) were repeated on the remaining tests values from the 13 laboratories on level C. The test statistic obtained this time was 0,739, which is still larger than Cochran's critical value at the 1 % significance level (0,624, $p$ = 13, $n$ = 2), caused by the maximum cell absolute difference (23,80) from laboratory 14 on level C this time. Therefore, the test result from laboratory 14 on level C is also an outlier, which should be discarded here.

Cochran's tests ($p$ = 12, $n$ = 2) were repeated on the remaining tests values from the rest of the 12 laboratories on level C. The test statistic obtained this time was 0,244. The values are less than Cochran's critical value at the 1 % significance level (0,653, $p$ = 12, $n$ = 2). This confirmed that no outlier existed in level C anymore.

### Grubbs' test

Grubbs' test is primarily a test of inter-laboratory variability. The test data used herein are those which have passed Cochran's 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 ; 12 | 2,254 | 0,973 | 0,835 0 | 0,156 8 | Grubbs' test statistics |
| B | / | / | / | / | |
| C ; 12 | 1,987 | 1,359 | 0,625 9 | 0,405 8 | |
| D ; 14 | 1,711 | 1,750 | 0,647 5 | 0,486 2 | |
| Stragglers (5 %) | | | | | Grubbs' critical values |
| $p$ = 12 | 2,412 | 2,412 | 0,253 7 | 0,253 7 | |
| $p$ = 14 | 2,507 | 2,507 | 0,311 2 | 0,311 2 | |
| Outliers (1 %) | | | | | |
| $p$ = 12 | 2,636 | 2,636 | 0,173 8 | 0,173 8 | |
| $p$ = 14 | 2,755 | 2,755 | 0,228 0 | 0,228 0 | |

For 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 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 confirms that there was no outlier.

### A.2.5 Calculation of the general mean and standard deviations

Calculation of the general mean, $s_r$, $s_R$ of fluoride (F⁻) contents in each sample listed in Table A.6.

**Table A.6 — Calculation results of the general mean, $s_r$, $s_R$ of fluoride (F⁻) contents**

| **Sample/Level** | **A** | **B** | **C** | **D** |
|---|---|---|---|---|
| Number of laboratories | 13 | / | 14 | 14 |
| Outliers | 1 | / | 2 | 0 |
| General mean, $\bar{x}$, mg/kg | 240,03 | / | 164,61 | 76,60 |
| Repeatability standard deviation, $s_r$, mg/kg | 4,47 | / | 2,89 | 3,81 |
| Reproducibility standard deviation, $s_R$, mg/kg | 19,61 | / | 20,04 | 7,64 |

### A.2.6 Dependence of precision on general mean (level), $\bar{x}$

As shown in Table A.6, the repeatability standard deviations, $s_r$, have shown no significant linear or logarithmic-linear relationship with the general mean (level), $\bar{x}$, so for all levels, the mean value of the repeatability standard deviation, $s_r$, is represented as the average value of $s_r$ listed in Table A.6.

The reproducibility standard deviations, $s_R$, show a logarithmic-linear relationship with the general mean (level), $\bar{x}$: $\log s_R = 0{,}889 \log \bar{x} - 0{,}761$, $R^2 = 0{,}882$

For all levels, the repeatability standard deviation, $s_r$ is 3,723.

For all levels, the reproducibility standard deviation, $s_R$ is $0{,}173\,\bar{x}^{0{,}889}$.

### A.2.7 Final values of precision

The precision of the fluoride (F⁻) contents measurements were discerned from Table A.6.

The conclusions above were determined from a uniform-level experiment involving 14 laboratories, in which one test value from laboratory 12 on level A, one test value from laboratory 2 and one test value from laboratory 14 on level C have been discarded as outliers.

The precision of the fluoride (F⁻) contents measurement method should be quoted as follows:

— repeatability standard deviation: $s_r = 3{,}723$,

— reproducibility standard deviation: $s_R = 0{,}173\,\bar{x}^{0{,}889}$.

## A.3 Statistical analysis of the test results of chloride (Cl⁻) contents

### A.3.1 Original test results

Fifteen laboratories participated in the determination of chloride (Cl⁻) contents in fertilizer test samples. The results are listed in Table A.7. The chloride (Cl⁻) contents in fertilizer sample B was determined to have the mean value over 2 000 mg/kg, which were used as training data and was not included in the statistics and calculation.

Table A.7 — Original test results of the determination of chloride ($Cl^-$) contents

| Laboratory *i* | Column used | Level *j* | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | A mg/kg | | B mg/kg | | C mg/kg | | D mg/kg | |
| 1 | AS-18 | 1 592 | 1 591 | / | / | 142,8 | 144,2 | 64,91 | 61,11 |
| 2 | AS-18 | 1 514 | 1 561 | / | / | 148,4 | 133,3 | 84,80 | 68,30 |
| 3 | Metrosep A Supp 5 | 1 493 | 1 493 | / | / | 129,1 | 128,3 | 62,18 | 63,21 |
| 4 | AS-19 | 1 495 | 1 495 | / | / | 138,1 | 139,5 | 74,98 | 75,30 |
| 5 | AS-19 | 1 673 | 1 642 | / | / | 159,4 | 163,0 | 53,90 | 55,99 |
| 6 | AS-18 | 1 503 | 1 506 | / | / | 135,0 | 133,0 | 60,00 | 60,00 |
| 7 | AS-19 | 1 520 | 1 522 | / | / | 130,8 | 130,2 | 57,41 | 57,19 |
| 8 | AS-18 | 1 581 | 1 599 | / | / | 132,2 | 128,4 | 68,73 | 63,60 |
| 9 | AS-18 | 1 661 | 1 661 | / | / | 115,5 | 115,8 | 75,05 | 75,08 |
| 10 | AS-18 | 1 661 | 1 661 | / | / | 115,4 | 115,7 | 65,10 | 65,08 |
| 11 | AS-18 | 1 511 | 1 518 | / | / | 136,1 | 138,6 | 62,24 | 62,69 |
| 12 | Metrosep A Supp 7 | 1 378 | 1 392 | / | / | 127,2 | 127,2 | 70,04 | 66,23 |
| 13 | AS-19 | 1 581 | 1 592 | / | / | 137,3 | 147,8 | 61,12 | 72,47 |
| 14 | Metrosep A Supp 5 | 1 460 | 1 463 | / | / | / | / | / | / |
| 15 | AS-18 | 1 482 | 1 563 | / | / | 163,0 | 167,0 | / | / |

## A.3.2 Cell means by laboratory

The cell means (means of the analyses) by laboratory for the determination of chloride ($Cl^-$) contents are listed in Table A.8.

Table A.8 — Cell means of the determination of chloride ($Cl^-$) contents

| Laboratory *i* | Level *j* | | | |
|---|---|---|---|---|
| | A mg/kg | B mg/kg | C mg/kg | D mg/kg |
| 1 | 1 591,5 | / | 143,50 | 63,010 |
| 2 | 1 537,5 | / | 140,85 | 76,550 |
| 3 | 1 493,0 | / | 128,70 | 62,695 |
| 4 | 1 495,0 | / | 138,80 | 75,140 |
| 5 | 1 657,5 | / | 161,20 | 54,945 |
| 6 | 1 504,5 | / | 134,00 | 60,000 |
| 7 | 1 521,0 | / | 130,50 | 57,300 |
| 8 | 1 590,0 | / | 130,30 | 66,165 |
| 9 | 1 661,0 | / | 115,65 | 75,065 |
| 10 | 1 661,0 | / | 115,55 | 65,090 |
| 11 | 1 514,5 | / | 137,35 | 62,465 |
| 12 | 1 385,0 | / | 127,20 | 68,135 |
| 13 | 1 586,5 | / | 142,55 | 66,795 |
| 14 | 1 461,5 | / | / | / |
| 15 | 1 522,5 | / | 165,00 | / |

### A.3.3 Cell absolute differences of the analyses by laboratory

The cell absolute differences of the analyses by laboratory for the determination of chloride ($Cl^-$) contents are listed in Table A.9.

**Table A.9 — Cell absolute differences of the determination of chloride ($Cl^-$) contents**

| Laboratory<br>*i* | Level *j* | | | |
|---|---|---|---|---|
| | A<br>mg/kg | B<br>mg/kg | C<br>mg/kg | D<br>mg/kg |
| 1 | 1 | / | 1,4 | 3,80 |
| 2 | 47 | / | 15,1 | 16,50 |
| 3 | 0 | / | 0,8 | 1,03 |
| 4 | 0 | / | 1,4 | 0,32 |
| 5 | 31 | / | 3,6 | 2,09 |
| 6 | 3 | / | 2,0 | 0,00 |
| 7 | 2 | / | 0,6 | 0,22 |
| 8 | 18 | / | 3,8 | 5,13 |
| 9 | 0 | / | 0,3 | 0,03 |
| 10 | 0 | / | 0,3 | 0,02 |
| 11 | 7 | / | 2,5 | 0,45 |
| 12 | 14 | / | 0,0 | 3,81 |
| 13 | 11 | / | 10,5 | 11,35 |
| 14 | 3 | / | / | / |
| 15 | 81 | / | 4,0 | / |

