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BSI Standards Publication

Fertilizers and soil conditioners — Analytical methods for Sulfur Coated Urea (SCU)

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National foreword

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A list of organizations represented on this committee can be obtained on request to its secretary.

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Fertilizers and soil conditioners — Analytical methods for Sulfur Coated Urea (SCU)

Matières fertilisantes — Méthodes analytiques pour l'urée enrobée de soufre (SCU)

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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

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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).

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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*.

Introduction

Sulfur Coated Urea (SCU) is a coated, slow release fertilizer consisting of urea particles coated with sulfur, which was first developed by the Tennessee Valley Authority's National Fertilizer Development Center (TVA/NFDC), Alabama in 1961, and produced commercially in 1967. SCU is made by coating urea with sulfur and sealant. It contains 30 % to 40 % nitrogen and 10 % to 30 % sulfur. The main coating material of SCU is sulfur. Sulfur is insoluble in water and its chemical properties are stable, thus, it is an impermeable coating material. In addition, sulfur itself is a secondary nutrient and it does not pollute the soil.

This International Standard specifies analytical methods, including mass fraction of total nitrogen, one-day dissolution rate (1DDR), seven-day dissolution rate (7DDR), mass fraction of sulfur, mass fraction of biuret, mass fraction of water (H_2O), and SGN and UI of SCU. There are two methods for determining of one-day dissolution rate (1DDR) and seven-day dissolution rate (7DDR): one is titrimetric method after distillation, the other is refractometer method which is a fast analytical method.

NOTE Some countries or regions might have published other standards covering analytical methods for SCU.

INTERNATIONAL STANDARD ISO 17322:2015(E)

Fertilizers and soil conditioners — Analytical methods for Sulfur Coated Urea (SCU)

1 Scope

This International Standard specifies analytical methods for the determination of mass fraction of total nitrogen, one-day dissolution rate (1DDR), seven-day dissolution rate (7DDR), mass fraction of sulfur, mass fraction of biuret, mass fraction of water (H_2O), and particle size of SCU.

These methods are applicable to SCU.

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 760, *Determination of water — Karl Fischer method (General method)*

ISO 3310-1, *Test sieves — Technical requirements and testing — Part 1: Test sieves of metal wire cloth*

ISO 5315, *Fertilizers — Determination of total nitrogen content — Titrimetric method after distillation*

ISO 17323, *Fertilizers and soil conditioners — Sulfur Coated Urea — General requirements*

3 Sampling and sample preparation

Sampling and sample preparation shall be carried out in accordance with ISO 17323.

4 Determination of the appearance

It shall be determined by visual method.

5 Determination of the mass fraction of total nitrogen

It shall be determined in accordance with ISO 5315.

6 Determination of 1DDR and 7DDR

6.1 Titrimetric method after distillation

6.1.1 Principle

Digest the testing sample in static water at a constant temperature (38,0 ± 0,5) °C. Within a certain period, the nitrogen component in the testing sample will dissolve into the water through the coatings, and then the released nitrogen can be determined by titrimetric method after distillation. The percentage of released nitrogen to the total nitrogen is defined as 1DDR or 7DDR.

6.1.2 Reagents

See ISO 5315.

6.1.3 Apparatus

6.1.3.1 Common laboratory apparatus.

6.1.3.2 The apparatus listed in ISO 5315.

6.1.3.3 Balance, capable of weighing to the nearest 0, 01 g.

6.1.3.4 Constant temperature incubator, capable of being controlled at (38,0 ± 0,5) °C.

6.1.4 Procedure

The replicate experiments shall be done for the determination.

6.1.4.1 Place 20 g uncrushed test sample (accurate to 0,01 g) into a small bag made of 100 meshes nylon yarn nets. Then, seal the bag and place it into a 250 ml Erlenmeyer flask with a plug.

6.1.4.2 Add 200 ml of water into the flask precisely before the flask sealed with the plug.

6.1.4.3 Shake the glass flask gently to disperse the particle of test portion. Then, place the glass flask into a constant temperature incubator with temperature set at (38,0 ± 0,5) °C and keep for 24 h and 7 d, respectively.

6.1.4.4 After a set period, take out the flask from the incubator and reverse it gently three times to ensure the uniformity of solution concentration throughout the flask.

6.1.4.5 Then, cool the flask down to room temperature, and the solution should be filtrated with dry filter paper with a pore size of 30 μm to 50 μm.

6.1.4.6 Pipette 5 ml of the as-prepared solution; the total released nitrogen during a 24 h and 7 d period should be determined in accordance with ISO 5315.

NOTE 1 Nylon yarn nets were used herein for the convenience of filtration (large undissolved particles of SCU can be discarded together with the nylon yarn net).

NOTE 2 Replicate tests during the actual operation can refer to two, three, or more tests.

6.1.5 Calculation

6.1.5.1 Calculate the total released nitrogen during 24 h period, w_1, expressed in the mass fraction (%), according to Formula (1):

$$w_1 = \frac{w'_1}{V_0 / V} \tag{1}$$

where

w'_1 is the total released nitrogen of the test solution pipetted during a 24 h period calculated according to ISO 5315, in the unit of mass fraction (%);

V_0 is the volume value of the test solution pipetted during the test, in the unit of millilitre (ml);

V is the total volume value of the test solution, in the unit of millilitre (ml).

Express the result to within two decimal places. The average value of the results of parallel tests shall be defined as the final result of the determination.

6.1.5.2 Calculate the 1DDR, x_1, as the mass fraction (%), according Formula (2)

$$x_1 = \frac{w_1}{w_0} \times 100 \quad (2)$$

where

w_1 is the value of the total released nitrogen during 24 h period, expressed in the mass fraction (%);

w_0 is the value of the total nitrogen determined in accordance with the provision 5, expressed in the mass fraction (%).

6.1.5.3 Calculate the total nitrogen release during 7 d, w_2, expressed in the mass fraction (%), with Formula (1), prescribed in 6.1.5.1.

Express the results to within two decimal places. The average value of the results of two parallel tests shall be defined as the result of the test.

6.1.5.4 Calculate the 7DDR, x_2, expressed in the mass fraction (%), according to Formula (3):

$$x_2 = \frac{w_2}{w_0} \times 100 \quad (3)$$

where

w_2 is the value of the total released nitrogen during 7 d, expressed in mass fraction (%).

6.2 Refractometer method

6.2.1 Principle

First, determine the solid contents in the sulfur coated urea product, and then calculate the mass of urea in the sample. Based on the feature that the mass fraction of urea (%) in a solution at a certain temperature is proportional to the refractive index of the solution, calculate the urea contents (g/l) in the solution by determining the refractive index of the solution.

6.2.2 Reagents

6.2.2.1 Urea solution, 200 g/l.

Weigh 100 g urea, dissolve it in 250 ml water, and then dilute the solution to 500 ml and mix.

6.2.3 Apparatus

6.2.3.1 Ordinary laboratory apparatus.

6.2.3.2 Balance, capable of weighing to the nearest 0,000 1 g.

6.2.3.3 Magnetic stirring apparatus.

6.2.3.4 Temperature-controlled refractometer, readability, 0,000 01RI, Accuracy: ±0,000 05RI, temperature accuracy: ±0,05 °C at 20 °C, thermometer resolution: 0,01 °C.

6.2.3.5 Constant temperature incubator, capable of being controlled at (38 ± 0,5) °C.

6.2.3.6 Drying oven, capable of being controlled at (100 ± 2) °C.

6.2.4 Procedure

6.2.4.1 Preparation of calibration curve

6.2.4.1.1 Preparation of the standard solution

As shown in Table 1, pipette into a series of eight 100 ml volumetric flasks, 0,00 ml (as compensation solution), 2,50 ml, 5,00 ml, 10,00 ml, 20,00 ml, 30,00 ml, 40,00 ml, and 50,00 ml of the urea standard solution. Make each flask up to the mark with water and mix thoroughly.

Table 1 — Amount of urea content per standard solution

Volumes of urea standard solution/ml	The corresponding urea contents/g/l
0,00	0,00
2,50	5,00
5,00	10,0
10,00	20,0
20,00	40,0
30,00	60,0
40,00	80,0
50, 00	100,0

6.2.4.1.2 Preparation of the calibration curve

Prior to the test, set the optimum parameters for the refractometer, following the instruction of the guidebook.

Pipette 2 to 3 drops of the as-prepared urea standard solution and directly drop on the measuring disk of the refractometer, then wait for 3 min to 4 min until the temperature is stable at (30 ± 0,1) °C. Then, the refractive index of standard solutions with different concentrations can be measured and recorded.

With the refractive indexes of the urea standard solutions as the ordinate, and the urea contents (g/l) in the corresponding standard solution as the abscissa, the calibration curve can be plotted, and determine the equation of linear regression.

6.2.4.2 Determination of solid contents in samples

The replicate experiments shall be done for the determination.

Weigh 2 g (accurate to 0,000 2 g) of the as-prepared test sample (crushed) into a tall-type beaker, and add 100 ml of water; the system should be mixed up on a magnetic stirrer at least 2 min to form a slurry solution. Make sure that all the granules are completely crushed and the urea is dissolved completely.

Place a piece of weighted filter paper into a Buchner funnel, the paper should be soaked with water and fitted to the shape of the Buchner funnel. Pour the sample containing slurry solution onto the filter paper in the Buchner funnel; the residue on the stirrer should be washed onto the filter paper.

Place the insoluble substances into a drying oven at 103 °C to 105 °C and hold for 45 min, and then cool down to room temperature in a dryer for 30 min. The mass of the insoluble substances together with the filter paper should be weighed and recorded (m_2).

The solid content, *w*, can be calculated, expressed in the mass fraction (%), according to Formula (4):

$$w = \frac{m_2 - m_3}{m_4} \times 100 \quad (4)$$

where

m_2 is the mass of the insoluble substances and filter paper, in the unit of gram (g);

m_3 is the mass of the filter paper, in the unit of gram (g);

m_4 is the mass of the test portion, in the unit of gram (g).

The average value of the results of two parallel experiments shall be defined as the result of the test.

NOTE Replicate tests during the actual operation can refer to two, three, or more tests.

6.2.4.3 Determination of the urea contents in solution

Prepare the sample as set out in 6.1.4.1 to 6.1.4.5.

Pipette 2 or 3 drops of the filtered solution and directly drop on the measuring disk of the refractometer, wait for 3 min to 4 min until the temperature of the solution stabilize at (30 ± 0,1) °C, and then the refractive index should be measured by the refractometer and recorded.

6.2.5 Calculation

6.2.5.1 Calculate the mass of urea in the sample, m_5, in the unit of gram (g), according to Formula (5):

$$m_5 = \frac{(100 - M) \times m_1}{100} \quad (5)$$

where

m_1 is the mass of the uncrushed test portion, in the unit of gram (g).

6.2.5.2 Calculate 1DDR or 7DDR, *X*, expressed in the mass fraction (%), according to Formula (6):

$$X = \frac{(n - n_0 \times V)}{m_5 \times 1\ 000} \times 100 \quad (6)$$

where

N is the urea concentration of test solution prepared in a period of 24 h and 7 d, determined directly from the calibration curve or calculated by the linear regression equation, corresponding to the refractive indexes, in the unit of gram (g/l);

n_0 is the urea concentration value corresponding to the blank refractive index, determined directly from the calibration curve or calculated by the linear regression equation, in the unit of gram(g/l);

V is the total volume value of the test solution, in the unit of millilitre (ml).

The average value of the results of two parallel experiments shall be defined as the result of the test.

7 Determination of the mass fraction of sulfur

7.1 Principle

Use water and sulfur-saturated acetone solution to extract water-soluble and acetone-soluble substances, according to the sulfur's behaviour of solubility. Then, extract all the sulfur by carbon disulfide. Calculate the content of sulfur by the subtraction method.

7.2 Reagents

7.2.1 Acetone

7.2.2 **Sulfur**, solid.

7.2.3 **Carbon disulfide**.

7.2.4 Sulfur-saturated acetone solution.

Add a certain amount of sulfur into acetone, and stir continuously. Some more sulfur should be added in the acetone as long as the former can be dissolved thoroughly, until sulfur precipitate from acetone.

7.3 Apparatus

7.3.1 **Ordinary laboratory apparatus**.

7.3.2 **Balance**, capable of weighing to the nearest 0,000 1 g.

7.3.3 **Glass crucible filter**, No. 4, volume of 30 ml.

7.3.4 **Drying oven**, capable of being controlled at (100 ± 2) °C.

7.4 Procedure

7.4.1 Determination of the sulfur content

Warning — This method of analysis involves the use of carbon disulfide (CS_2). Special safety measures shall therefore be taken, in particular with regard to the following:

— **the storage of CS_2;**

— **protective equipment for staff;**

— **occupational hygiene;**

— **prevention of fire and explosions;**

— **disposal of the reagent.**

Warning — This method requires a highly skilled staff and a suitable equipped laboratory.

The replication experiments shall be done for the determination.

Weigh a certain amount of (with 200 mg to 300 mg sulfur contained) as-prepared test sample (crushed) into a 125 ml Erlenmeyer flask with a plug. Add 50 ml of water into the flask precisely before the flask sealed with the plug. Shake the flask vigorously to dissolve the urea content thoroughly. Remove all

contents from the triangular flask into a glass crucible filter (7.3.2) which has been dried to a constant weight at (100 ± 2) °C, and then wash the flask five to six times with water.