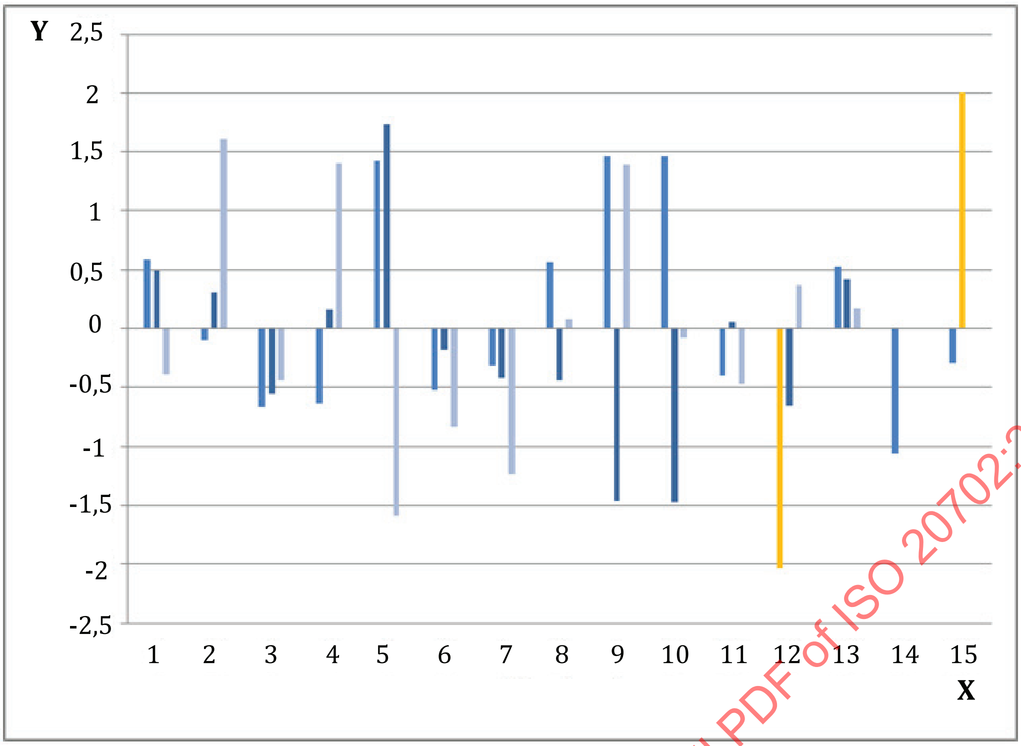
### A.3.4 Evaluation of the results for consistency and outliers

Graphical evaluation of the analytical results for consistency by Mandel's *h* and *k* statistics were studied:

The inter-laboratory consistency statistic *h* and the intra-laboratory consistency statistic *k*, for each level of each laboratory, were calculated. The *h* and *k* values for each cell for the respective laboratories were plotted to obtain the Mandel's *h* and *k* graphs.

The Mandel's inter-laboratory consistency statistic *h* graph (Figure A.3) indicated that laboratory 12 had one straggler on level A and laboratory 15 had one straggler on level C.

The Mandel's intra-laboratory consistency statistic *k* graph (Figure A.4) exhibited rather large variability between replicate test results for laboratory 2 on level C (outlier) and level D (outlier), and laboratory 15 on level A (outlier); while laboratory 13 had one straggler on level C.

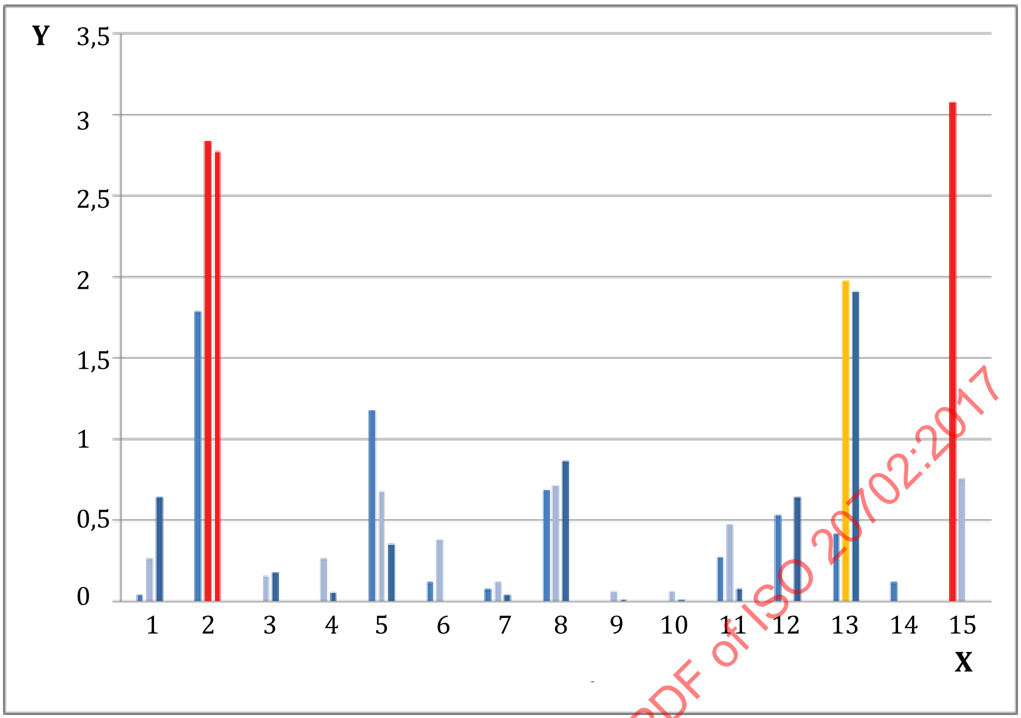


**Key**

X laboratory, *i*

Y Mandel's statistic, *h*

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



**Key**

X laboratory, *i*

Y Mandel's statistic, *k*

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

### Cochran's test

Cochran's test is the test of the intra-laboratory variability and should be applied first, then any necessary action should be taken, and also with repeated tests if necessary.

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*** Before scrutiny | **A** | **B** | **C** | **D** | **Type of test** |
|---|---|---|---|---|---|
| C (Cochran) | 0,628 | / | 0,574 | 0,589 | Cochran's test statistics |
| Stragglers (5 %) | 0,471 ($p$ = 15, $n$ = 2) | / | 0,492 ($p$ = 14, $n$ = 2) | 0,515 ($p$ = 13, $n$ = 2) | Cochran's critical values |
| Outliers (1 %) | 0,575 ($p$ = 15, $n$ = 2) | / | 0,599 ($p$ = 14, $n$ = 2) | 0,624 ($p$ = 13, $n$ = 2) | Cochran's critical values |
| **Level *j*** After scrutiny | **A** | **B** | **C** | **D** | **Type of test** |
| C (Cochran) | 0,569 | / | 0,574 | 0,589 | Cochran's test statistics |
| Stragglers (5 %) | 0,492 ($p$ = 14, $n$ = 2) | / | 0,492 ($p$ = 14, $n$ = 2) | 0,515 ($p$ = 13, $n$ = 2) | Cochran's critical values |
| Outliers (1 %) | 0,599 ($p$ = 14, $n$ = 2) | / | 0,599 ($p$ = 14, $n$ = 2) | 0,624 ($p$ = 13, $n$ = 2) | Cochran's critical values |

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 showed that the test statistic reached 0,628, calculated by the maximum cell absolute difference (1 482, 1 563) from laboratory 15 on level A.

Cochran's critical value at the 1 % significance level was 0,575, for $p = 15$ and $n = 2$; therefore, the test result from laboratory 15 on level A is an outlier, which should be discarded here.

Accordingly, for laboratory 15, level A was eliminated from their results.

Cochran's tests ($p = 14$, $n = 2$) were repeated on the remaining tests values from the 15 laboratories on level A. The test statistic obtained this time was 0,569. The values is less than Cochran's critical value at the 1 % significance level (0,599, $p = 14$, $n = 2$). This confirmed that no outlier existed in level A anymore.

**Grubbs' test**

Grubbs' test is primarily a test of inter-laboratory variability. The test data used herein are those which have passed Cochran's 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 ; 14 | 1,989 | 1,397 | 0,658 1 | 0,559 0 | Grubbs' test statistics |
| B | / | / | / | / | |
| C ; 14 | 1,472 | 2,001 | 0,375 9 | 0,620 7 | |
| D ; 13 | 1,584 | 1,615 | 0,557 4 | 0,613 1 | |
| Stragglers (5 %) | | | | | Grubbs' critical values |
| $p = 13$ | 2,462 | 2,462 | 0,283 6 | 0,283 6 | |
| $p = 14$ | 2,507 | 2,507 | 0,311 2 | 0,311 2 | |
| Outliers (1 %) | | | | | |
| $p = 13$ | 2,699 | 2,699 | 0,201 6 | 0,201 6 | |
| $p = 14$ | 2,755 | 2,755 | 0,228 0 | 0,228 0 | |

For 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 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 confirmed that there was no outlier.

### A.3.5 Calculation of the general mean and standard deviations

Calculation of the general mean, $s_r$, $s_R$ of chloride ($\text{Cl}^-$) contents in each sample listed in Table A.12.

**Table A.12 — Calculation results of the general mean, $s_r$, $s_R$ of chloride (Cl$^-$) contents**

| **Sample/Level** | **A** | **B** | **C** | **D** |
|---|---|---|---|---|
| Number of laboratories | 14 | / | 14 | 13 |
| Outliers | 1 | / | 0 | 0 |
| General mean, $\bar{x}$, mg/kg | 1 547 | / | 136,5 | 65,64 |
| Repeatability standard deviation, $s_r$, mg/kg | 11,78 | / | 3,77 | 4,22 |
| Reproducibility standard deviation, $s_R$, mg/kg | 81,95 | / | 14,48 | 7,38 |

### A.3.6 Dependence of precision on general mean (level), $\bar{x}$

As shown in Table A.12, the repeatability standard deviations, $s_r$, show a linear relationship with the general mean (level), $\bar{x}$ : $s_r = 0{,}005\,\bar{x} + 3{,}459$, $R^2 = 0{,}991$

The reproducibility standard deviations, $s_R$, show a linear relationship with the general mean (level), $\bar{x}$ : $s_R = 0{,}049\,\bar{x} + 5{,}916$, $R^2 = 0{,}998$

For all levels, the repeatability standard deviation $s_r$ is $0{,}005\,\bar{x} + 3{,}459$.

For all levels, the reproducibility standard deviation $s_R$ is $0{,}049\,\bar{x} + 5{,}916$.

### A.3.7 Final values of precision

The precision of the chloride (Cl$^-$) contents measurements were discerned from Table A.12.

The conclusions above were determined from a uniform-level experiment involving 15 laboratories, in which one test value from laboratory 15 on level A has been discarded as outliers.

The precision of the chloride (Cl$^-$) contents measurement method should be quoted as follows:

— repeatability standard deviation: $s_r = 0{,}005\,\bar{x} + 3{,}459$.

— reproducibility standard deviation: $s_R = 0{,}049\,\bar{x} + 5{,}916$.

## A.4 Statistical analysis of the test results of bromide (Br$^-$) contents

### A.4.1 Original test results

Fifteen laboratories participated in the determination of bromide (Br$^-$) contents in fertilizer test samples. The results are listed in Table A.13. The bromide (Br$^-$) contents in fertilizer sample B was determined to have the mean value over 2 000 mg/kg, which were used as training data and was not included in the statistics and calculation.

**Table A.13 — Original test results of the determination of bromide ($Br^-$) contents**

| Laboratory<br>*i* | Column used | Level *j* | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | A<br>mg/kg | | B<br>mg/kg | | C<br>mg/kg | | D<br>mg/kg | |
| 1 | AS-18 | 1 609 | 1 601 | / | / | 119,2 | 118,8 | 62,51 | 65,28 |
| 2 | AS-18 | 1 543 | 1 558 | / | / | 90,20 | 90,90 | 37,00 | 36,50 |
| 3 | Metrosep A Supp 5 | 1 530 | 1 531 | / | / | 114,1 | 114,3 | 57,62 | 55,44 |
| 4 | AS-19 | 1 577 | 1 579 | / | / | 97,25 | 97,81 | 51,07 | 51,43 |
| 5 | AS-19 | 1 615 | 1 628 | / | / | 94,65 | 96,38 | 52,34 | 52,18 |
| 6 | AS-18 | 1 521 | 1 511 | / | / | 101,0 | 101,0 | 52,00 | 53,00 |
| 7 | AS-19 | 1 559 | 1 559 | / | / | 117,7 | 118,6 | 71,26 | 71,86 |
| 8 | AS-18 | 1 620 | 1 648 | / | / | 105,7 | 108,2 | 48,21 | 49,98 |
| 9 | AS-18 | 1 542 | 1 542 | / | / | 112,1 | 112,2 | 44,84 | 44,90 |
| 10 | AS-18 | 1 542 | 1 542 | / | / | 112,0 | 112,2 | 44,74 | 44,77 |
| 11 | AS-18 | 1 601 | 1 607 | / | / | 108,2 | 108,3 | 51,56 | 51,31 |
| 12 | Metrosep A Supp 7 | 1 487 | 1 505 | / | / | 111,6 | 111,6 | 73,94 | 63,81 |
| 13 | AS-19 | 1 551 | 1 550 | / | / | 106,2 | 132,9 | 48,78 | 46,77 |
| 14 | Metrosep A Supp 5 | 1 846 | 1 782 | / | / | / | / | / | / |
| 15 | AS-18 | 1 215 | 1 186 | / | / | 67,46 | 69,74 | 31,14 | 31,32 |

### A.4.2 Cell means by laboratory

The cell means (means of the analyses) by laboratory for the determination of bromide ($Br^-$) contents are listed in Table A.14.

**Table A.14 — Cell means of the determination of bromide ($Br^-$) contents**

| Laboratory<br>*i* | Level *j* | | | |
|---|---|---|---|---|
| | A<br>mg/kg | B<br>mg/kg | C<br>mg/kg | D<br>mg/kg |
| 1 | 1 605,0 | / | 119,00 | 63,895 |
| 2 | 1 550,5 | / | 90,550 | 36,750 |
| 3 | 1 530,5 | / | 114,20 | 56,530 |
| 4 | 1 578,0 | / | 97,530 | 51,250 |
| 5 | 1 621,5 | / | 95,515 | 52,260 |
| 6 | 1 516,0 | / | 101,00 | 52,500 |
| 7 | 1 559,0 | / | 118,15 | 71,560 |
| 8 | 1 634,0 | / | 106,95 | 49,095 |
| 9 | 1 542,0 | / | 112,15 | 44,870 |
| 10 | 1 542,0 | / | 112,10 | 44,755 |
| 11 | 1 604,0 | / | 108,25 | 51,435 |
| 12 | 1 496,0 | / | 111,60 | 68,875 |

**Table A.14** *(continued)*

| Laboratory<br>*i* | Level *j* | | | |
|---|---|---|---|---|
| | A<br>mg/kg | B<br>mg/kg | C<br>mg/kg | D<br>mg/kg |
| 13 | 1 550,5 | / | 119,55 | 47,775 |
| 14 | 1 814,0 | / | / | / |
| 15 | 1 200,5 | / | 68,600 | 31,230 |

## A.4.3 Cell absolute differences of the analyses by laboratory

The cell absolute differences of the analyses by laboratory for the determination of bromide ($Br^-$) contents are listed in Table A.15.

**Table A.15 — Cell absolute differences of the determination of bromide ($Br^-$) contents**

| Laboratory<br>*i* | Level *j* | | | |
|---|---|---|---|---|
| | A<br>mg/kg | B<br>mg/kg | C<br>mg/kg | D<br>mg/kg |
| 1 | 8 | / | 0,4 | 2,77 |
| 2 | 15 | / | 0,70 | 0,50 |
| 3 | 1 | / | 0,2 | 2,18 |
| 4 | 2 | / | 0,56 | 0,36 |
| 5 | 13 | / | 1,73 | 0,16 |
| 6 | 10 | / | 0,0 | 1,00 |
| 7 | 0 | / | 0,9 | 0,60 |
| 8 | 28 | / | 2,5 | 1,77 |
| 9 | 0 | / | 0,1 | 0,06 |
| 10 | 0 | / | 0,2 | 0,03 |
| 11 | 6 | / | 0,1 | 0,25 |
| 12 | 18 | / | 0,0 | 10,13 |
| 13 | 1 | / | 26,7 | 2,01 |
| 14 | 64 | / | / | / |
| 15 | 29 | / | 2,28 | 0,18 |

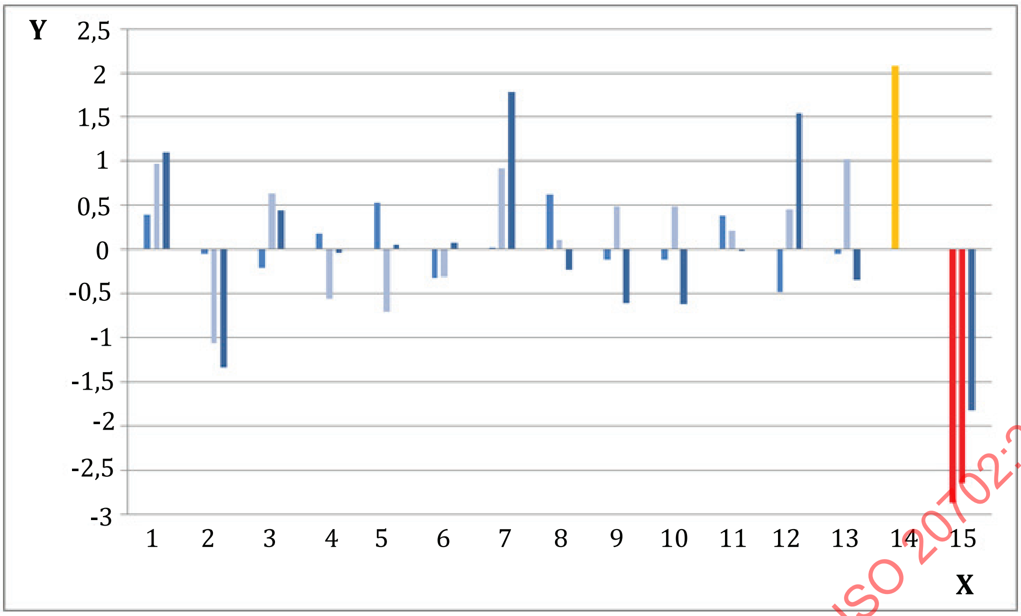
## A.4.4 Evaluation of the results for consistency and outliers

Graphical evaluation of the analytical results for consistency by Mandel's *h* and *k* statistics were studied.

The inter-laboratory consistency statistic *h* and the intra-laboratory consistency statistic *k*, for each level of each laboratory, were calculated. The *h* and *k* values for each cell for the respective laboratories were plotted to obtain the Mandel's *h* and *k* graphs.

The Mandel's inter-laboratory consistency statistic *h* (Figure A.5) graph indicated that laboratory 15 had one outlier on level A and one outlier on level C, laboratory 14 had one straggler on level A.

The Mandel's intra-laboratory consistency statistic *k* (Figure A.6) graph exhibited rather large variability between replicate test results for laboratory 12 on level D (outlier), laboratory 13 on level C (outlier); and laboratory 14 on level A (outlier).