Wash the glass crucible filter and its contents with 10 ml sulfur-saturated acetone solution (7.2.4), the content should be dried up by a vacuum pump, repeat this operation four times. Then, dehydrate the sample in the drying oven at (100 ± 2) °C for 1 h; after drying, remove the sample from the dryer and cool it down to room temperature and weigh.

Pipette another 10 ml carbon disulfide to wash the test portion, then the content should be dried up by a vacuum pump, repeat this operation 3 to 5 times, until all the sulfur content within the test portion has been rinsed out.

Then, dehydrate the test portion in the drying oven at (100 ± 2) °C for 1 h; after drying, remove the sample from the dryer and cool it down to room temperature and weigh.

The mass difference between the above two weights should be the mass of sulfur content.

7.4.2 Blank test

Replace the test portion with other inert material free of sulfur (ordinary urea, for example), and carry out the blank test in parallel with the determination using the same procedure and the same quantities of all reagents.

7.5 Calculation

Calculate the sulfur content (represented by the fraction of S element), w_3, expressed in the mass fraction (%), according to Formula (7):

$$w_3 = \frac{m_7 - m_8 - m_9}{m_6} \times 100 \qquad (7)$$

where

m_6 is the mass of the test portion, in the unit of gram (g);

m_7 is the mass of the test portion after washing by sulfur-saturated acetone, in the unit of gram (g);

m_8 is the mass of the test portion after washing by carbon disulfide, in the unit of gram (g);

m_9 is the mass of sulfur in the blank test, in the unit of gram (g).

Express the result to within two decimal places. The average value of the results of parallel experiments shall be defined as the result of the test.

8 Determination of the mass fraction of biuret

8.1 Principle

Under alkaline conditions in the presence of potassium sodium tartrate, biuret forms a purple complex with copper salts. The absorbance of the solution is measured at a wavelength of 550 nm.

8.2 Reagents

8.2.1 Alkaline solution of potassium sodium tartrate.

In a 1 L volumetric flask, dissolve 40 g of sodium hydroxide in 500 ml water and leave it to cool. Add 50 g of potassium sodium tartrate ($NaKC_4H_4O_6$ $4H_2O$). Make the flask up to the mark with water and leave to stand for 24 h before use.

8.2.2 Copper sulfate solution.

In a 1 L volumetric flask, dissolve 15 g of copper sulfate pentahydrate ($CuSO_4$ $5H_2O$) in 500 ml water. Make the flask up to the mark with water.

8.2.3 Freshly prepared biuret standard solution, corresponding to 0,002 g biuret per millilitre.

Biuret—to recrystallize, weigh 15 g reagent grade biuret (chemically pure), transfer to 1 L beaker, add 500 ml 95 % alcohol(analytical grade), and dissolve. Concentrate by gentle heating to 250 ml. Cool at 5 °C and filter through fritted glass funnel. Repeat crystallization and dry final product for 1 h at 105°in oven. Remove from oven, place in desiccator, and cool to room temperature.

In a 250 ml volumetric flask, dissolve 0,500 0 g of recrystallized biuret in water, make the flask up to the mark with water.

8.2.4 Hydrochloric acid solution, c = 1mol/l.

8.3 Apparatus

8.3.1 Common used laboratory apparatus.

8.3.2 Balance, capable of weighing to the nearest 0,000 1 g.

8.3.3 Spectrophotometer.

8.3.4 Water bath, capable of being controlled at (30 ± 5) °C.

8.4 Procedure

8.4.1 Preparation of the calibration curve.

As shown in Table 2, pipette into a series of six 100 ml volumetric flasks, 0,00 ml, 2,50 ml, 5,00 ml, 10,00 ml, 20,00 ml, and 30,00 ml of the biuret standard solution. Dilute them to 50 ml with water. Add 20,0 ml of the alkaline potassium sodium tartrate solution (8.2.1) and 20,0 ml of the copper sulfate solution (8.2.2) into the volumetric flasks successively, make up to the mark with water, leave to stand for 20 min in a water bath controlled at (30 ± 5)°C and shake again.

Table 2 — Amount of biuret content per standard solution

Volumes of biuret standard solution/ml	The corresponding biuret contents/mg
0,00	0,00
2,50	5,00
5,00	10,0
10,00	20,0
20,00	40,0
30,00	60,0

Transfer the solutions to spectrophotometer cells and measure their absorbance at the wavelength of 550 nm using the spectrophotometer, against the compensation solution containing 0 ml of biuret standard solution, 200 ml of the alkaline tartrate solution (8.2.1) and 200 ml of the copper sulfate solution (8.2.2).

Plot the calibration curve with the absorbance value on the ordinate and the corresponding quantities of biuret (in milligrams) on the abscissa. Deduce the equation of regression from the data obtained.

8.4.2 Preparation of the solution to be analysed

Weigh 3 g (accurate to 0,000 2 g) of the as-prepared test sample (crushed) into a 50 ml beaker and add 20 ml of water; the system should be stirred by a glass rod until the urea dissolved. Then, the solution should be filtered into a 100 ml volumetric flask. Add 0,3 ml of hydrochloric acid solution (8.2.4) into the 100 ml volumetric flask and vigorously shake the flask, for the solution might be a little turbid.

Pipette 20,0 ml of the alkaline potassium sodium tartrate solution (8.2.1) and 20,0 ml of the copper sulfate solution (8.2.2) into the volumetric flasks successively. Then make up to the mark with water, leave to stand for 20 min in a water bath controlled at (30 ± 5) °C and shake again.

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

Measure the absorbance of both the test portion and the blank, then, determine the mass of the biuret from the corresponding calibration curve.

8.5 Calculation

Calculate the mass concentration, w_4 (%), of the biuret within the sample according to Formula (8):

$$w_4 = \frac{(m_{11} - m_{12}) \times 10^{-3}}{m_{10}} \times 100 = \frac{m_{11} - m_{12}}{m_{10} \times 10} \tag{8}$$

where

m_{11} is the mass of biuret, in the unit of milligrams;

m_{12} is the mass of biuret in blank test, in the unit of milligrams;

m_{10} is the mass of test portion, in the unit of grams.

Express the result to within two decimal places. The average value of the results of parallel experiments shall be defined as the result of the test.

9 Determination of the water content

9.1 Principle

Extract the water from the SCU into dioxane and titrate it by the Karl Fischer reagent, previously standardized by titration with an exactly known mass of water.

The equations are as follows:

$$H_2O + I_2 + SO_2 + 3C_5H_5N \rightarrow 2C_5H_5N{\cdot}HI + C_5H_5N{\cdot}SO_3$$

$$C_5H_5N{\cdot}SO_3 + CH_3OH \rightarrow C_6H_5NH{\cdot}OSO_2OCH_3$$

9.2 Reagents

9.2.1 5A molecular sieve

Granules of 3 mm to 5 mm diameter is used as desiccant. Before using, the molecular sieve should be heated at 500 °C for 2 h and then cooled down to room temperature in a desiccator filled with molecular sieve. The molecular sieve once used can be regenerated by washing with water, drying, and calcinated.

9.2.2 Methanol

The water content (w/w %) should be not more than 0,05 %. If the water content (w/w%) is more than 0,05 %, about 50 g 5A molecular sieve (9.2.1)should be added to 500 ml methanol. Then, the bottle is sealed and kept at room temperature (-25 °C) overnight. Extract the upper clear solution for use.

9.2.3 Dioxane

Dehydrating by the same way as described in 9.2.2.

NOTE Other commercially available solvent with equal effect can also be used

Caution — Dioxane is a hazardous chemical requiring specific safety precaution.

9.2.4 Karl Fischer reagent, prepared according to ISO 760

9.2.5 Sodium tartrate dihydrate, $Na_2C_4H_4O_6{\cdot}2H_2O$

9.3 Apparatus

9.3.1 Balance, capable of weighing to the nearest 0,000 1 g.

9.3.2 Karl Fischer titrator.

9.3.3 Centrifuge, (0 to 4 000) r/min.

9.3.4 Syringe, 5 ml and 50 ml.

9.4 Installation and test of the Karl Fischer titrator

Follow the instruction manual to install the Karl Fischer titrator.

9.5 Procedure

9.5.1 Standardization of the Karl Fischer reagent

Titrate the known quantity of water or sodium tartrate dihydrate (9.2.5) (accurate to 0,000 2 g) introduced with the Karl Fisher reagent (9.2.4) to be standardized, until the galvanometer pointer shows a sudden and constant deflection lasting for at least 1 min. Note the volume (V_3) of reagent used and calculate the water equivalent (T) of the Karl Fisher reagent.

9.5.2 Determination

Weigh 1,5 g to 2,5 g crushed test sample (accurate to 0,000 2 g) where the content of free water is no more than 150 mg into a 125 ml conical flask with a rubber stopper. Seal it with rubber stopper and inject 50 ml dioxane (9.2.3) with a syringe. Shake for a few minutes, leave to stand for 15 min and then shake for a few minutes again. After the test portion subsides slightly, some portion of the solution should be centrifuged in a centrifugal (speed: 2 000 r/min, time: 5 min) tube with a rubber plug.

Empty the titration vessel via its outlet. Add 50 ml of methanol into the titration vessel; the amount of methanol should be capable of submerging the electrodes. Switch on the electromagnetic stirrer. Titrate with the Karl Fischer reagent until the same deflection of the pointer of the Karl Fischer titrator is reached as standardization of the Karl Fischer reagent and remains stable for at least 1 min.

Take 5,0 ml dioxane extraction from the centrifuge tube with a syringe, inject through the feed inlet into the titration vessel, and titrate it to the equivalent point by Karl Fischer reagent. Record the volume (V_4) of Karl Fischer reagent used.

As the dioxane is used as extraction reagent, the residue in the titration vessel should be emptied after three measurements. Fill the vessel with methanol and titrate it to the equivalent point. Then start the next test of sample.

Determine the volume (V_5) of Karl Fischer reagent used by titrating 5 ml dioxane with the same method.

9.6 Calculation

9.6.1 Water equivalent of the Karl Fischer reagent

The water equivalent, T, of the Karl Fischer reagent, expressed in milligrams of water per millilitre of reagent, is given by Formula (9):

$$T = \frac{m_{14} \times 0{,}156\ 6}{V_3} \quad \text{or} \quad T = \frac{m_{15}}{V_3} \tag{9}$$

where

m_{14} is the mass of the sodium tartrate introduced if this reagent is used for the standardization, in the unit of milligrams (mg);

m_{15} is the mass of the water introduced if pure water is used for the standardization, in the unit of milligrams (mg);

V_3 is the volume of Karl Fischer reagent used for the standardization, in the unit of millilitre (ml).

9.6.2 Water content of the sample

The water content of the sample, w_5, expressed as mass fraction (%), is given by Formula (10).

$$w_5 = \frac{T(V_4 - V_5)}{m_{16} \times \frac{5}{50} \times 1\ 000} \times = \frac{T(V_4 - V_5)}{m_{16}} \quad (10)$$

where

T is the water equivalent of the Karl Fischer reagent, calculated in accordance with 9.6.1, in the unit of milligram per millilitre (mg/ml);

V_4 is the volume of Karl Fischer reagent used by 5 ml dioxane extraction solution, in the unit of millilitre (ml);

V_5 is the volume of Karl Fischer reagent used by 5 ml dioxane, in the unit of millilitre (ml);

m_{16} is the mass of the test portion, in the unit of grams (g).

Express the result withint two decimal places. The average value of the results of two parallel tests shall be defined as the result of the test.

10 Determination of particle size

It shall be determined in accordance with ISO 3310-1, and the size of test sieving should been chosen 1,00 mm to 4,75 mm.

11 Precision

11.1 Ring test

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

11.2 Repeatability

Item	Repeatability limit r %
mass fraction of total nitrogen	0,356
1DDR (Titrimetric method after distillation)	0,127x – 0,060 5
7DDR (Titrimetric method after distillation)	2,990
1DDR (Refractometer method)	3,102
7DDR (Refractometer method)	4,248
mass fraction of sulfur	0, 392
mass fraction of biuret	0,059
mass fraction of water (H_2O)	0,067

11.3 Reproducibility

Item	Repeatability limit *R* %
mass fraction of total nitrogen	1,151
1DDR (Titrimetric method after distillation)	0,0736x + 3,481 5
7DDR (Titrimetric method after distillation)	0,153x + 2,392 6
1DDR (Refractometer method)	0,101x + 3,957 0
7DDR (Refractometer method)	8,366
mass fraction of sulfur	1, 372
mass fraction of biuret	0,235
mass fraction of water (H_2O)	0,123

12 Test report

The test report shall contain at least the following information:

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

b) the test method used with reference to this International Standard (i.e. ISO 17322);

c) the test results obtained;

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

e) the date when the analysis was finished;

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

g) all the operating details not specified in this International 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 interlaboratory testing of this International Standard was accomplished from September 2012 to December 2012. Eleven laboratories participated in the two parallel tests on each four samples. These eleven laboratories are Thornton Laboratories Testing and Inspection Services, Inc(USA), PT. Hanampi Sejahtera Kahuripan (Indonesia), Soil and water research institute of Iran (Iran), Shanghai Research Institute (China), Heilongjiang Research Institute (China), Shandong Research Institute 1 (China), Jiangsu Research Institute 1 (China), Guangxi Research Institute (China), Jiangsu Research Institute 2 (China), Yunnan Research Institute (China), and Shandong Research Institute 2 (China) respectively. 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 test methods described in Clauses 4 to 10 were adopted in this Annex for total nitrogen, one-day dissolution rate (titrimetric method after distillation), seven-day dissolution rate (titrimetric method after distillation), one-day dissolution rate (refractometer method), seven-day dissolution rate (refractometer method), sulfur, mass fraction of biuret, and water in Sulfur Coated Urea.