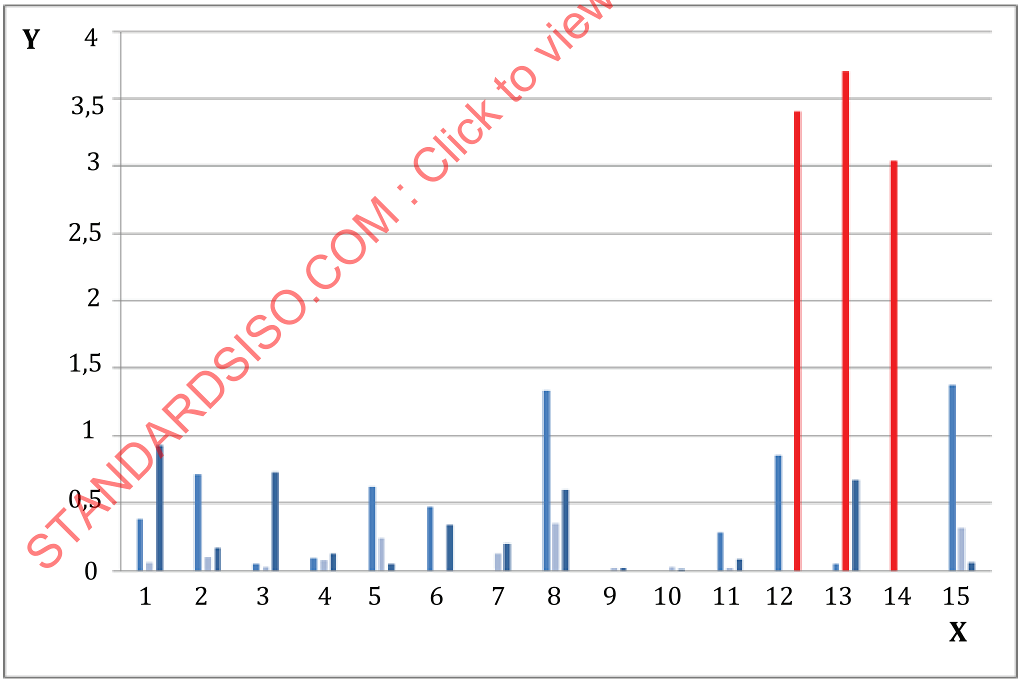


**Key**

X laboratory, *i*

Y Mandel's statistic, *h*

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



**Key**

X laboratory, *i*

Y Mandel's statistic, *k*

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

### Cochran's test

Cochran's test is the test of the intra-laboratory variability and should be applied first, then any necessary action should be taken, and also with repeated tests if necessary.

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***<br>Before scrutiny | **A** | **B** | **C** | **D** | **Type of test** |
|---|---|---|---|---|---|
| C (Cochran) | 0,616 | / | 0,978 | 0,827 | Cochran's test statistics |
| Stragglers<br>(5 %) | 0,471 ($p$ = 15, $n$ = 2) | / | 0,492 ($p$ = 14, $n$ = 2) | 0,492 ($p$ = 14, $n$ = 2) | Cochran's critical values |
| Outliers<br>(1 %) | 0,575 ($p$ = 15, $n$ = 2) | / | 0,599 ($p$ = 14, $n$ = 2) | 0,599 ($p$ = 14, $n$ = 2) | Cochran's critical values |
| **Level *j***<br>After scrutiny | **A** | **B** | **C** | **D** | **Type of test** |
| C (Cochran) | 0,330 | / | 0,383 | 0,357 | Cochran's test statistics |
| Stragglers<br>(5 %) | 0,492 ($p$ = 14, $n$ = 2) | / | 0,515 ($p$ = 13, $n$ = 2) | 0,515 ($p$ = 13, $n$ = 2) | Cochran's critical values |
| Outliers<br>(1 %) | 0,599 ($p$ = 14, $n$ = 2) | / | 0,624 ($p$ = 13, $n$ = 2) | 0,624 ($p$ = 13, $n$ = 2) | Cochran's critical values |

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 showed that the test statistic reached 0,616, calculated by the maximum cell absolute difference (1 846, 1 782) from laboratory 14 on level A.

Cochran's critical value at the 1 % significance level was 0,575, for $p$ = 15 and $n$ = 2; therefore, the test result from laboratory 14 on level A is an outlier, which should be discarded here.

Accordingly, for laboratory 14, level A was eliminated from their results.

Cochran's tests ($p$ = 14, $n$ = 2) were repeated on the remaining tests values from the 14 laboratories on level A. The test statistic obtained this time was 0,330. The values is less than Cochran's critical value at the 1 % significance level (0,599, $p$ = 14, $n$ = 2). This confirmed that no outlier existed in level A anymore.

Cochran's test showed that the test statistic reached 0,978, calculated by the maximum cell absolute difference (106,2, 132,9) from laboratory 13 on level C.

Cochran's critical value at the 1 % significance level was 0,599, for $p$ = 14 and $n$ = 2; therefore, the test result from laboratory 13 on level C is an outlier, which should be discarded here.

Accordingly, for laboratory 13, level C was eliminated from their results.

Cochran's tests ($p$ = 13, $n$ = 2) were repeated on the remaining tests values from the 13 laboratories on level C. The test statistic obtained this time was 0,383. The values is less than Cochran's critical value at the 1 % significance level (0,624, $p$ = 13, $n$ = 2). This confirmed that no outlier existed in level C anymore.

Cochran’s test showed that the test statistic reached 0,827, calculated by the maximum cell absolute difference (73,94, 63,81) from laboratory 12 on level D.

Cochran’s critical value at the 1 % significance level was 0,599, for $p = 14$ and $n = 2$; therefore, the test result from laboratory 12 on level D is an outlier, which should be discarded here.

Accordingly, for laboratory 12, level C was eliminated from their results.

Cochran’s tests ($p = 13$, $n = 2$) were repeated on the remaining tests values from the 13 laboratories on level C. The test statistic obtained this time was 0,357. The values is less than Cochran’s critical value at the 1 % significance level (0,624, $p = 13$, $n = 2$). This confirmed that no outlier existed in level D anymore.

**Grubbs’ test**

Grubbs’ test is primarily a test of inter-laboratory variability. The test data used herein are those which have passed Cochran’s 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***<br>Before scrutiny | **Single low** | **Single high** | **Double low** | **Double high** | **Type of test** |
|---|---|---|---|---|---|
| A ; 14 | 3,209 | 0,915 | / | / | Grubbs’ test statistics |
| B | / | / | / | / | |
| C ; 13 | 2,576 | 1,063 | 0,789 9 | 0,268 8 | |
| D ; 13 | 1,831 | 2,041 | 0,426 0 | 0,505 3 | |
| Stragglers (5 %) | | | | | Grubbs’ critical values |
| $p = 14$ | 2,507 | 2,507 | / | / | |
| $p = 13$ | 2,462 | 2,462 | 0,311 2 | 0,311 2 | |
| Outliers (1 %) | | | | | |
| $p = 14$ | 2,755 | 2,755 | / | / | |
| $p = 13$ | 2,699 | 2,699 | 0,228 0 | 0,228 0 | |
| **Level *j* ; *p***<br>After scrutiny | **Single low** | **Single high** | **Double low** | **Double high** | **Type of test** |
| A ; 13 | 1,617 | 1,675 | 0,537 5 | 0,616 5 | Grubbs’ test statistics |
| B | / | / | / | / | |
| C ; 13 | 2,576 | 1,063 | 0,789 9 | 0,268 8 | |
| D ; 13 | 1,831 | 2,041 | 0,426 0 | 0,505 3 | |
| Stragglers (5 %) | | | | | Grubbs’ critical values |
| $p = 13$ | 2,462 | 2,462 | 0,283 6 | 0,283 6 | |
| Outliers (1 %) | | | | | |
| $p = 13$ | 2,699 | 2,699 | 0,201 6 | 0,201 6 | |

For 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 level A, the single low test statistic reached 3,209, while Grubbs’ critical value at the 1 % significance level was 2,755, for $p = 14$; therefore, the smallest test result in level A (from laboratory 15) is an outlier, which should be discarded here.

Accordingly, for laboratory 15, level A was eliminated from their results.

Grubbs' test for one outlying observation ($p = 13$) was repeated on the remaining tests values from the 13 laboratories on level A. The single low test statistic obtained this time was 1,617. The values is less than Grubbs' single low critical value at the 1 % significance level (2,699, $p = 13$). This confirmed that no outlier existed in level A anymore.

For 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 for two outlying observation to our cell means confirmed that there was no outlier.

### A.4.5 Calculation of the general mean and standard deviations

Calculation of the general mean, $s_r$, $s_R$ of bromide ($Br^-$) contents in each sample listed in Table A.18.

**Table A.18 — Calculation results of the general mean, $s_r$, $s_R$ of bromide ($Br^-$) contents**

| **Sample/Level** | **A** | **B** | **C** | **D** |
|---|---|---|---|---|
| Number of laboratories | 15 | / | 14 | 14 |
| Outliers | 2 | / | 1 | 1 |
| General mean, $\overline{x}$, mg/kg | 1 564 | / | 104,3 | 50,30 |
| Repeatability standard deviation, $s_r$, mg/kg | 8,11 | / | 0,79 | 0,91 |
| Reproducibility standard deviation, $s_R$, mg/kg | 42,31 | / | 13,86 | 10,44 |

### A.4.6 Dependence of precision on general mean (level), $\overline{x}$

As shown in Table A.18, the repeatability standard deviations, $s_r$, show a linear relationship with the general mean (level), $\overline{x}$ : $s_r = 0{,}004\,\overline{x} + 0{,}477$, $R^2 = 0{,}997$

The reproducibility standard deviations, $s_R$, show a linear relationship with the general mean (level), $\overline{x}$ $s_R = 0{,}020\,\overline{x} + 10{,}55$, $R^2 = 0{,}995$

For all levels, the repeatability standard deviation $s_r$ is $0{,}004\,\overline{x} + 0{,}477$.

For all levels, the reproducibility standard deviation $s_R$ is $0{,}020\,\overline{x} + 10{,}555$.

### A.4.7 Final values of precision

The precision of the bromide ($Br^-$) contents measurements were discerned from Table A.18.

The conclusions above were determined from a uniform-level experiment involving 15 laboratories, in which one test value from laboratory 14 and one test value from laboratory 15 on level A, one test value from laboratory 13 on level C, one test value from laboratory 12 on level D have been discarded as outliers.

The precision of the bromide ($Br^-$) contents measurement method should be quoted as follows:

- repeatability standard deviation: $s_r = 0{,}004\,\overline{x} + 0{,}477$.
- reproducibility standard deviation: $s_R = 0{,}020\,\overline{x} + 10{,}555$.

## A.5 Statistical analysis of the test results of iodide ($I^-$) contents

### A.5.1 Original test results

Fifteen laboratories participated in the determination of iodide ($I^-$) contents in fertilizer test samples. The results are listed in Table A.19.