Four different samples of SCU were used during the ring test, with the serial number of SCU-I, SCU-II, SCU-III, and SCU-IV. Four different kinds of fertilizer samples were with several mean levels. All the SCU samples encountered hereafter could be referred to the description in this subclause.

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

A.2 Statistical analysis of the test results of the mass fraction of total nitrogen

A.2.1 Original test results

Ten laboratories have participated in the determination of the mass fraction of total nitrogen. The test results are listed in Table A.1, expressed in the mass fraction (%).

Table A.1 — Original test results of the determination of the mass fraction of total nitrogen

Laboratory *i*	Level j							
	SCU-I		SCU-II		SCU-III		SCU-IV	
1	40,24	40,22	37,59	37,56	35,77	35,76	35,93	35,94
2	39,13	39,2	36,89	36,92	35,06	35,02	35,01	34,93
3	38,69	39,09	37,4	36,79	35,47	36,17	37,08	37,52
4	40,02	40,24	37,36	37,49	35,92	36,15	35,66	35,53
5	39,86	40,19	37,48	37,7	35,83	35,7	35,98	35,94
6	39,46	39,61	37,48	37,62	35,34	35,39	35,67	35,54
7	39,84	39,66	37,32	37,16	35,68	35,64	35,62	35,72
8	40,15	40,11	37,33	37,3	35,61	35,56	35,92	35,86
9	39,99	40,07	38,00	37,76	35,76	35,92	35,91	36,09

Table A.1 *(continued)*

Laboratory *i*	Level j							
	SCU-I		SCU-II		SCU-III		SCU-IV	
10	39,51	39,41	37,06	37,28	35,45	35,4	35,58	35,68

A.2.2 Cell means

The cell means of the determination of the mass fraction of total nitrogen are listed in Table A.2, expressed in the mass fraction (%).

Table A.2 — Cell means of the determination of the mass fraction of total nitrogen

Laboratory *i*	Level j			
	SCU-I	SCU-II	SCU-III	SCU-IV
1	40,230	37,575	35,765	35,935
2	39,165	36,905	35,040	34,970
3	38,890	37,095	35,820	37,300
4	40,130	37,425	36,035	35,595
5	40,025	37,590	35,765	35,960
6	39,535	37,550	35,365	35,605
7	39,750	37,240	35,660	35,670
8	40,130	37,315	35,585	35,890
9	40,030	37,880	35,840	36,000
10	39,460	37,170	35,425	35,630

A.2.3 Cell absolute differences

The cell absolute differences of the determination of the mass fraction of total nitrogen are listed in Table A.3, expressed in the mass fraction (%).

Table A.3 — Cell absolute differences of the determination of the mass fraction of total nitrogen

Laboratory *i*	Level j			
	SCU-I	SCU-II	SCU-III	SCU-IV
1	0,02	0,03	0,01	0,01
2	0,07	0,03	0,04	0,08
3	0,40	0,61	0,70	0,44
4	0,22	0,13	0,23	0,13
5	0,33	0,22	0,13	0,04
6	0,15	0,14	0,05	0,13
7	0,18	0,16	0,04	0,10
8	0,04	0,03	0,05	0,06
9	0,08	0,24	0,16	0,18
10	0,10	0,22	0,05	0,10

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.

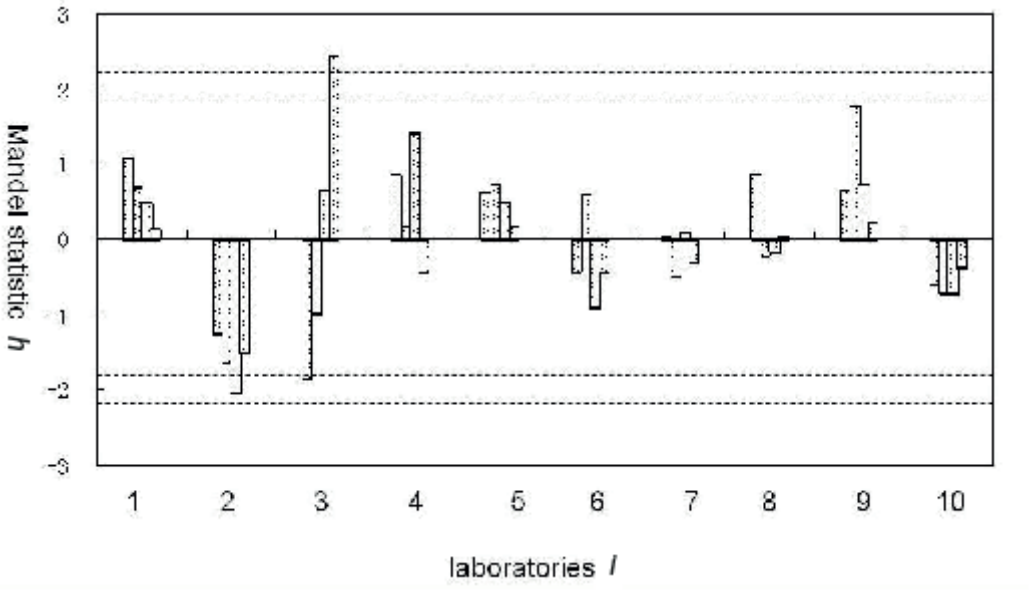

Figure A.1 — Mandel's between-laboratory consistency statistic, *h*, grouped by laboratories

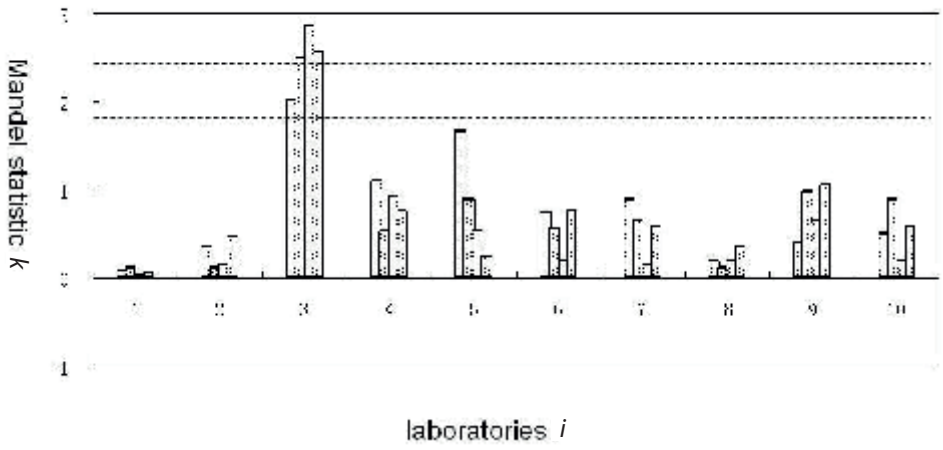

Figure A.2 — Mandel's within-laboratory consistency statistic, *k*, grouped by laboratories

Horizontal dotted lines in Figures A.1 and A.2 represent 1 % and 5 % critical values of Mandel's *h* and *k* statistics, respectively.

The *h* graph shows that laboratory 3 had an outlier on level SCU-IV, laboratory 2 had a straggler on level SCU-III, and laboratory 3 had a straggler on level SCU-I.

The *k* graph exhibited a large variability between replicate test results for laboratory 3 on four levels; it was decided to retain them here for next step.

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	SCU-I	SCU-II	SCU-III	SCU-IV	Type of test
C	0,405	0,629	0,822	0,701	Cochran's test statistics
Stragglers	0,602	0,602	0,602	0,602	Cochran's critical values
Outliers	0,718	0,718	0,718	0,718	

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 is shown that the test statistics reached 0,822, calculated by the cell absolute difference (0,70) from laboratory 3 on level SCU-III.

The Cochran's critical value at the 1 % significance level was 0,718, therefore, the test results from laboratory 3 on level SCU-III is a outlier, which should be discarded here. At the 5 % significance level, the Cochran's critical value was 0,602, therefore, the test results from laboratory 3 on level SCU-III and SCU-IV are stragglers, it was decided to retain them here for next step.

Cochran's test was repeated on the remaining tests values from the nine laboratories on level SCU-III, the test statistic obtained this time was 0,498, which is less than the Cochran' s critical value at the 5 % significance level (0,698, $P = 9$). 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 has 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
SCU-I;10	1,846	1,083	0,316 3	0,733 8	Grubbs' test statistics
SCU-II;10	1,640	1,766	0,500 1	0,502 5	
SCU-III;9	1,918	1,437	0,304 3	0,604 2	
SCU-IV;10	1,503	2,451	0,400 7	0,675 1	
Stragglers					Grubbs' critical values
$P = 9$	2,215	2,215	0,149 2	0,149 2	
$P = 10$	2,290	2,290	0,186 4	0,186 4	
Outliers					
$P = 9$	2,387	2,387	0,085 1	0,085 1	
$P = 10$	2,482	2,482	0,115 0	0,115 0	

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

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

We have confirmed that laboratory 3 had a straggler on level SCU-IV, but no outliers exist by Grubbs' test here.

A.2.5 Calculation of the general mean and standard deviations

Calculation of the general mean, s_r, s_R, of the mass fraction of total nitrogen in each sample led to Table A.6, expressed in the mass fraction (%).

Table A.6 — Calculation results of the general mean, s_r, s_R, of the mass fraction of total nitrogen

Sample/Level	SCU-I	SCU-II	SCU-III	SCU-IV
Number of laboratories	10	10	9	10
Outliers	0	0	1	0
General mean, m	39,74	37,38	35,61	35,86
Repeatability standard deviation, s_r	0,141	0,172	0,077	0,118
Reproducibility standard deviation, s_R	0,459	0,303	0,294	0,588

A.2.6 Dependence of precision on general mean, m

An examination of the data in Table A.6 does not indicate any dependence and average values can be used.

A.2.7 Final values of precision

The precision (expressed in the mass fraction) of the mass fraction of total nitrogen measurement method should be quoted as follows:

— repeatability standard deviation: s_r = 0,127

— reproducibility standard deviation: s_R = 0,411

The conclusion above was determined from a uniform-level experiment involving 10 laboratories; no outliers have been reported and two test values have remained as stragglers.

A.3 Statistical analysis of the test results of 1DDR (Titrimetric method after distillation)

A.3.1 Original test results

Ten laboratories have participated in the determination of 1DDR (Titrimetric method after distillation). The test results are listed in Table A.7, expressed in the mass fraction (%).

Table A.7 — Original test results of the determination of 1DDR (Titrimetric method after distillation)

Laboratory *i*	Level j							
	SCU-I		SCU-II		SCU-III		SCU-IV	
1	44,15	46,94	36,3	37,28	8,76	9,34	8,05	8,18
2	41,88	42,19	39,04	39,04	10,30	10,30	9,61	9,49
3	52,98	45,63	32,95	34,91	12,62	12,31	7,98	7,61
4	42,84	46,13	30,99	35,96	8,96	9,35	11,07	9,27
5	48,00	46,10	40,30	35,40	8,50	11,10	8,90	8,90
6	46,73	46,13	39,8	37,16	9,29	10,1	10,85	10,01
7	45,71	45,89	37,54	37,73	8,10	8,24	13,01	13,12
8	44,28	44,33	35,60	36,55	8,49	8,41	7,76	7,86
9	45,72	46,76	38,04	38,67	9,96	9,60	9,39	8,67
10	44,17	43,97	37,18	36,80	10,30	10,98	10,61	10,97

A.3.2 Cell means

The cell means of the determination of 1DDR (Titrimetric method after distillation) are listed in Table A.8, expressed in the mass fraction (%).

Table A.8 — Cell means of the determination of 1DDR (Titrimetric method after distillation)

Laboratory *i*	Level j			
	SCU-I	SCU-II	SCU-III	SCU-IV
1	45,545	36,790	9,050	8,115
2	42,035	39,040	10,300	9,550
3	49,305	33,930	12,465	7,795
4	44,485	33,475	9,155	10,170
5	47,050	37,850	9,800	8,900
6	46,430	38,480	9,695	10,430
7	45,800	37,635	8,170	13,065
8	44,305	36,075	8,450	7,810
9	46,240	38,355	9,780	9,030
10	44,070	36,990	10,640	10,790

A.3.3 Cell absolute differences

The cell absolute differences of the determination of 1DDR (Titrimetric method after distillation) are listed in Table A.9, expressed in the mass fraction (%).

Table A.9 — Cell absolute differences of the determination of 1DDR (Titrimetric method after distillation)

Laboratory *i*	Level j			
	SCU-I	SCU-II	SCU-III	SCU-IV
1	2,79	0,98	0,58	0,13
2	0,31	0,00	0,00	0,12
3	7,35	1,96	0,31	0,37
4	3,29	4,97	0,39	1,80
5	1,90	4,90	2,60	0,00
6	0,60	2,64	0,81	0,84
7	0,18	0,19	0,14	0,11
8	0,05	0,95	0,08	0,10
9	1,04	0,63	0,36	0,72
10	0,20	0,38	0,68	0,36

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.