**Table A.19 — Original test results of the determination of iodide ($I^-$) contents**

| Laboratory<br>*i* | Column used | Level *j* | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | A<br>mg/kg | | B<br>mg/kg | | C<br>mg/kg | | D<br>mg/kg | |
| 1 | AS-18 | 1 850 | 1 844 | 254,2 | 265,6 | 130,5 | 132,9 | 71,55 | 76,61 |
| 2 | AS-18 | 1 744 | 1 759 | 221,7 | 247,4 | 113,2 | 121,9 | 57,20 | 58,90 |
| 3 | Metrosep A Supp 5 | 1 633 | 1 649 | 270,2 | 267,5 | 134,2 | 132,4 | 63,21 | 63,93 |
| 4 | AS-19 | 1 601 | 1 609 | 208,8 | 204,8 | 85,43 | 86,10 | / | / |
| 5 | AS-18 | 1 525 | 1 536 | 181,0 | 180,0 | 107,0 | 105,0 | / | / |
| 6 | AS-18 | 1 824 | 1 796 | 230,1 | 238,6 | 118,0 | 119,8 | 62,76 | 63,50 |
| 7 | AS-18 | 1 750 | 1 751 | 219,7 | 220,4 | 121,8 | 122,0 | 69,95 | 69,95 |
| 8 | AS-18 | 1 750 | 1 751 | 219,6 | 220,3 | 121,9 | 122,1 | 69,99 | 69,95 |
| 9 | AS-18 | 1 663 | 1 612 | 240,0 | 229,0 | 135,7 | 135,7 | 64,18 | 70,94 |
| 10 | Metrosep A Supp 7 | 1 626 | 1 642 | 212,8 | 214,7 | 121,4 | 121,4 | / | / |
| 11 | AS-19 | 1 603 | 1 709 | 200,4 | 277,2 | 99,78 | 101,1 | 49,15 | 49,01 |
| 12 | AS-18 | 1 219 | 1 310 | / | / | / | / | / | / |

### A.5.2 Cell means by laboratory

The cell means (means of the analyses) by laboratory for the determination of iodide ($I^-$) contents are listed in Table A.20.

**Table A.20 — Cell means of the determination of iodide ($I^-$) contents**

| Laboratory<br>*i* | Level *j* | | | |
|---|---|---|---|---|
| | A<br>mg/kg | B<br>mg/kg | C<br>mg/kg | D<br>mg/kg |
| 1 | 1 847,0 | 259,90 | 131,72 | 74,080 |
| 2 | 1 751,5 | 234,55 | 117,55 | 58,050 |
| 3 | 1 641,0 | 268,85 | 133,30 | 63,570 |
| 4 | 1 605,0 | 206,80 | 85,765 | / |
| 5 | 1 530,5 | 180,50 | 106,00 | / |
| 6 | 1 810,0 | 234,35 | 118,90 | 63,130 |
| 7 | 1 750,5 | 220,05 | 121,90 | 69,950 |
| 8 | 1 750,5 | 219,95 | 122,00 | 69,970 |
| 9 | 1 637,5 | 234,50 | 135,69 | 67,560 |
| 10 | 1 634,0 | 213,75 | 121,40 | / |
| 11 | 1 656,0 | 238,80 | 100,44 | 49,080 |
| 12 | 1 264,5 | / | / | / |

### A.5.3 Cell absolute differences of the analyses by laboratory

The cell absolute differences of the analyses by laboratory for the determination of iodide ($I^-$) contents are listed in Table A.21.

**Table A.21 — Cell absolute differences of the determination of iodide ($I^-$) contents**

| Laboratory<br>*i* | Level *j* | | | |
|---|---|---|---|---|
| | A<br>mg/kg | B<br>mg/kg | C<br>mg/kg | D<br>mg/kg |
| 1 | 6 | 11,4 | 2,38 | 5,06 |
| 2 | 15 | 25,7 | 8,70 | 1,70 |
| 3 | 16 | 2,7 | 1,80 | 0,72 |
| 4 | 8 | 4,0 | 0,67 | / |
| 5 | 11 | 1,0 | 2,00 | / |
| 6 | 28 | 8,5 | 1,80 | 0,74 |
| 7 | 1 | 0,7 | 0,20 | 0,00 |
| 8 | 1 | 0,7 | 0,20 | 0,04 |
| 9 | 51 | 11,0 | 0,07 | 6,76 |
| 10 | 16 | 1,9 | 0,00 | / |
| 11 | 106 | 76,8 | 1,32 | 0,14 |
| 12 | 91 | / | / | / |

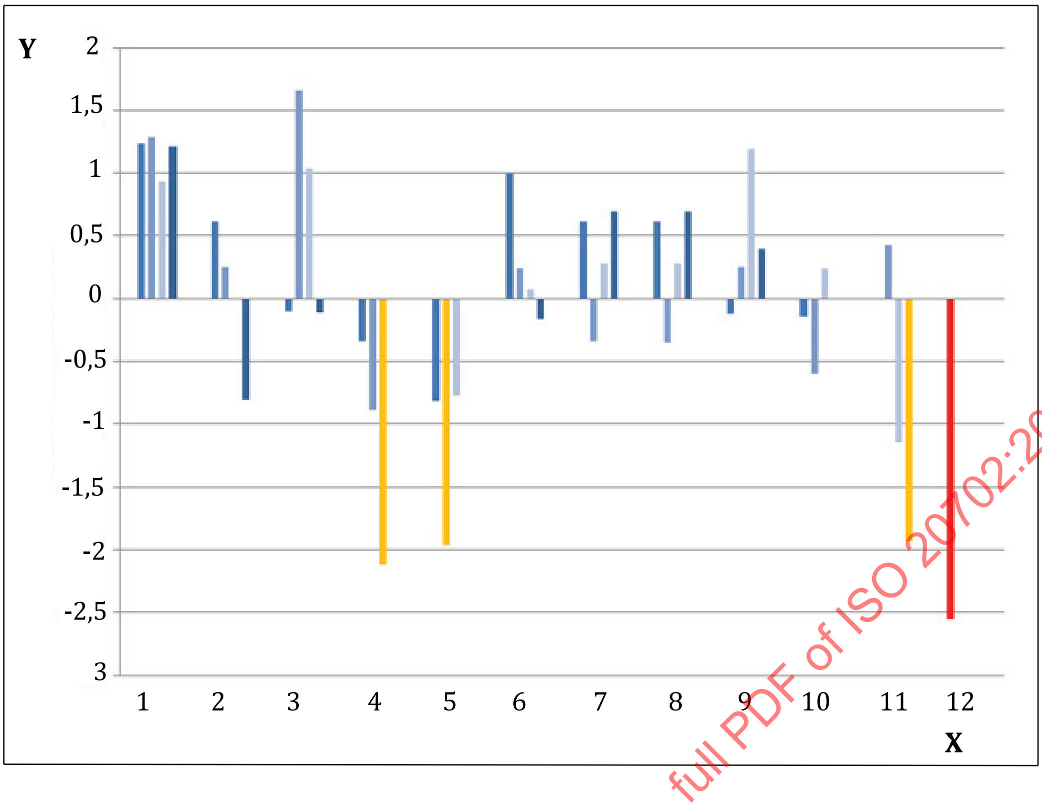
### A.5.4 Evaluation of the results for consistency and outliers

Graphical evaluation of the analytical results for consistency by Mandel's *h* and *k* statistics were studied:

The inter-laboratory consistency statistic *h* and the intra-laboratory consistency statistic *k*, for each level of each laboratory were calculated. The *h* and *k* values for each cell for the respective laboratories were plotted to obtain the Mandel's *h* and *k* graphs.

The Mandel's inter-laboratory consistency statistic *h* (Figure A.7) graph indicated that laboratory 12 had one outlier on level A, laboratory 5 had one straggler on level B, laboratory 4 had one straggler on level C, and laboratory 11 had one straggler on level D.

The Mandel's intra-laboratory consistency statistic *k* (Figure A.8) graph exhibited rather large variability between replicate test results for laboratory 2 on level C (outlier), laboratory 11 on both level A (outlier) and level B (outlier); while laboratory 9 had one straggler on level D, and laboratory 12 had one straggler on level A.

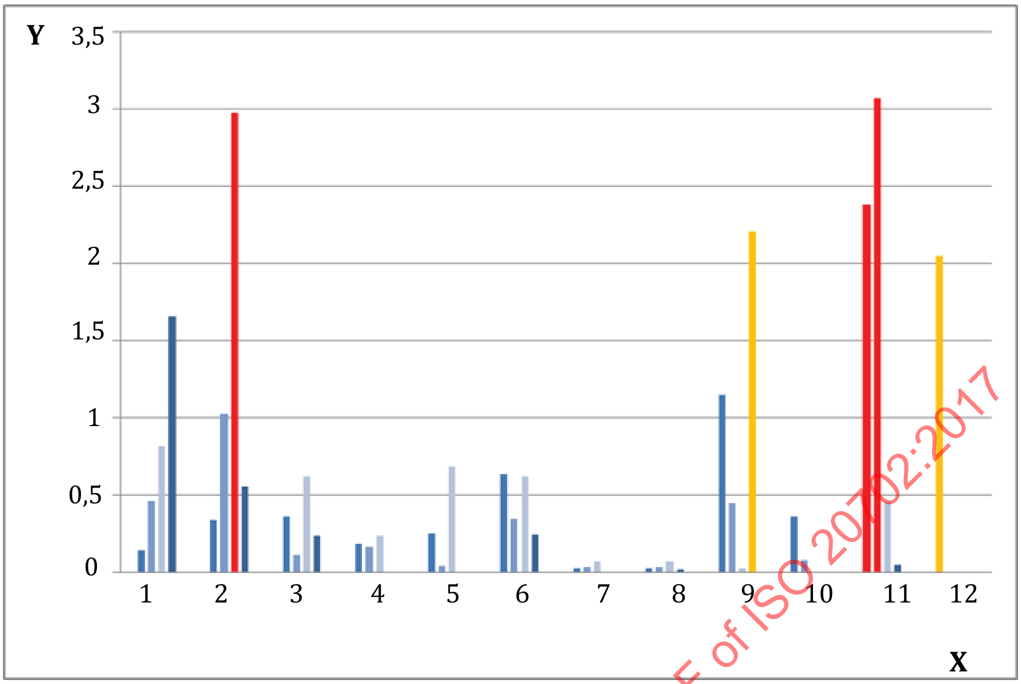


**Key**

X laboratory, *i*

Y Mandel's statistic, *h*

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



**Key**

X laboratory, *i*

Y Mandel’s statistic, *k*

**Figure A.8 — Mandel’s intra-laboratory consistency statistic, *k*, grouped by laboratories**

### Cochran’s test

Cochran’s test is the test of the intra-laboratory variability and should be applied first, then any necessary action should be taken, and also with repeated tests if necessary.