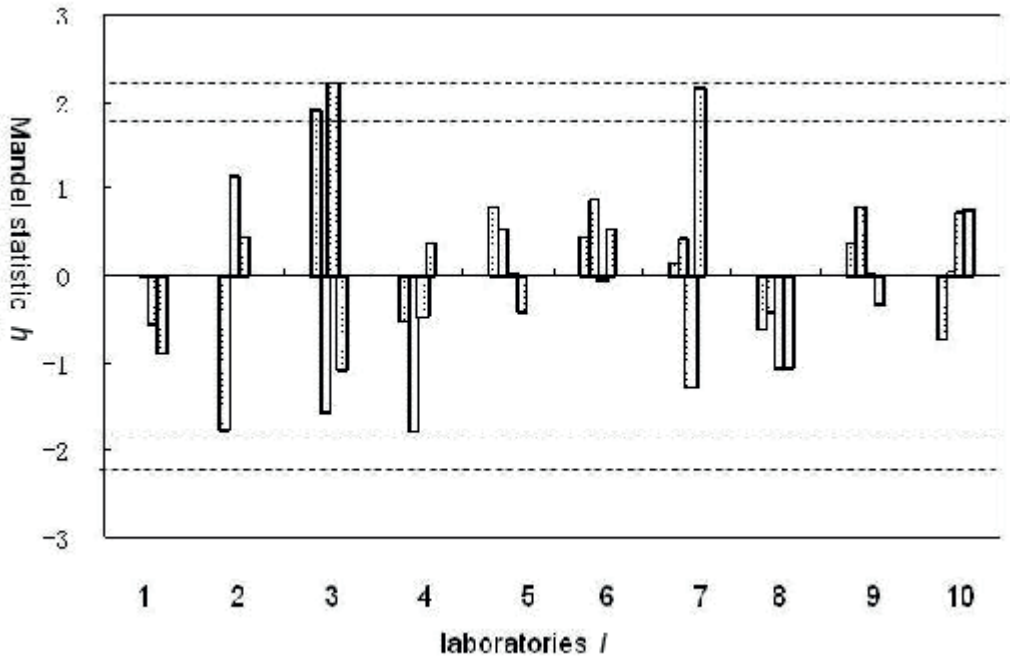

Figure A.3 — Mandel's between-laboratory consistency statistic, *h*, grouped by laboratories

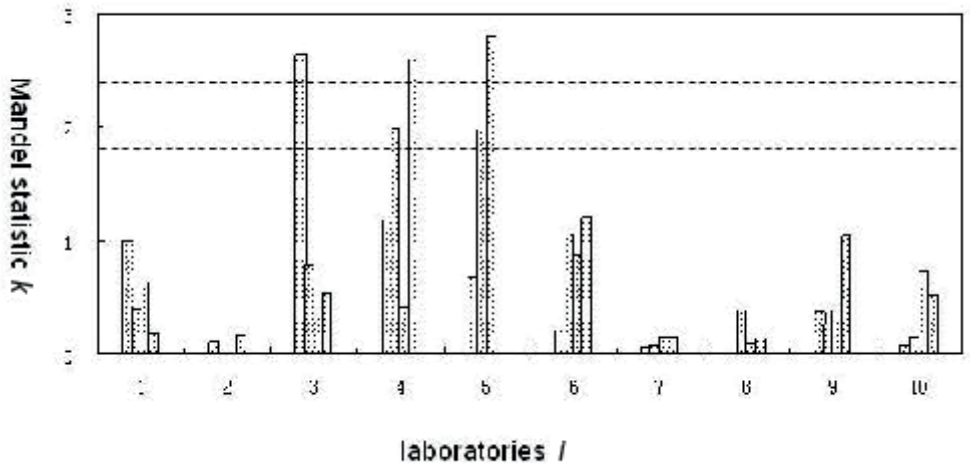

Figure A.4 — Mandel's within-laboratory consistency statistic, *k*, grouped by laboratories

Horizontal dotted lines in Figures A.3 and A.4 represent 1 % and 5 % critical values of Mandel's *h* and *k* statistics, respectively.

The *h* graph shows that laboratory 3 had an outlier on level SCU-III, laboratory 3 had a straggler on level SCU-I, and laboratory 7 had a straggler on level SCU-IV.

The *k* graph shows that laboratory 3 had an outlier on level SCU-I, laboratory 4 had an outlier on level SCU-IV, and laboratory 5 had an outlier on level SCU-III. Laboratory 4 and laboratory 5 had a straggler on level SCU-II.

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	**SCU-I**	**SCU-II**	**SCU-III**	**SCU-IV**	**Type of test**
C	0,694	0,399	0,784	0,677	Cochran's test statistics
Stragglers	0,602	0,602	0,602	0,602	Cochran's critical values
Outliers	0,718	0,718	0,718	0,718	

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 is shown that the test statistic reached 0,784, calculated by the cell absolute difference (2,60) from laboratory 5 on level SCU-III.

The Cochran's critical value at the 1 % significance level was 0,718, therefore, the test results from laboratory 5 on level SCU-III is an outlier, which should be discarded here.

At the 5 % significance level, the Cochran' s critical value was 0,602, therefore, the test results from laboratory 3 on level SCU-Iand from laboratory 4 on level SCU-IV is stragglers, it was decided to retain them here for next step.

Cochran's test was repeated on the remaining test values from the nine laboratories on level SCU-III, the test statistic obtained this time was 0,353, which is less than the Cochran' s critical value at the 5 % significance level (0,638, $P = 9$). It was have confirmed that no straggler (and no outlier) exist this time.

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**
SCU-I;10	1,773	1,919	0,502 0	0,423 5	Grubbs' test statistics
SCU-II;10	1,800	1,157	0,213 8	0,712 5	
SCU-III;9	1,212	0,689	0,604 9	0,254 3	
SCU-IV;10	1,086	2,147	0,675 0	0,308 4	
stragglers $P = 9$	2,215	2,215	0,149 2	0,149 2	Grubbs' critical values
$P = 10$	2,290	2,290	0,186 4	0,186 4	
outliers $P = 9$	2,387	2,387	0,085 1	0,085 1	
$P = 10$	2,482	2,482	0,115 0	0,115 0	

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

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

We have confirmed that no outliers and stragglers exist by Grubbs' test here.

A.3.5 Calculation of the general mean and standard deviations

Calculation of the general mean, s_r, s_R, of 1DDR (Titrimetric method after distillation) in each sample has led to Table A.12, expressed in the mass fraction (%).

Table A.12 — Calculation results of the general mean, s_r, s_R, of 1DDR (Titrimetric method after distillation)

Sample/Level	SCU-I	SCU-II	SCU-III	SCU-IV
Number of Laboratories	10	10	9	10
Outliers	0	0	1	0
General mean, m	45,53	36,86	9,75	9,57
Repeatability standard deviation, s_r	1,973	1,758	0,321	0,489
Reproducibility standard deviation, s_R	2,413	2,255	1,319	1,666

A.3.6 Dependence of precision on general mean, m

Table A.12 states that the standard deviations tend to increase with higher values of m, 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 s_r, s_R, with m, respectively, the formulae are as follows:

— $s_r = 0{,}045\ 5\ m - 0{,}021\ 6\ R^2 = 0{,}985\ 2$

— $s_R = 0{,}026\ 3\ m + 1{,}243\ 4\ R^2 = 0{,}917\ 3$

A.3.7 Final values of precision

The precision (expressed in the mass fraction) of 1DDR (Titrimetric method after distillation) measurement method should be quoted as follows:

— repeatability standard deviation: $s_r = 0{,}045\ 5\ m - 0{,}021\ 6$

— reproducibility standard deviation: $s_R = 0{,}026\ 3\ m + 1{,}243\ 4$

The conclusion above were determined from a uniform-level experiment involving 10 laboratories, in which one test value from a laboratory has been discarded as an outlier and two test values have remained as stragglers.

A.4 Statistical analysis of the test results of 7DDR (Titrimetric method after distillation)

A.4.1 Original test results

Eleven laboratories have participated in the determination of 7DDR (Titrimetric method after distillation). The test results are listed in Table A.13, expressed in the mass fraction (%).

Table A.13 — Original test results of the determination of 7DDR (Titrimetric method after distillation)

Laboratory *i*	Level j							
	SCU-I		SCU-II		SCU-III		SCU-IV	
1	59,50	60,49	56,72	56,48	17,35	14,57	15,11	14,63

Table A.13 *(continued)*

Laboratory *i*	Level j							
	SCU-I		SCU-II		SCU-III		SCU-IV	
2	52,44	52,16	48,16	48,45	17,92	17,85	16,18	16,27
3	50,39	49,67	50,85	49,57	21,22	18,56	12,57	13,46
4	51,66	50,09	50,86	49,00	13,84	19,12	19,55	16,76
5	61,00	61,06	52,75	56,58	16,06	17,20	16,05	18,00
6	57,93	58,28	54,65	55,18	14,97	16,01	16,37	15,56
7	58,82	58,97	50,11	50,16	16,63	16,85	17,63	17,75
8	59,76	59,81	54,85	54,74	15,69	15,78	14,54	14,52
9	59,16	61,35	57,66	54,94	18,86	17,63	15,17	16,39
10	51,47	52,18	51,74	51,01	14,88	14,23	14,99	15,24

A.4.2 Cell means

The cell means of the determination of 7DDR (Titrimetric method after distillation) are listed in Table A.14, expressed in the mass fraction (%).

Table A.14 — Cell means of the determination of 7DDR (Titrimetric method after distillation)

Laboratory *i*	Level j			
	SCU-I	SCU-II	SCU-III	SCU-IV
1	59,995	56,600	15,960	14,870
2	52,300	48,305	17,885	16,225
3	50,030	50,210	19,890	13,015
4	50,875	49,930	16,480	18,155
5	61,030	54,665	16,630	17,025
6	58,105	54,915	15,490	15,965
7	58,895	50,135	16,740	17,690
8	59,785	54,795	15,735	14,530
9	60,255	56,300	18,245	15,780
10	51,825	51,375	14,555	15,115

A.4.3 Cell absolute differences

The cell absolute differences of the determination of 7DDR (Titrimetric method after distillation) are listed in Table A.15, expressed in the mass fraction (%).

Table A.15 — Cell absolute differences of the determination of 7DDR (Titrimetric method after distillation)

Laboratory *i*	Level j			
	SCU-I	SCU-II	SCU-III	SCU-IV
1	0,99	0,24	2,78	0,48
2	0,28	0,29	0,07	0,09
3	0,72	1,28	2,66	0,89
4	1,57	1,86	5,28	2,79

Table A.15 *(continued)*

Laboratory *i*	**Level** j			
	SCU-I	**SCU-II**	**SCU-III**	**SCU-IV**
5	0,06	3,83	1,14	1,95
6	0,35	0,53	1,04	0,81
7	0,15	0,05	0,22	0,12
8	0,05	0,11	0,09	0,02
9	2,19	2,72	1,23	1,22
10	0,71	0,73	0,65	0,25

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.

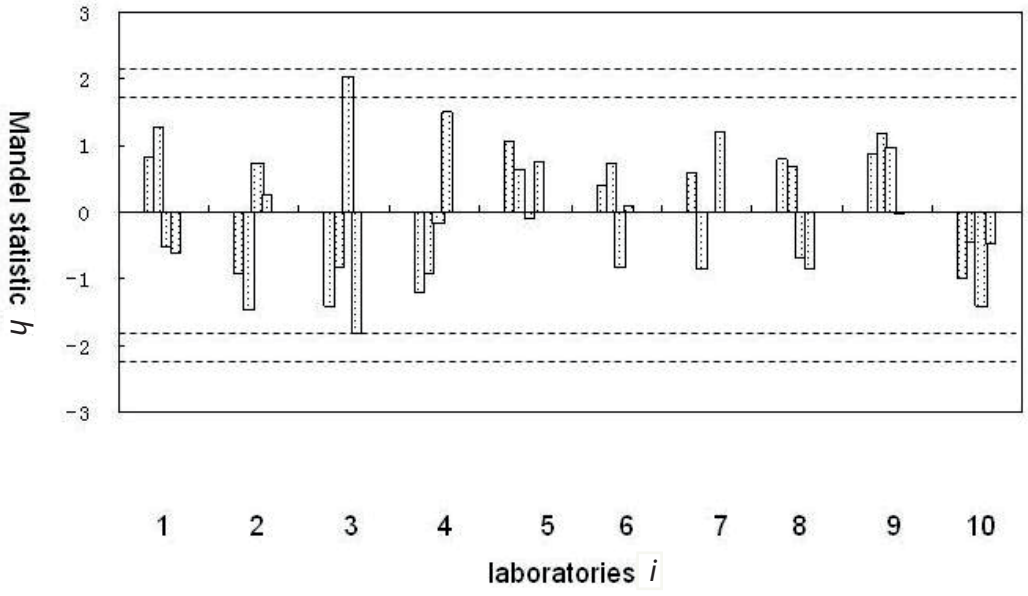

Figure A.5 — Mandel's between-laboratory consistency statistic, *h*, grouped by laboratories

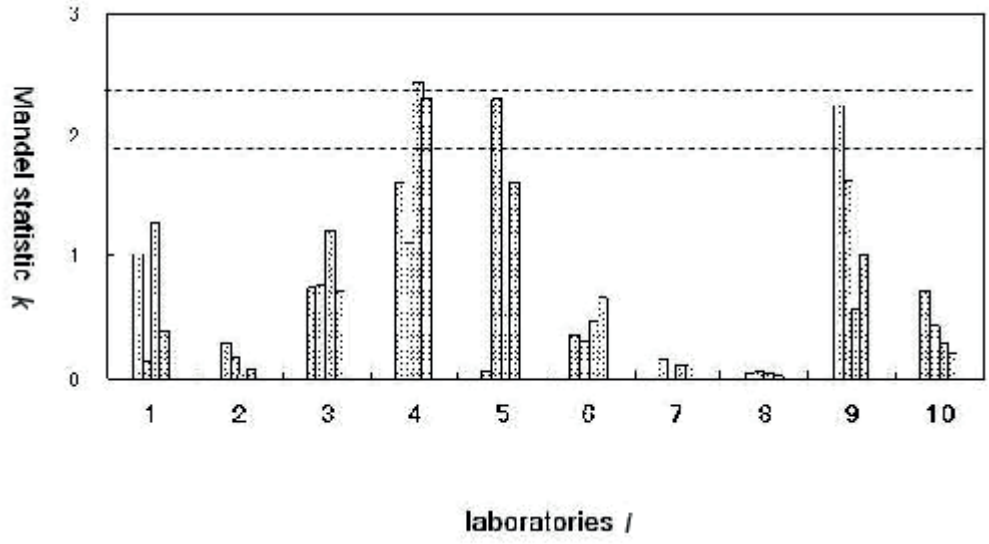

Figure A.6 — Mandel's within-laboratory consistency statistic, *k*, grouped by laboratories

Horizontal dotted lines in Figures A.5 and A.6 represent 1 % and 5 % critical values of Mandel's *h* and *k* statistics, respectively.