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*** Before scrutiny | **A** | **B** | **C** | **D** | **Type of test** |
|---|---|---|---|---|---|
| C (Cochran) | 0,471 | 0,853 | 0,804 | 0,607 | Cochran’s test statistics |
| Stragglers (5 %) | 0,541 ($p$ = 12, $n$ = 2) | 0,570 ($p$ = 11, $n$ = 2) | 0,570 ($p$ = 11, $n$ = 2) | 0,680 ($p$ = 8, $n$ = 2) | Cochran’s critical values |
| Outliers (1 %) | 0,653 ($p$ = 12, $n$ = 2) | 0,684 ($p$ = 11, $n$ = 2) | 0,684 ($p$ = 11, $n$ = 2) | 0,794 ($p$ = 8, $n$ = 2) | Cochran’s critical values |
| **Level *j*** After scrutiny | **A** | **B** | **C** | **D** | **Type of test** |
| C (Cochran) | 0,471 | 0,652 | 0,308 | 0,607 | Cochran’s test statistics |
| Stragglers (5 %) | 0,541 ($p$ = 12, $n$ = 2) | 0,602 ($p$ = 10, $n$ = 2) | 0,602 ($p$ = 10, $n$ = 2) | 0,680 ($p$ = 8, $n$ = 2) | Cochran’s critical values |
| Outliers (1 %) | 0,653 ($p$ = 12, $n$ = 2) | 0,718 ($p$ = 10, $n$ = 2) | 0,718 ($p$ = 10, $n$ = 2) | 0,794 ($p$ = 8, $n$ = 2) | Cochran’s critical values |

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 showed that the test statistic reached 0,853, calculated by the maximum cell absolute difference (200,4, 277,2) from laboratory 11 on level B.

Cochran's critical value at the 1 % significance level was 0,684, for $p = 11$ and $n = 2$; therefore, the test result from laboratory 11 on level B is an outlier, which should be discarded here.

Accordingly, for laboratory 11, level B was eliminated from their results.

Cochran's tests ($p = 10$, $n = 2$) were repeated on the remaining tests values from the 10 laboratories on level B. The test statistic obtained this time was 0,652. The values is less than Cochran's critical value at the 1 % significance level (0,718, $p = 10$, $n = 2$). This confirmed that no outlier existed in level B anymore.

Cochran's test showed that the test statistic reached 0,804, calculated by the maximum cell absolute difference (113,2, 121,9) from laboratory 2 on level C.

Cochran's critical value at the 1 % significance level was 0,684, for $p = 11$ and $n = 2$; therefore, the test result from laboratory 2 on level C is an outlier, which should be discarded here.

Accordingly, for laboratory 2, level C was eliminated from their results.

Cochran's tests ($p = 10$, $n = 2$) were repeated on the remaining tests values from the 10 laboratories on level C. The test statistic obtained this time was 0,308. The values is less than Cochran's critical value at the 1 % significance level (0,718, $p = 10$, $n = 2$). This confirmed that no outlier existed in level C anymore.

**Grubbs' test**

Grubbs' test is primarily a test of inter-laboratory variability. The test data used herein are those which have passed Cochran's 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 ; 12 | 2,550 | 1,239 | 0,737 5 | 0,248 8 | Grubbs' test statistics |
| B ; 10 | 1,837 | 1,630 | 0,417 3 | 0,417 3 | |
| C ; 10 | 2,012 | 1,132 | 0,708 2 | 0,708 2 | |
| D ; 8 | 1,929 | 1,214 | 0,664 6 | 0,664 6 | |
| Stragglers (5 %) | | | | | Grubbs' critical values |
| $p = 12$ | 2,412 | 2,412 | 0,253 7 | 0,253 7 | |
| $p = 10$ | 2,290 | 2,290 | 0,186 4 | 0,186 4 | |
| $p = 8$ | 2,126 | 2,126 | 0,110 1 | 0,110 1 | |
| Outliers (1 %) | | | | | |
| $p = 12$ | 2,636 | 2,636 | 0,173 8 | 0,173 8 | |
| $p = 10$ | 2,482 | 2,482 | 0,115 0 | 0,115 0 | |
| $p = 8$ | 2,274 | 2,274 | 0,056 3 | 0,056 3 | |

For 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 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 confirmed that there was no outlier.

### A.5.5 Calculation of the general mean and standard deviations

Calculation of the general mean, $s_r$, $s_R$ of iodide (I⁻) contents in each sample listed in Table A.24.

**Table A.24 — Calculation results of the general mean, $s_r$, $s_R$ of iodide (I⁻) contents**

| Sample/Level | A | B | C | D |
|---|---|---|---|---|
| Number of laboratories | 12 | 11 | 11 | 8 |
| Outliers | 0 | 1 | 1 | 0 |
| General mean, $\bar{x}$ , mg/kg | 1 657 | 227,3 | 117,7 | 64,42 |
| Repeatability standard deviation, $s_r$, mg/kg | 31,53 | 7,12 | 0,96 | 2,17 |
| Reproducibility standard deviation, $s_R$, mg/kg | 155,31 | 25,97 | 15,89 | 8,10 |

### A.5.6 Dependence of precision on general mean (level), $\bar{x}$

As shown in Table A.24, the repeatability standard deviations, $s_r$, show a linear relationship with the general mean (level), $\bar{x}$ : $s_r = 0{,}018\bar{x} + 0{,}825$, $R^2 = 0{,}986$

The reproducibility standard deviations, $s_R$, show a linear relationship with the general mean (level), $\bar{x}$: $s_R = 0{,}091\bar{x} + 4{,}141$, $R^2 = 0{,}999$

For all levels, the repeatability standard deviation $s_r$ is $0{,}018\bar{x} + 0{,}825$.

For all levels, the reproducibility standard deviation $s_R$ is $0{,}091\bar{x} + 4{,}141$.

### A.5.7 Final values of precision

The precision of the iodide ($I^-$) contents measurements were discerned from Table A.24.

The conclusions above were determined from a uniform-level experiment involving 12 laboratories, in which one test value from laboratory 11 on level B, one test value from laboratory 2 on level C have been discarded as outliers.

The precision of the iodide ($I^-$) contents measurement method should be quoted as follows:

— repeatability standard deviation: $s_r = 0{,}018\,\overline{x} + 0{,}825$.

— reproducibility standard deviation: $s_R = 0{,}091\,\overline{x} + 4{,}141$.

## A.6 Statistical analysis of the test results of nitrite ($NO_2^-$) contents

### A.6.1 Original test results

10 laboratories participated in the determination of nitrite ($NO_2^-$) contents in fertilizer test samples. The results are listed in Table A.25.

**Table A.25 — Original test results of the determination of nitrite ($NO_2^-$) contents**

| Laboratory *i* | Column used | Level *j* | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | A mg/kg | | B mg/kg | | C mg/kg | | D mg/kg | |
| 1 | AS-18 | 14,28 | 17,11 | 20,65 | 15,31 | 42,93 | 47,19 | 58,66 | 77,77 |
| 2 | AS-18 | 12,30 | 11,30 | 15,10 | 15,80 | 18,70 | 7,70 | 68,00 | 60,20 |
| 3 | Metrosep A Supp 5 | 10,07 | 9,31 | / | / | 13,12 | 13,62 | 53,62 | 54,74 |
| 4 | AS-19 | 14,61 | 14,77 | 14,23 | 12,81 | 14,20 | 14,22 | / | / |
| 5 | AS-18 | 12,27 | 12,07 | 10,96 | 10,08 | 28,11 | 26,74 | 64,50 | 66,38 |
| 6 | AS-18 | 14,77 | 14,74 | 9,09 | 9,09 | 30,07 | 31,14 | 70,03 | 70,03 |
| 7 | AS-18 | 14,67 | 14,71 | 9,06 | 9,09 | 30,07 | 30,13 | 70,05 | 70,05 |
| 8 | AS-18 | 1,66 | 1,38 | / | / | 10,46 | 12,61 | / | / |
| 9 | Metrosep A Supp 7 | / | / | / | / | 21,04 | 21,04 | / | / |
| 10 | AS-18 | 5,37 | 7,27 | 8,84 | 5,89 | / | / | / | / |

### A.6.2 Cell means by laboratory

The cell means (means of the analyses) by laboratory for the determination of nitrite ($NO_2^-$) contents are listed in Table A.26.

**Table A.26 — Cell means of the determination of nitrite ($NO_2^-$) contents**

| Laboratory *i* | Level *j* | | | |
|---|---|---|---|---|
| | A mg/kg | B mg/kg | C mg/kg | D mg/kg |
| 1 | 15,695 | 17,980 | 45,060 | 68,215 |
| 2 | 11,800 | 15,450 | 13,200 | 64,100 |
| 3 | 9,691 | / | 13,370 | 54,180 |
| 4 | 14,690 | 13,520 | 14,210 | / |
| 5 | 12,170 | 10,520 | 27,425 | 65,440 |

**Table A.26** *(continued)*

| Laboratory<br>*i* | Level *j* | | | |
|---|---|---|---|---|
| | A<br>mg/kg | B<br>mg/kg | C<br>mg/kg | D<br>mg/kg |
| 6 | 14,755 | 9,090 | 30,605 | 70,030 |
| 7 | 14,69 | 9,075 | 30,100 | 70,050 |
| 8 | 1,522 | / | 11,535 | / |
| 9 | / | / | 21,040 | / |
| 10 | 6,320 | 7,365 | / | / |

### A.6.3 Cell absolute differences of the analyses by laboratory

The cell absolute differences of the analyses by laboratory for the determination of nitrite ($NO_2^-$) contents are listed in Table A.27.