The *h* graph shows that laboratory 3 had stragglers on level SCU-III and level SCU-IV.

The *k* graph shows that laboratory 4 had an outlier on level SCU-III, laboratory 4 had a straggler on level SCU-IV, laboratory 5 had a straggler on level SCU-II, and laboratory 9 had a straggler on level SCU-I.

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	SCU-I	SCU-II	SCU-III	SCU-IV	Type of test
C	0,260	0,521	0,592	0,525	Cochran's test statistics
Stragglers (P = 10)	0,602	0,602	0,602	0,602	Cochran's critical values
Outliers (P = 10)	0,718	0,718	0,718	0,718	

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.

It was confirmed that no outliers and stragglers exist by Cochran's test here.

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
SCU-I;10	1,410	1,060	0,517 7	0,735 5	Grubbs' test statistics
SCU-II;10	1,456	1,278	0,591 8	0,580 3	
SCU-III;10	1,426	2,023	0,628 7	0,319 4	
SCU-IV;10	1,825	1,499	0,451 4	0,489 6	
Stragglers P = 10	2,290	2,290	0,186 4	0,186 4	Grubbs' critical values
Outliers P = 10	2,482	2,482	0,115 0	0,115 0	

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

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

It was confirmed that no outliers and stragglers exist by Grubbs' test here.

A.4.5 Calculation of the general mean and standard deviations

Calculation of the general mean, s_r, s_R, of 7DDR (Titrimetric method after distillation) in each sample has led to Table A.18, expressed in the mass fraction (%).

Table A.18 — Calculation results of the general mean, s_r, s_R, of 7DDR (Titrimetric method after distillation)

Sample/Level	SCU-I	SCU-II	SCU-III	SCU-IV
Number of Laboratories	10	10	10	10
Outliers	0	0	0	0
General mean, m	56,31	52,72	16,76	15,84
Repeatability standard deviation, s_r	0,689	1,186	1,534	0,861
Reproducibility standard deviation, s_R	4,481	3,148	1,889	1,662

A.4.6 Dependence of precision on general mean, m

An examination of the data in Table A.18 does not indicate any dependence and average values can be used.

But it seems clear that s_R tend to increase with higher values of m, so it is likely that it might be permissible to establish some form of functional relationship.

s_R = 0,054 8 m + 0,854 5 R^2 = 0,869 0

A.4.7 Final values of precision

The precision of 7DDR (Titrimetric method after distillation) measurement method should be quoted as follows:

— repeatability standard deviation: s_r = 1,068

— reproducibility standard deviation: s_R = 0,054 8 m + 0,854 5

The conclusion above was determined from a uniform-level experiment involving 10 laboratories, no outliers and stragglers have been reported.

A.5 Statistical analysis of the test results of 1DDR (Refractometer method)

A.5.1 Original test results

Eight laboratories have participated in the determination of 1DDR (Refractometer method). The test results are listed in Table A.19, expressed in the mass fraction (%).

Table A.19 — Original test results of the determination of 1DDR (Refractometer method)

Laboratory *i*	Level j							
	SCU-I		SCU-II		SCU-III		SCU-IV	
1	44,67	47,12	36,50	35,74	8,28	9,22	10,08	8,25
2	44,90	45,23	40,09	39,77	10,72	10,96	9,58	9,81
3	52,30	50,96	38,14	38,14	14,10	14.10	13,37	13,37
4	42,39	45,62	30,96	35,67	9,00	8,05	10,75	8,89
5	49,99	48,26	41,50	36,10	10,04	11,63	10,00	8,56
6	45,35	45,29	35,06	35,35	9,08	8,98	8,35	8,43
7	45,07	45,99	36,49	37,67	9,53	8,76	8,67	7,92
8	40.<97	42,61	33,80	35,05	8,87	8,93	10,53	10,44

A.5.2 Cell means

The cell means of the determination of 1DDR (Refractometer method) are listed in Table A.20, expressed in the mass fraction (%).

Table A.20 — Cell means of the determination of 1DDR (Refractometer method)

Laboratory *i*	Level j			
	SCU-I	SCU-II	SCU-III	SCU-IV
1	45,895	36,120	8,750	9,165
2	45,065	39,930	10,840	9,695
3	51,630	38,140	14,100	13,370
4	44,005	33,315	8,525	9,820
5	49,125	38,800	10,835	9,280
6	45,320	35,205	9,030	8,390
7	45,530	37,080	9,145	8,295
8	41,790	34,425	8,900	10,485

A.5.3 Cell absolute differences

The cell absolute differences of the determination of 1DDR (Refractometer method) are listed in Table A.21, expressed in the mass fraction (%).

Table A.21 — Cell absolute differences of the determination of 1DDR (Refractometer method)

Laboratory *i*	**Level** j			
	SCU-I	**SCU-II**	**SCU-III**	**SCU-IV**
1	2,45	0,76	0,94	1,83
2	0,33	0,32	0,24	0,23
3	1,34	0,00	0,00	0,00
4	3,23	4,71	0,95	1,86
5	1,73	5,40	1,59	1,44
6	0,06	0,29	0,10	0,08
7	0,92	1,18	0,77	0,75
8	1,64	1,25	0,06	0,09

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.

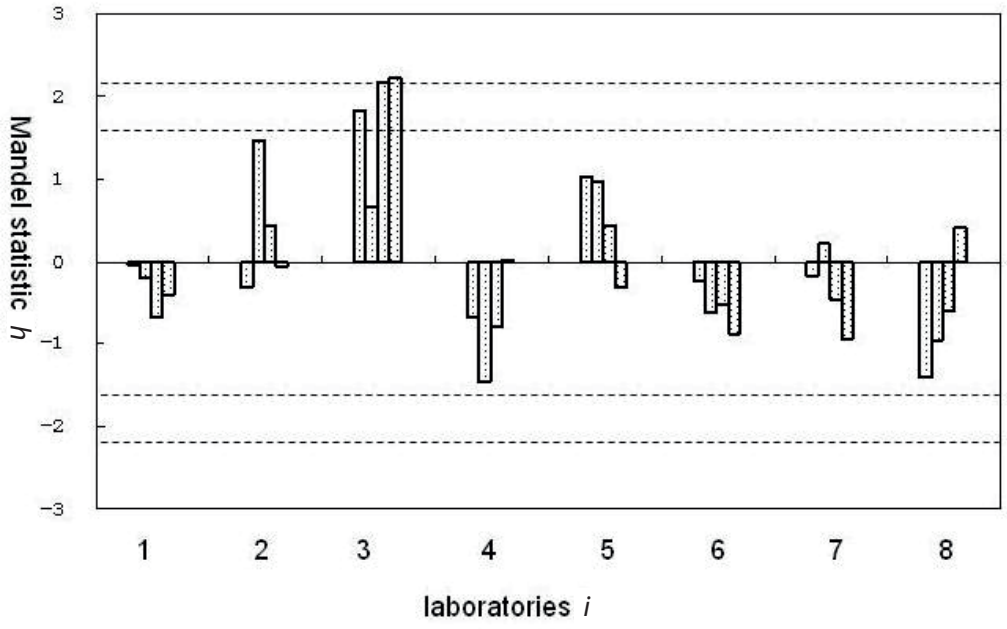

Figure A.7 — Mandel's between-laboratory consistency statistic, *h*, grouped by laboratories

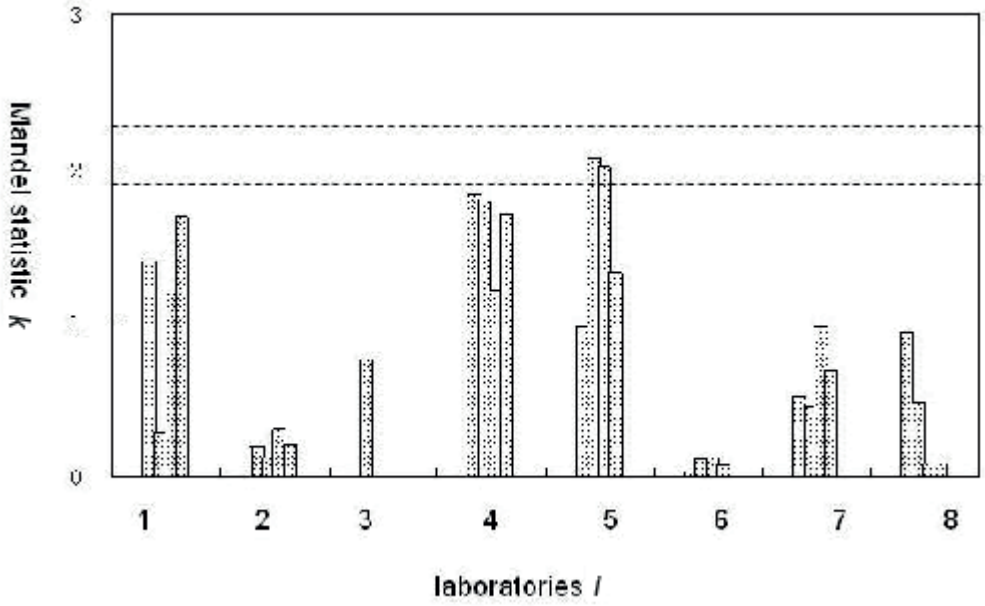

Figure A.8 — Mandel's within-laboratory consistency statistic, *k*, grouped by laboratories

Horizontal dotted lines in Figures A.7 and A.8 represent 1 % and 5 % critical values of Mandel's *h* and *k* statistics, respectively.

The *h* graph shows that laboratory 3 had an outlier on level SCU-III and level SCU-IV whereas laboratory 3 had a straggler on level SCU-I.

The *k* graph shows that laboratory 5 had stragglers on level SCU-IIand l level SCU-III.

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	**SCU-I**	**SCU-II**	**SCU-III**	**SCU-IV**	**Type of test**
C	0,419	0,530	0,508	0,364	Cochran's test statistics
Stragglers(P = 8)	0,680	0,680	0,680	0,680	Cochran's critical values
Outliers (P = 8)	0,794	0,794	0,794	0,794	

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 outliers and stragglers exist by Cochran's test here.

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
SCU-I;8	1,399	1,837	0,236 0	0,178 1	Grubbs' test statistics
SCU-II;8	1,456	1,452	0,266 6	0,430 4	
SCU-III;8	0,791	2,169	0,265 8	0,139 1	
SCU-IV;8	0,942	2,209	0,162 2	0,113 5	
Stragglers $P = 8$	2,126	2,126	0,110 1	0,110 1	Grubbs' critical values
Outliers $P = 8$	2,274	2,274	0,056 3	0,056 3	

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

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

It was confirmed that laboratory 3 had stragglers on level SCU-III and level SCU-IV, but no outliers exist by Grubbs' test here.

A.5.5 Calculation of the general mean and standard deviations

Calculation of the general mean, s_r, s_R, of 1DDR (Refractometer method) in each sample has led to Table A.24, expressed in the mass fraction (%).

Table A.24 — Calculation results of the general mean, s_r, s_R, of 1DDR (Refractometer method)

Sample/Level	SCU-I	SCU-II	SCU-III	SCU-IV
Number of Laboratories	8	8	8	8
Outliers	0	0	0	0
General mean, m	46,05	36,63	10,02	9,81
Repeatability standard deviation s_r	1,247	1,855	0,558	0,771
Reproducibility standard deviation s_R	3,166	2,626	1,872	1.703

A.5.6 Dependence of precision on general mean, m

An examination of the data in Table A.24 does not indicate any dependence and average values can be used.

But it seems clear that s_R tend to increase with higher values of m, so it is likely that it might be permissible to establish some form of functional relationship.

$s_R = 0{,}036\ 2\ m + 1{,}413\ 2 \quad R^2 = 0{,}975\ 7$

A.5.7 Final values of precision

The precision of 1DDR (Refractometer method) measurement method should be quoted as follows:

— repeatability standard deviation: $s_r = 1{,}108$

— reproducibility standard deviation: $s_R = 0{,}036\ 2\ m + 1{,}413\ 2$

The conclusion above was determined from a uniform-level experiment involving eight laboratories, in which two test values have remained as stragglers.

A.6 Statistical analysis of the test results of 7DDR (Refractometer method)

A.6.1 Original test results

Eight laboratories have participated in the determination of 7DDR (Refractometer method). The test results are listed in Table A.25, expressed in the mass fraction (%).

Table A.25 — Original test results of the determination of 7DDR (Refractometer method)

Laboratory *i*	Level j							
	SCU-I		SCU-II		SCU-III		SCU-IV	
1	60,39	60,35	53,92	53,19	19,34	16,60	14,67	14,66
2	56,36	56,65	50,66	50,33	20,16	19,92	18,12	17,99
3	56,34	56,34	54,52	54,52	19,70	22,52	24,09	18,74
4	52,19	50,53	50,70	48,57	13,42	19,53	19,69	17,17
5	61,30	63,65	52,50	57,27	16,99	17,82	17,06	17,70
6	60,39	60,38	52,17	52,19	15,43	15,27	13,92	13,49
7	57,45	58,06	53,26	51,87	17,89	16,21	13,04	14,73
8	49,26	51,95	49,60	49,28	15,17	14,18	15,10	14,08

A.6.2 Cell means

The cell means of the determination of 7DDR (Refractometer method) were listed in Table A.26, expressed in the mass fraction (%).

Table A.26 — Cell means of the determination of 7DDR (Refractometer method)

Laboratory *i*	Level j			
	SCU-I	SCU-II	SCU-III	SCU-IV
1	60,370	53,555	17,970	14,665
2	56,505	50,495	20,040	18,055
3	56,340	54,520	21,110	21,415
4	51,360	49,635	16,475	18,430
5	62,475	54,885	17,405	17,380
6	60,385	52,180	15,350	13,705
7	57,755	52,565	17,050	13,885
8	50,605	49,440	14,675	14,590

A.6.3 Cell absolute differences

The cell absolute differences of the determination of 7DDR (Refractometer method) were listed in Table A.27, expressed in the mass fraction (%).

Table A.27 — Cell absolute differences of the determination of 7DDR (Refractometer method)

Laboratory *i*	Level j			
	SCU-I	SCU-II	SCU-III	SCU-IV
1	0,04	0,73	2,74	0,01
2	0,29	0,33	0,24	0,13
3	0,00	0,00	2,82	5,35

Table A.27 *(continued)*

Laboratory *i*	**Level** j			
	SCU-I	**SCU-II**	**SCU-III**	**SCU-IV**
4	1,66	2,13	6,11	2,52
5	2,35	4,77	0,83	0,64
6	0,01	0,02	0,16	0,43
7	0,61	1,39	1,68	1,69
8	2,69	0,32	0,99	1,02

A.6.4 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.

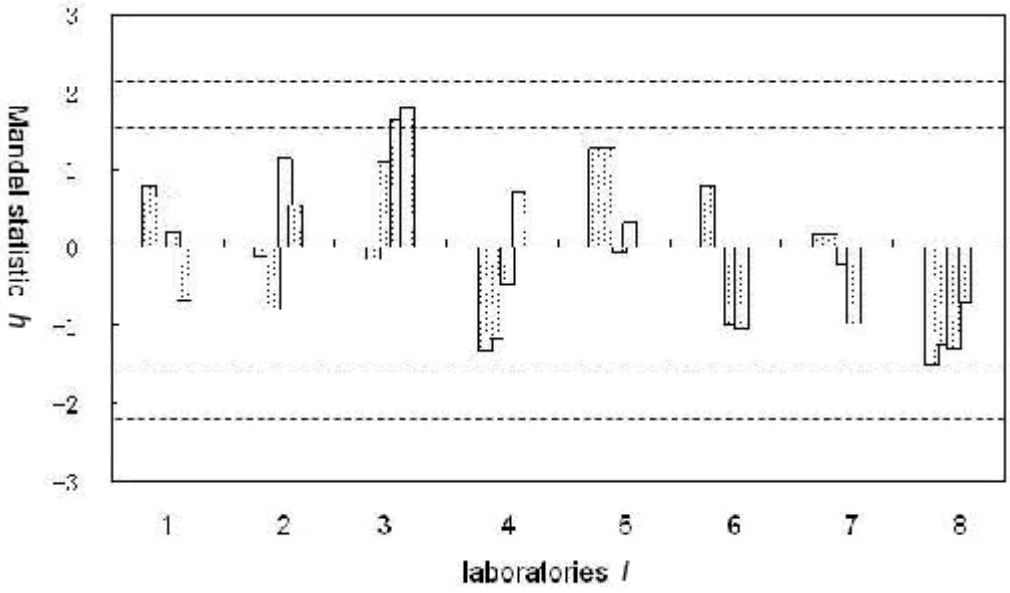

Figure A.9 — Mandel's between-laboratory consistency statistic, *h*, grouped by laboratories

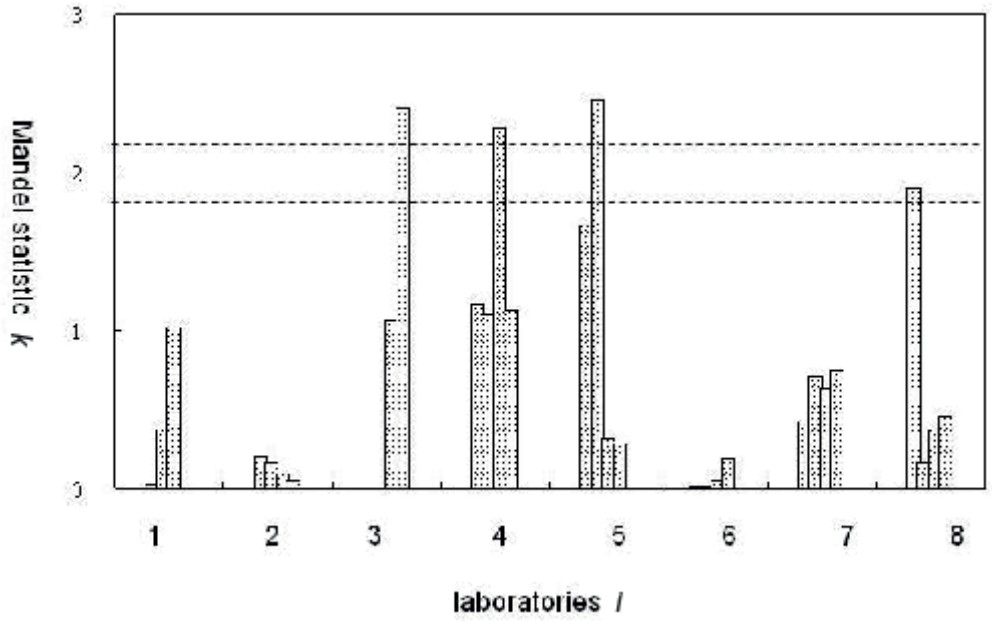

Figure A.10 — Mandel's within-laboratory consistency statistic, *k*, grouped by laboratories

Horizontal dotted lines in Figures A.9 and A.10 represent 1 % and 5 % critical values of Mandel's *h* and *k* statistics, respectively.

The *h* graph shows that laboratory 5 had stragglers on level SCU-III and l level SCU-IV.

The *k* graph shows that laboratory 3 had an outlier on level SCU-IV, laboratory 4 had an outlier on level SCU-III, and laboratory 5 had an outlier on level SCU-II; laboratory 8 had a straggler on level SCU-I.

Cochran's test

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	**SCU-I**	**SCU-II**	**SCU-III**	**SCU-IV**	**Type of test**
C	0,346	0,759	0,651	0,725	Cochran's test statistics
Stragglers (P = 8)	0,680	0,680	0,680	0,680	Cochran's critical values
Outliers (P = 8)	0,794	0,794	0,794	0,794	

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.

It was confirmed that that laboratory 5 had a straggler on level SCU-II and laboratory 3 had a straggler on level SCU-IV, but no outliers exist by Cochran' s test here.

Grubbs' 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
SCU-I;8	1,497	1,293	0,242 4	0,565 1	Grubbs' test statistics
SCU-II;8	1,279	1,282	0,420 2	0,453 0	
SCU-III;8	1,294	1,644	0,498 0	0,236 4	
SCU-IV;8	1,024	1,785	0,625 4	0,328 6	
Stragglers $P = 8$	2,126	2,126	0,110 1	0,110 1	Grubbs' critical values
Outliers $P = 8$	2,274	2,274	0,056 3	0,056 3	

It was confirmed that no outliers and stragglers exist by Grubbs' test here.

A.6.5 Calculation of the general mean and standard deviations

Calculation of the general mean, s_r, s_R, of 7DDR (Refractometer method) in each sample has led to Table A.30, expressed in the mass fraction (%).

Table A.30 — Calculation results of the general mean, s_r, s_R, of 7DDR (Refractometer method)

Sample/Level	SCU-I	SCU-II	SCU-III	SCU-IV
Number of Laboratories	8	8	8	8
Outliers	0	0	0	0
General mean, m	56,974	52,159	17,509	16,516
Repeatability standard deviation s_r	0,999	1,606	1,894	1,571
Reproducibility standard deviation s_R	4,313	2,110	2,567	2,961

A.6.6 Dependence of precision on general mean, m

An examination of the data in Table A.30 does not indicate any dependence and average values can be used.

A.6.7 Final values of precision

The precision of 7DDR (Refractometer method) measurement method should be quoted as follows:

— repeatability standard deviation: $s_r = 1,517$

— reproducibility standard deviation: $s_R = 2,988$

The conclusion above was determined from a uniform-level experiment involving eight laboratories, in which two test values have remained as stragglers.

A.7 Statistical analysis of the test results of the mass fraction of sulfur

A.7.1 Original test results

Ten laboratories have participated in the determination of the mass fraction of sulfur. The test results were listed in Table A.31, expressed in the mass fraction (%).

Table A.31 — Original test results of the determination of the mass fraction of sulfur

Laboratory *i*	Level j							
	SCU-I		SCU-II		SCU-III		SCU-IV	
1	14,45	14,48	18,99	19,03	22,75	22,74	21,70	21,75
2	13,87	13,93	18,74	18,68	22,8	22,76	22,48	22,.46
3	13,62	13,75	18,01	17,34	22,00	23,03	18,46	19,99
4	13,13	13,09	17,74	17,68	22,24	22,22	22,50	22,46
5	12,95	12,48	17,71	17,90	22,20	21,38	21,79	21,32
6	13,19	12,89	18,67	18,48	22,55	22,54	22,05	22,14
7	13,92	14,04	18,46	18,66	22,68	22,76	21,89	21,99
8	14,60	14,55	19,09	19,13	22,59	22,53	21,36	21,30
9	13,48	13,41	18,92	18,80	22,55	22,57	22,60	22,62
10	13,80	13,58	18,56	18,.50	22,26	22,38	22,70	22,54

A.7.2 Cell means

The cell means of the determination of the mass fraction of sulfur were listed in Table A.32, expressed in the mass fraction (%).

Table A.32 — Cell means of the determination of the mass fraction of sulfur

Laboratory *i*	Level j			
	SCU-I	SCU-II	SCU-III	SCU-IV
1	14,465	19,010	22,745	21,725
2	13,900	18,710	22,780	22,470
3	13,685	17,675	22,515	19,225
4	13,110	17,710	22,230	22,480
5	12,715	17,805	21,790	21,555
6	13,040	18,575	22,545	22,095
7	13,980	18,560	22,720	21,940
8	14,575	19,110	22,560	21,330
9	13,445	18,860	22,560	22,610
10	13,690	18,530	22,320	22,620

A.7.3 Cell absolute differences

The cell absolute differences of the determination of the mass fraction of sulfur were listed in Table A.33, expressed in the mass fraction (%).

Table A.33 — Cell absolute differences of the determination of the mass fraction of sulfur

Laboratory *i*	Level j			
	SCU-I	SCU-II	SCU-III	SCU-IV
1	0,03	0,04	0,01	0,05
2	0,06	0,06	0,04	0,02
3	0,13	0,67	1,03	1,53
4	0,04	0,06	0,02	0,04

Table A.33 *(continued)*

Laboratory *i*	**Level** j			
	SCU-I	**SCU-II**	**SCU-III**	**SCU-IV**
5	0,47	0,19	0,82	0,47
6	0,30	0,19	0,01	0,09
7	0,12	0,20	0,08	0,10
8	0,05	0,04	0,06	0,06
9	0,07	0,12	0,02	0,02
10	0,22	0,06	0,12	0,16

A.7.4 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.