**Table A.27 — Cell absolute differences of the determination of nitrite ($NO_2^-$) contents**

| Laboratory<br>*i* | Level *j* | | | |
|---|---|---|---|---|
| | A<br>mg/kg | B<br>mg/kg | C<br>mg/kg | D<br>mg/kg |
| 1 | 2,83 | 5,34 | 4,26 | 19,11 |
| 2 | 1,00 | 0,70 | 11,00 | 7,80 |
| 3 | 0,76 | / | 0,50 | 1,12 |
| 4 | 0,16 | 1,42 | 0,02 | / |
| 5 | 0,20 | 0,88 | 1,37 | 1,88 |
| 6 | 0,03 | 0,00 | 1,07 | 0,00 |
| 7 | 0,04 | 0,03 | 0,06 | 0,00 |
| 8 | 0,28 | / | 2,15 | / |
| 9 | / | / | 0,00 | / |
| 10 | 1,90 | 2,95 | / | / |

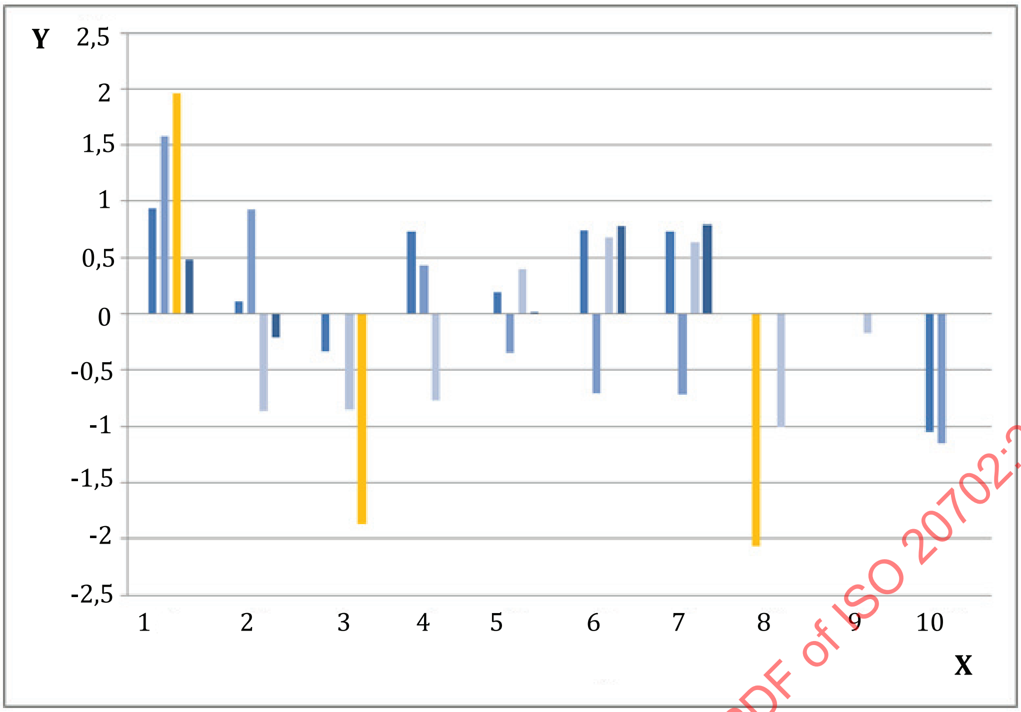
### A.6.4 Evaluation of the results for consistency and outliers

Graphical evaluation of the analytical results for consistency by Mandel's *h* and *k* statistics were studied.

The inter-laboratory consistency statistic *h* and the intra-laboratory consistency statistic *k*, for each level of each laboratory were calculated. The *h* and *k* values for each cell for the respective laboratories were plotted to obtain the Mandel's *h* and *k* graphs.

The Mandel's inter-laboratory consistency statistic *h* (Figure A.9) graph indicated that laboratory 8 had one straggler on level A, laboratory 1 had one straggler on level C and laboratory 3 had one straggler on level D.

The Mandel's intra-laboratory consistency statistic *k* (Figure A.10) graph indicated that laboratory 1 had one outlier on level A, laboratory 1 had one outlier on level B, laboratory 2 had one outlier on level C and laboratory 1 had one outlier on level D.

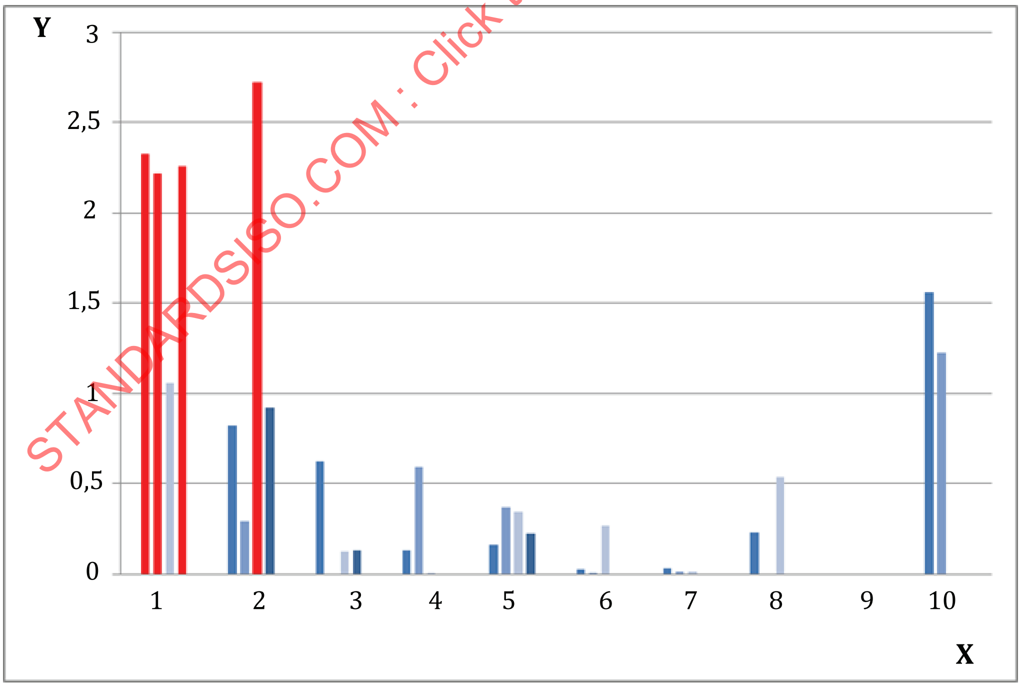


**Key**

X laboratory, *i*

Y Mandel's statistic, *h*

Figure A.9 — Mandel's inter-laboratory consistency statistic, *h*, grouped by laboratories



**Key**

X laboratory, *i*

Y Mandel's statistic, *k*

Figure A.10 — Mandel's intra-laboratory consistency statistic, *k*, grouped by laboratories

### Cochran's test

Cochran's test is the test of the intra-laboratory variability and should be applied first, then any necessary action should be taken, and also with repeated tests if necessary.

Application of Cochran's test led to the values of the test statistic C given in Table A.28.

**Table A.28 — Values of Cochran test statistic, C**

| **Level *j*** Before scrutiny | **A** | **B** | **C** | **D** | **Type of test** |
|---|---|---|---|---|---|
| C (Cochran) | 0,600 | 0,704 | 0,823 | 0,848 | Cochran's test statistics |
| Stragglers (5 %) | 0,638 ($p = 9$, $n = 2$) | 0,727 ($p = 7$, $n = 2$) | 0,638 ($p = 9$, $n = 2$) | 0,781 ($p = 6$, $n = 2$) | Cochran's critical values |
| Outliers (1 %) | 0,754 ($p = 9$, $n = 2$) | 0,838 ($p = 7$, $n = 2$) | 0,754 ($p = 9$, $n = 2$) | 0,883 ($p = 6$, $n = 2$) | Cochran's critical values |
| **Level *j*** After scrutiny | **A** | **B** | **C** | **D** | **Type of test** |
| C (Cochran) | 0,600 | 0,704 | 0,697 | 0,848 | Cochran's test statistics |
| Stragglers (5 %) | 0,638 ($p = 9$, $n = 2$) | 0,727 ($p = 7$, $n = 2$) | 0,680 ($p = 8$, $n = 2$) | 0,781 ($p = 6$, $n = 2$) | Cochran's critical values |
| Outliers (1 %) | 0,754 ($p = 9$, $n = 2$) | 0,838 ($p = 7$, $n = 2$) | 0,794 ($p = 8$, $n = 2$) | 0,883 ($p = 6$, $n = 2$) | Cochran's critical values |

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 showed that the test statistic reached 0,823, calculated by the maximum cell absolute difference (11,00) from laboratory 2 on level C.

Cochran's critical value at the 1 % significance level was 0,754, for $p = 9$ and $n = 2$; therefore, the test result from laboratory 2 on level C is an outlier, which should be discarded here.

Accordingly, for laboratory 2, level C was eliminated from their results.

Cochran's tests ($p = 8$, $n = 2$) were repeated on the remaining tests values from the 8 laboratories on level C. The test statistic obtained this time was 0,697. The values is less than Cochran's critical value at the 1 % significance level (0,794, $p = 8$, $n = 2$). This confirmed that no outlier existed in level C anymore.

### Grubbs' test

Grubbs' test is primarily a test of inter-laboratory variability. The test data used herein are those which have passed Cochran's test.

Application of Grubbs' test to cell means led to the values of the test statistic G shown in Table A.29.