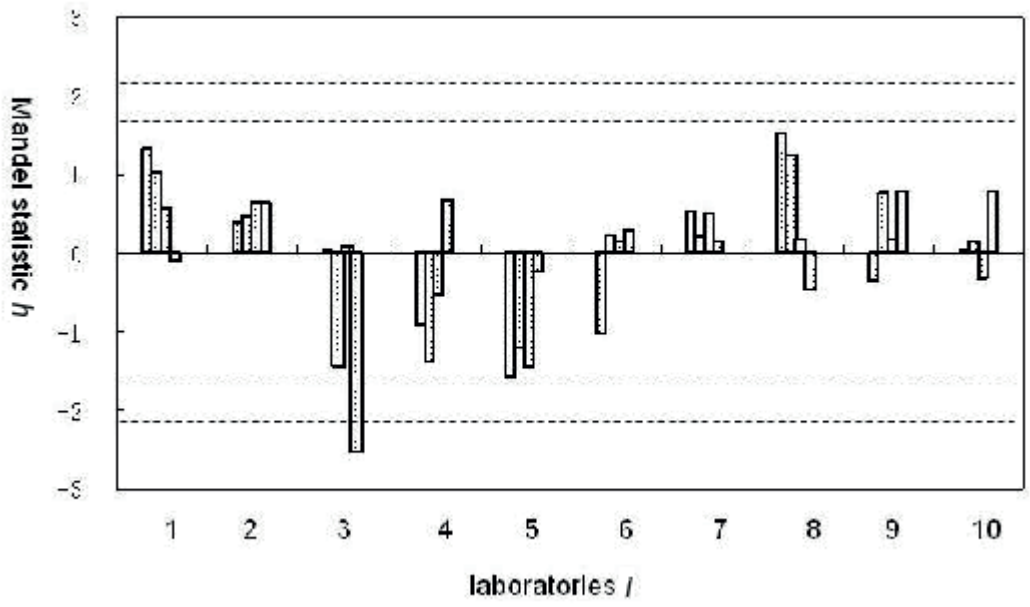

Figure A.11 — Mandel's between-laboratory consistency statistic, *h*, grouped by laboratories

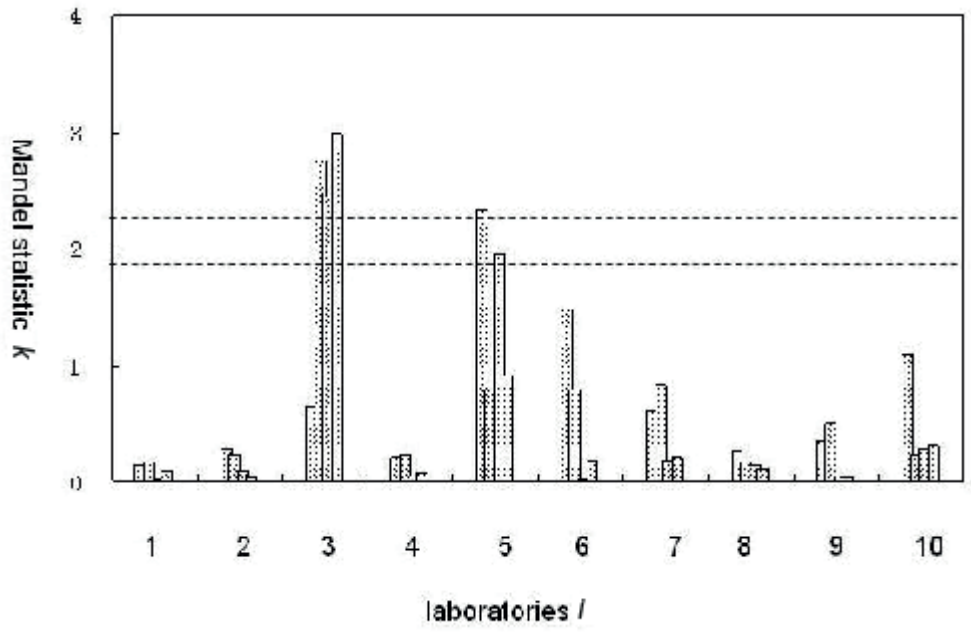

Figure A.12 — Mandel's within-laboratory consistency statistic, *k*, grouped by laboratories

Horizontal dotted lines in Figures A.11 and A.12 represent 1 % and 5 % critical values of Mandel's *h* and *k* statistics, respectively.

The *h* graph shows that laboratory 3 had an outlier on level SCU-IV.

The *k* graph shows that laboratory 3 had outliers on level SCU-II, SCU-III, and SCU-IV, laboratory 5 had an outlier on level SCU-I, and laboratory 5 had a straggler on level SCU-III.

Cochran's test

Application of Cochran's test led to the values of the test statistic C given in Table A.34.

Table A.34 — Values of Cochran test statistic, C

Level j	**SCU-I**	**SCU-II**	**SCU-III**	**SCU-IV**	**Type of test**
C	0,547	0,761	0,603	0,896	Cochran's test statistics
Stragglers (P = 10)	0,602	0,602	0,602	0,602	Cochran's critical values
Outliers (P = 10)	0,718	0,718	0,718	0,718	

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 shows that the test statistics reached 0,761 and 0,896, calculated by the cell absolute difference (0,67 and 1,53) from laboratory 3 on level SCU-II and SCU-IV.

The Cochran's critical value at the 1 % significance level was 0,718, therefore, the test results from laboratory 3 on level SCU-II and is SCU-IVoutliers, which should be discarded here. At the 5 % significance level, the Cochran's critical value was 0,602, therefore, the test results from laboratory 3 on level SCU-III is a straggler, it was decided to retain it here for next step.

Cochran's test was repeated on the remaining tests values from the nine laboratories on level SCU-II and SCU-IV, the test statistic obtained this time were 0,284 and 0,809, and the Cochran's critical value at the 1 % significance level was 0,638 (P = 9), so the test value from five laboratories on level SCU-IV should be discarded here. Then, Cochran's test was repeated again on the remaining test values from the eight laboratories on level SCU-IV, the test statistic obtained this time was 0,490, which is less than the Cochran's critical value at the 5 % significance level (0,680, P = 8). It was confirmed that no straggler (and no outlier) exist this time.

Grubbs' test

Application of Grubbs' test to cell means has led to the values of the test statistic G, shown in Table A.35.

Table A.35 — Application of Grubbs' test to cell means

Level j;p	**Single low**	**Single high**	**Double low**	**Double high**	**Type of test**
SCU-I;10	1,568	1,516	0,433 9	0,515 6	Grubbs' test statistics
SCU-II;9	1,702	1,165	0,634 5	0,170 1	
SCU-III;10	2,302	1,018	0,888 1	1,169 6	
SCU-IV;8	1,765	0,982	0,876 5	0,357 2	
Stragglers					Grubbs' critical values
P = 8	2,126	2,126	0,110 1	0,110 1	
P = 9	2,215	2,215	0,149 2	0,149 2	
P = 10	2,290	2,290	0,186 4	0,186 4	
Outliers					
P = 8	2,274	2,274	0,056 3	0,056 3	
P = 9	2,387	2,387	0,085 1	0,085 1	
P = 10	2,482	2,482	0,115 0	0,115 0	

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

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

We have confirmed that that laboratory 5 had a straggler on level SCU-III, but no outliers exist by Grubbs' test here.

A.7.5 Calculation of the general mean and standard deviations

Calculation of the general mean, s_r, s_R, of the mass fraction of sulfur in each sample has led to Table A.36, expressed in the mass fraction (%).

Table A.36 — Calculation results of the general mean, s_r, s_R, of the mass fraction of sulfur

Sample/Level	**SCU-I**	**SCU-II**	**SCU-III**	**SCU-IV**
Number of Laboratories	10	10	10	10
Outliers	0	1	0	2
General mean, m	13,66	18,54	22,48	22,16
Repeatability standard deviation s_r	0,133	0,087	0,295	0,057
Reproducibility standard deviation s_R	0,610	0,492	0,360	0,471

A.7.6 Dependence of precision on general mean, m

An examination of the data in Table A.36 does not indicate any dependence and average values can be used.

A.7.7 Final values of precision

The precision (expressed in the mass fraction) of the mass fraction of sulfur measurement method should be quoted as follows:

— repeatability standard deviation: s_r = 0,14

— reproducibility standard deviation: s_R = 0,49

The conclusion above were determined from a uniform-level experiment involving 10 laboratories, in which one test value from two laboratories have been discarded as outliers, in which one test value remained as a straggler.

A.8 Statistical analysis of the test results of the mass fraction of biuret

A.8.1 Original test results

Ten laboratories have participated in the determination of the mass fraction of biuret. The test results were listed in Table A.37, expressed in the mass fraction (%).

Table A.37 — Original test results of the determination of the mass fraction of biuret

Laboratory *i*	**Level** j							
	SCU-I		**SCU-II**		**SCU-III**		**SCU-IV**	
1	0,74	0,75	0,77	0,78	0,69	0,68	0,70	0,71
2	0,80	0,82	0,76	0,76	0,74	0,72	0,68	0,70
3	0,.55	0,52	0,49	0,49	0,52	0,52	0,55	0,55
4	0,64	0,64	0,.64	0,65	0,60	0,62	0,67	0,63
5	0,64	0,80	0,77	0,71	0,67	0,72	0,69	0,78
6	0,74	0,78	0,75	0,73	0,70	0,73	0,70	0,66
7	0,79	0,83	0,85	0,89	0,76	0,79	0,78	0,80
8	0,76	0,77	0,78	0,79	0,71	0,70	0,70	0,69
9	0,82	0,78	0,80	0,85	0,67	0,67	0,67	0,69
10	0,69	0,65	0,68	0,62	0,60	0,61	0,61	0,62

A.8.2 Cell means

The cell means of the determination of the mass fraction of biuret were listed in Table A.38, expressed in the mass fraction (%).

Table A.38 — Cell means of the determination of the mass fraction of biuret

Laboratory *i*	**Level** j			
	SCU-I	**SCU-II**	**SCU-III**	**SCU-IV**
1	0,745	0,775	0,685	0,705
2	0,810	0,760	0,730	0,690
3	0,535	0,490	0,520	0,550
4	0,640	0,645	0,610	0,650

Table A.38 *(continued)*

Laboratory *i*	Level j			
	SCU-I	SCU-II	SCU-III	SCU-IV
5	0,720	0,740	0,695	0,735
6	0,760	0,740	0,715	0,680
7	0,810	0,870	0,775	0,790
8	0,765	0,785	0,705	0,695
9	0,800	0,825	0,670	0,680
10	0,670	0,650	0,605	0,615

A.8.3 Cell absolute differences

The cell absolute differences of the determination of the mass fraction of biuret were listed in Table A.39, expressed in the mass fraction (%).

Table A.39 — Cell absolute differences of the determination of the mass fraction of biuret

Laboratory *i*	Level j			
	SCU-I	SCU-II	SCU-III	SCU-IV
1	0,01	0,01	0,01	0,01
2	0,02	0,00	0,02	0,02
3	0,03	0,00	0,00	0,00
4	0,00	0,01	0,02	0,04
5	0,16	0,06	0,05	0,09
6	0,04	0,02	0,03	0,04
7	0,04	0,04	0,03	0,02
8	0,01	0,01	0,01	0,01
9	0,04	0,05	0,00	0,02
10	0,04	0,06	0,01	0,01

A.8.4 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.

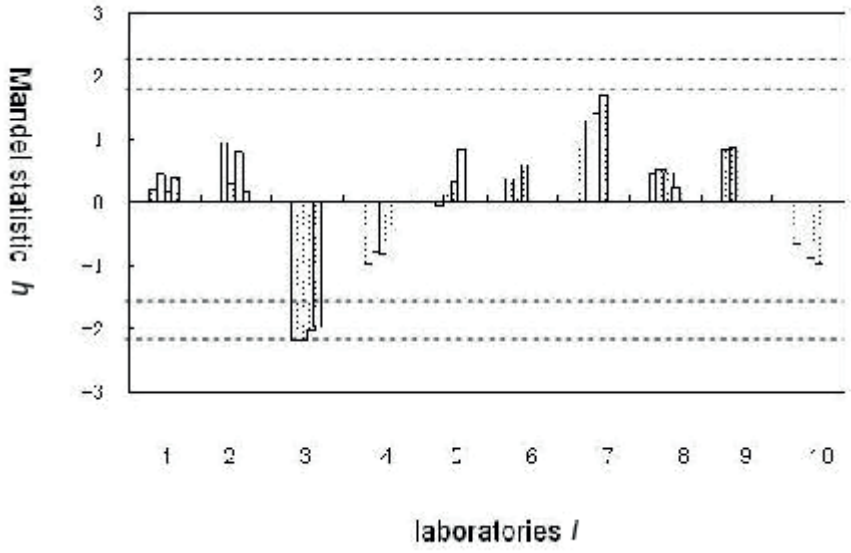

Figure A.13 — Mandel's between-laboratory consistency statistic, *h*, grouped by laboratories

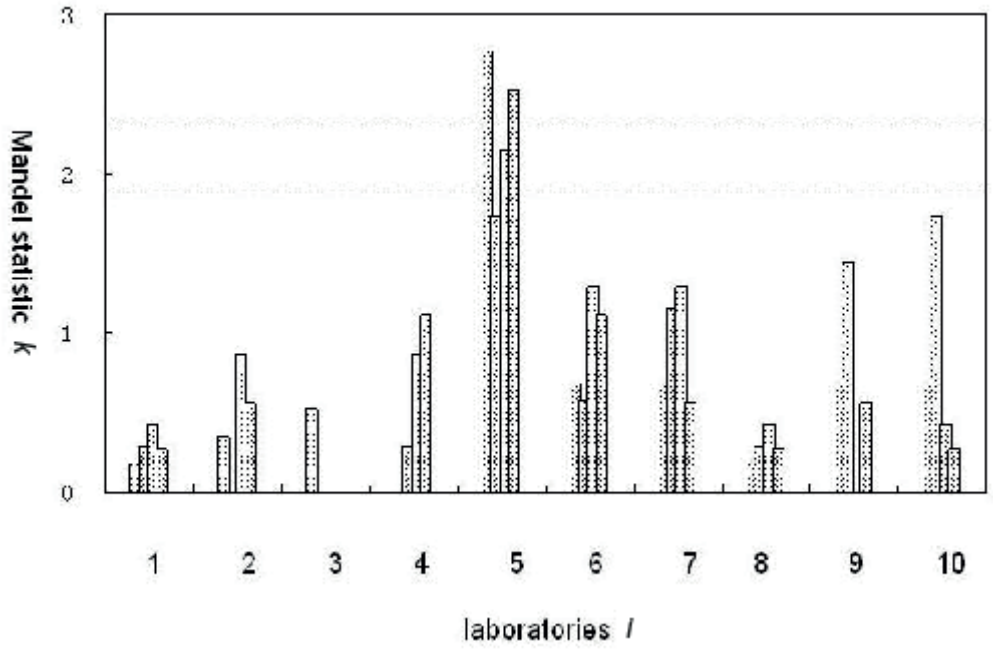

Figure A.14 — Mandel's within-laboratory consistency statistic, *k*, grouped by laboratories

Horizontal dotted lines in Figures A.13 and A.14 represent 1 % and 5 % critical values of Mandel's *h* and *k* statistics, respectively.