**Table A.29 — Application of Grubbs' test to cell means**

| **Level *j* ; *p*** | **Single low** | **Single high** | **Double low** | **Double high** | **Type of test** |
|---|---|---|---|---|---|
| A ; 9 | 1,360 | 2,273 | 0,236 5 | 0,636 1 | Grubbs' test statistics |
| B ; 7 | 1,156 | 1,576 | 0,251 5 | 0,615 7 | |
| C ; 8 | 1,109 | 1,834 | 0,354 1 | 0,625 2 | |
| D ; 6 | 1,867 | 0,789 | 0,698 0 | 0,088 2 | |

**Table A.29** *(continued)*

| Level *j* ; *p* | Single low | Single high | Double low | Double high | Type of test |
|---|---|---|---|---|---|
| Stragglers (5 %) | | | | | Grubbs' critical values |
| $p = 9$ | 2,215 | 2,215 | 0,149 2 | 0,149 2 | |
| $p = 7$ | 2,020 | 2,020 | 0,070 8 | 0,070 8 | |
| $p = 8$ | 2,126 | 2,126 | 0,110 1 | 0,110 1 | |
| $p = 6$ | 1,887 | 1,887 | 0,034 9 | 0,034 9 | |
| Outliers (1 %) | | | | | |
| $p = 9$ | 2,387 | 2,387 | 0,085 1 | 0,085 1 | |
| $p = 7$ | 2,139 | 2,139 | 0,030 8 | 0,030 8 | |
| $p = 8$ | 2,274 | 2,274 | 0,056 3 | 0,056 3 | |
| $p = 6$ | 1,973 | 1,973 | 0,011 6 | 0,011 6 | |

For 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 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 confirmed that there was no outlier.

### A.6.5 Calculation of the general mean and standard deviations

Calculation of the general mean, $s_r$, $s_R$ of nitrite ($NO_2^-$) contents in each sample listed in Table A.30.

**Table A.30 — Calculation results of the general mean, $s_r$, $s_R$ of nitrite ($NO_2^-$) contents**

| **Sample/Level** | **A** | **B** | **C** | **D** |
|---|---|---|---|---|
| Number of laboratories | 9 | 7 | 9 | 6 |
| Outliers | 0 | 0 | 1 | 0 |
| General mean, $\bar{x}$, mg/kg | 14,10 | 11,86 | 24,17 | 65,34 |
| Repeatability standard deviation, $s_r$, mg/kg | 1,01 | 1,70 | 1,28 | 5,99 |
| Reproducibility standard deviation, $s_R$, mg/kg | 5,77 | 4,07 | 11,43 | 7,33 |

### A.6.6 Dependence of precision on general mean (level), $\bar{x}$

As shown in Table A.30, the repeatability standard deviations, $s_r$, have shown a logarithmic-linear relationship with the general mean (level), $\bar{x}$ : $\log s_r = 0{,}882 \log \bar{x} - 0{,}917$, $R^2 = 0{,}730$

The reproducibility standard deviations, $s_R$, have shown no significant linear or logarithmic-linear relationship with the general mean (level), $\bar{x}$, so for all levels, the mean value of the repeatability standard deviation $s_r$ is represented as the average value of $s_r$ listed in Table A.30.

For all levels, the repeatability standard deviation $s_r$ is $0{,}121\,\bar{x}^{\,0{,}882}$.

For all levels, the reproducibility standard deviation $s_R$ is 7,150.

### A.6.7 Final values of precision

The precision of the nitrite ($NO_2^-$) contents measurements were discerned from Table A.30.

The conclusions above were determined from a uniform-level experiment involving 10 laboratories, in which one test value from laboratory 2 on level C has been discarded as outlier.

The precision of the nitrite ($NO_2^-$) contents measurement method should be quoted as follows:

- — repeatability standard deviation: $s_r = 0{,}121\,\bar{x}^{\,0{,}882}$.
- — reproducibility standard deviation: $s_R = 7{,}150$.

## A.7 Statistical analysis of the test results of thiocyanate ($SCN^-$) contents

### A.7.1 Original test results

Fifteen laboratories participated in the determination of thiocyanate ($SCN^-$) contents in fertilizer test samples. The results are listed in Table A.31.

**Table A.31 — Original test results of the determination of thiocyanate ($SCN^-$) contents**

| Laboratory<br>*i* | Column used | Level *j* | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | A<br>mg/kg | | B<br>mg/kg | | C<br>mg/kg | | D<br>mg/kg | |
| 1 | AS-18 | 1 548 | 1 554 | 15,67 | 16,21 | 115,6 | 119,1 | 71,44 | 76,70 |
| 2 | AS-18 | 1 487 | 1 470 | 28,20 | 36,10 | 100,8 | 104,5 | 64,70 | 63,30 |
| 3 | Metrosep A Supp 5 | 1 476 | 1 474 | 21,52 | 21,98 | 111,8 | 113,7 | 69,76 | 69,32 |
| 4 | AS-19 | 1 284 | 1 278 | 2,601 | 2,613 | 88,37 | 86,13 | / | / |
| 5 | AS-19 | 1 565 | 1 582 | 10,59 | 9,951 | 92,30 | 99,32 | / | / |
| 6 | AS-18 | 1 472 | 1 477 | 10,00 | 11,00 | 107,0 | 105,0 | / | / |
| 7 | AS-19 | 1 544 | 1 545 | 20,24 | 20,10 | 104,7 | 105,9 | 66,70 | 66,52 |
| 8 | AS-18 | 1 506 | 1 515 | 21,90 | 20,90 | 108,9 | 110,2 | 67,88 | 66,05 |
| 9 | AS-18 | 1 516 | 1 516 | 18,90 | 19,00 | 121,9 | 122,2 | 69,85 | 69,81 |
| 10 | AS-18 | 1 515 | 1 516 | 18,92 | 18,98 | 122,0 | 122,2 | 69,85 | 69,81 |
| 11 | AS-18 | 1 529 | 1 542 | 18,99 | 18,45 | 121,7 | 130,7 | 65,43 | 68,74 |
| 12 | Metrosep A Supp 7 | 1 412 | 1 427 | / | / | 131,4 | 131,4 | / | / |
| 13 | AS-19 | 1 344 | 1 292 | / | / | 87,72 | 87,34 | / | / |
| 14 | Metrosep A Supp 5 | 1 578 | 1 521 | / | / | / | / | / | / |
| 15 | AS-18 | 1 349 | 1 329 | / | / | / | / | / | / |

### A.7.2 Cell means by laboratory

The cell means (means of the analyses) by laboratory for the determination of thiocyanate ($SCN^-$) contents are listed in Table A.32.

**Table A.32 — Cell means of the determination of thiocyanate ($SCN^-$) contents**

| Laboratory<br>*i* | Level *j* | | | |
|---|---|---|---|---|
| | A<br>mg/kg | B<br>mg/kg | C<br>mg/kg | D<br>mg/kg |
| 1 | 1 551,0 | 15,940 | 117,36 | 74,070 |
| 2 | 1 478,5 | 32,150 | 102,65 | 64,000 |
| 3 | 1 475,0 | 21,750 | 112,75 | 69,540 |
| 4 | 1 281,0 | 2,607 | 87,250 | / |
| 5 | 1 573,5 | 10,271 | 95,810 | / |

**Table A.32** *(continued)*

| Laboratory<br>*i* | Level *j* | | | |
|---|---|---|---|---|
| | **A**<br>mg/kg | **B**<br>mg/kg | **C**<br>mg/kg | **D**<br>mg/kg |
| 6 | 1 474,5 | 10,500 | 106,00 | / |
| 7 | 1 544,5 | 20,170 | 105,30 | 66,610 |
| 8 | 1 510,5 | 21,400 | 109,55 | 66,965 |
| 9 | 1 516,0 | 18,960 | 122,05 | 69,830 |
| 10 | 1 515,5 | 18,950 | 122,10 | 69,830 |
| 11 | 1 535,5 | 18,720 | 126,22 | 67,085 |
| 12 | 1 419,5 | / | 131,40 | / |
| 13 | 1 318,0 | / | 87,530 | / |
| 14 | 1 549,5 | / | / | / |
| 15 | 1 339,0 | / | / | / |

### A.7.3 Cell absolute differences of the analyses by laboratory

The cell absolute differences of the analyses by laboratory for the determination of thiocyanate ($SCN^-$) contents are listed in Table A.33.

**Table A.33 — Cell absolute differences of the determination of thiocyanate ($SCN^-$) contents**

| Laboratory<br>*i* | Level *j* | | | |
|---|---|---|---|---|
| | **A**<br>mg/kg | **B**<br>mg/kg | **C**<br>mg/kg | **D**<br>mg/kg |
| 1 | 6,00 | 0,54 | 3,51 | 5,26 |
| 2 | 17,00 | 7,90 | 3,70 | 1,40 |
| 3 | 2,00 | 0,46 | 1,90 | 0,44 |
| 4 | 6,00 | 0,01 | 2,24 | / |
| 5 | 17,00 | 0,64 | 7,02 | / |
| 6 | 5,00 | 1,00 | 2,00 | / |
| 7 | 1,00 | 0,14 | 1,20 | 0,18 |
| 8 | 9,00 | 0,94 | 1,30 | 1,83 |
| 9 | 0,00 | 0,04 | 0,30 | 0,04 |
| 10 | 1,00 | 0,06 | 0,20 | 0,04 |
| 11 | 13,00 | 0,54 | 9,04 | 3,32 |
| 12 | 15,00 | / | 0,00 | / |
| 13 | 52,00 | / | 0,38 | / |
| 14 | 57,00 | / | / | / |
| 15 | 20,00 | / | / | / |

### A.7.4 Evaluation of the results for consistency and outliers

Graphical evaluation of the analytical results for consistency by Mandel's *h* and *k* statistics were studied:

The inter-laboratory consistency statistic *h* and the intra-laboratory consistency statistic k, for each level of each laboratory were calculated. The *h* and k values for each cell for the respective laboratories were plotted to obtain the Mandel's *h* and *k* graphs.