The *h* graph shows that laboratory 3 and had laboratory 4 had a straggler.

The *k* graph shows that laboratory 5 had outliers on level SCU-I and SCU-IV, laboratory 5 had a straggler on level SCU-III.

Cochran's test

Application of Cochran's test led to the values of the test statistic C, given in Table A.40.

Table A.40 — Values of Cochran test statistic, C

Level j	**SCU-I**	**SCU-II**	**SCU-III**	**SCU-IV**	**Type of test**
C	0,764	0,300	0,463	0,633	Cochran's test statistics
Stragglers (P = 10)	0,602	0,602	0,602	0,602	Cochran's critical values
Outliers (P = 10)	0,718	0,718	0,718	0,718	

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 shows that the test statistic reached 0,764, calculated by the cell absolute difference (0,16) from laboratory 5 on level SCU-I.

The Cochran's critical value at 1 % significance level was 0,718, therefore the test results from laboratory 5 on level SCU-I are outliers, which should be discarded here.

At the 5 % significance level, the Cochran's critical value was 0,602, therefore the test results from laboratory 5 on level SCU-IV is stragglers, we decided to retain them here for next step.

Cochran' s test was repeated on the remaining tests values from the nine laboratories on level SCU-I, the test statistic obtained this time was 0,203, which is less than the Cochran' s critical value at the 5 % significance level (0,638, P = 9). It was confirmed that no straggler (and no outlier) exist this time.

Grubbs' test

Application of Grubbs' test to cell means led to the values of the test statistic G shown in Table A.41.

Table A.41 — Application of Grubbs' test to cell means

Level j;p	**Single low**	**Single high**	**Double low**	**Double high**	**Type of test**
SCU-I;9	2,048	0,899	0,211	0,766	Grubbs' test statistics
SCU-II;10	2,193	1,309	1,082	0,665	
SCU-III;10	2,046	1,409	1,681	0,708	
SCU-IV;10	1,983	1,706	1,884	0,878	
Stragglers					Grubbs' critical values
P = 9	2,215	2,215	0,149 2	0,149 2	
P = 10	2,290	2,290	0,186 4	0,186 4	
Outliers					
P = 9	2,387	2,387	0,085 1	0,085 1	
P = 10	2,482	2,482	0,115 0	0,115 0	

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

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

It was confirmed that no outliers exist by Cochran's test here.

A.8.5 Calculation of the general mean and standard deviations

Calculation of the general mean, s_r, s_R of biuret in each sample has led to Table A.42, expressed in the mass fraction (%).

Table A.42 — Calculation results of the general mean, s_r, s_R of biuret

Sample/Level	SCU-I	SCU-II	SCU-III	SCU-IV
Number of laboratories	9	10	10	10
Outliers	1	0	0	0
General mean, m	0,73	0,73	0,67	0,68
Repeatability standard deviation, s_r	0,021	0,020	0,016	0,025
Reproducibility standard deviation, s_R	0,094	0,106	0,071	0,064

A.8.6 Dependence of precision on general mean, m

An examination of the data in Table A.6 does not indicate any dependence and average values can be used.

A.8.7 Final Values of precision

The precision (expressed in the mass fraction) of the mass fraction of biuret measurement method should be quoted as follows:

— repeatability standard deviation: $s_r = 0,021$

— reproducibility standard deviation: $s_R = 0,084$

The conclusion above was determined from a uniform-level experiment involving 10 laboratories, in which one test value from a laboratory has been discarded as an outlier and in which one test value has remained as straggler.

A.9 Statistical analysis of the test results of the mass fraction of water

A.9.1 Original test results

Nine laboratories have participated in the determination of the mass fraction of water. The test results were listed in Table A.43, expressed in the mass fraction (%).

Table A.43 — Original test results of the determination of the mass fraction of water

Laboratory *i*	Level j							
	SCU-I		SCU-II		SCU-III		SCU-IV	
1	0,35	0,.36	0,18	0,19	0,29	0,30	0,19	0,19
2	0,29	0,32	0,20	0,26	0,23	0,27	0,21	0,27
3	0,36	0,29	0,14	0,22	0,43	0,35	0,21	0,29
4	0,36	0,36	0,19	0.18	0,29	0,31	0,17	0,19
5	0,38	0,40	0,17	0,17	0,29	0,30	0,17	0,19
6	0,27	0,30	0,13	0,10	0,20	0,24	0,15	0,16
7	0,37	0,38	0,20	0,19	0,29	0,30	0,22	0,20

Table A.43 *(continued)*

Laboratory *i*	Level j							
	SCU-I		SCU-II		SCU-III		SCU-IV	
8	0,31	0,32	0,24	0,22	0,30	0,31	0,25	0,23
9	0,28	0,24	0,23	0,28	0,20	0,25	0,21	0,28

A.9.2 Cell means

The cell means of the determination of the mass fraction of water were listed in Table A.44, expressed in the mass fraction (%).

Table A.44 — Cell means of the determination of the mass fraction of water

Laboratory *i*	Level j			
	SCU-I	SCU-II	SCU-III	SCU-IV
1	0,355	0,185	0,295	0,190
2	0,305	0,230	0,250	0,240
3	0,325	0,180	0,390	0,250
4	0,360	0,185	0,300	0,180
5	0,390	0,170	0,295	0,180
6	0,285	0,115	0,220	0,155
7	0,375	0,195	0,295	0,210
8	0,315	0,230	0,305	0,240
9	0,260	0,255	0,225	0,245

A.9.3 Cell absolute differences

The cell absolute differences of the determination of the mass fraction of water were listed in Table A.45, expressed in the mass fraction (%).

Table A.45 — Cell absolute differences of the determination of the mass fraction of water

Laboratory *i*	Level j			
	SCU-I	SCU-II	SCU-III	SCU-IV
1	0,01	0,01	0,01	0,00
2	0,03	0,06	0,04	0,06
3	0,07	0,08	0,08	0,08
4	0,00	0,01	0,02	0,02
5	0,02	0,00	0,01	0,02
6	0,03	0,03	0,04	0,01
7	0,01	0,01	0,01	0,02
8	0,01	0,02	0,01	0,02
9	0<04	0,05	0,05	0,07

A.9.4 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.

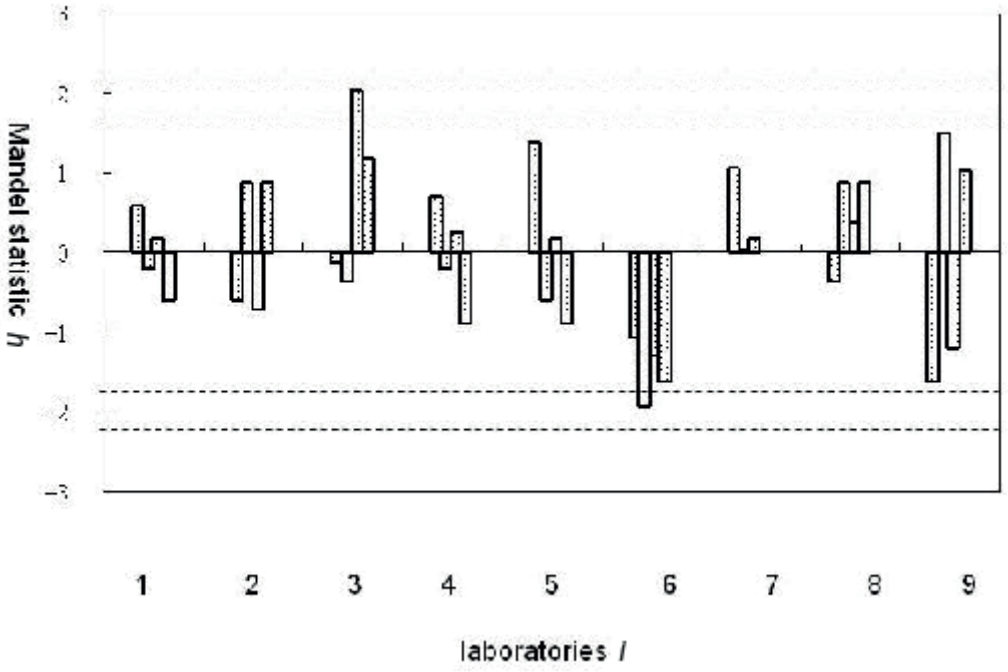

Figure A.15 — Mandel's between-laboratory consistency statistic, *h*, grouped by laboratories

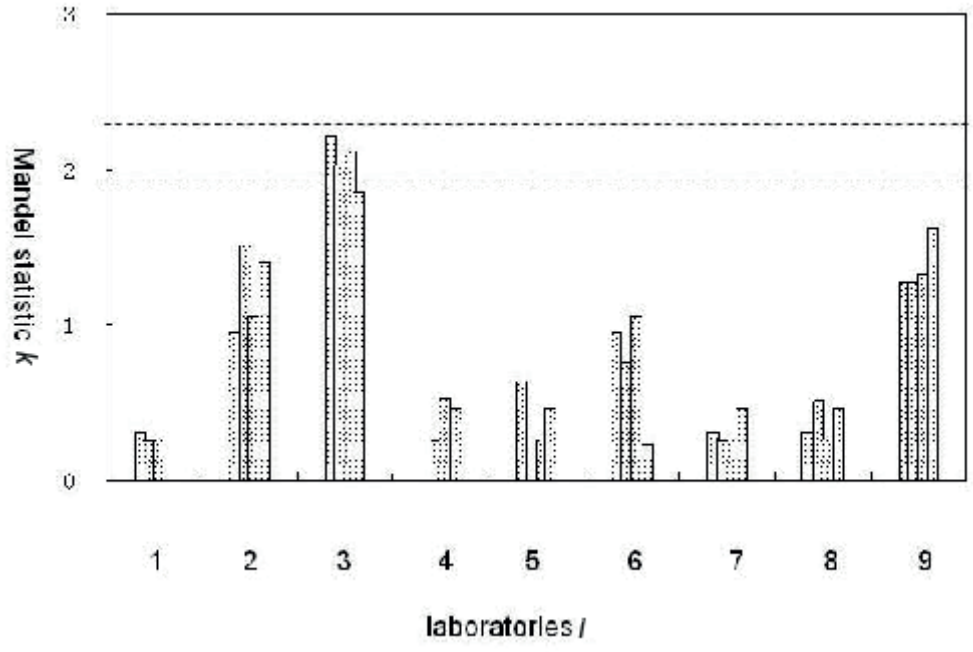

Figure A.16 — Mandel's within-laboratory consistency statistic, *k*, grouped by laboratories

Horizontal dotted lines in Figures A.15 and A.16 above represent 1 % and 5 % critical values of Mandel's *h* and *k* statistics, respectively.

The *h* graph shows that laboratory 3 had a straggler on level SCU-III and laboratory 6 had a straggler on level SCU-II.

The *k* graph shows that laboratory 3 had stragglers on level SCU-I, SCU-II, and level SCU-III.

Cochran's test

Application of Cochran's test led to the values of the test statistic C, given in Table A.46.

Table A.46 — Values of Cochran test statistic, C

Level j	SCU-I	SCU-II	SCU-III	SCU-IV	Type of test
C	0,544	0,454	0,496	0,386	Cochran's test statistics
Stragglers (P = 9)	0,638	0,638	0,638	0,638	Cochran's critical values
Outliers (P = 9)	0,754	0,754	0,754	0,754	

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.

It was confirmed that no outliers and stragglers exist by Cochran's test here.

Grubbs' test

Application of Grubbs' test to cell means led to the values of the test statistic G shown in Table A.47.

Table A.47 — Application of Grubbs' test to cell means

Level j;p	Single low	Single high	Double low	Double high	Type of test
SCU-I;9	1,619	1,388	0,296 0	0,682 8	Grubbs' test statistics
SCU-II;9	1,921	1,488	0,463 8	0,726 9	
SCU-III;9	1,291	2,028	0,366 7	0,755 6	
SCU-IV;9	1,567	1,140	0,751 0	0,754 2	
Stragglers P = 9	2,215	2,215	0,149 2	0,149 2	Grubbs' critical values
Outliers P = 9	2,387	2,387	0,085 1	0,085 1	

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

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

It was confirmed that no outliers exist by Grubbs' test here.

A.9.5 Calculation of the general mean and standard deviations

Calculation of the general mean, s_r, s_R, of the the mass fraction of water in each sample has led to Table A.48, expressed in the mass fraction (%).

Table A.48 — Calculation results of the general mean, s_r, s_R, of the mass fraction of water

Sample/Level	SCU-I	SCU-II	SCU-III	SCU-IV
Number of laboratories	9	9	9	9
Outliers	0	0	0	0
General mean, m	0,33	0,19	0,29	0,21
Repeatability standard deviation s_r	0,022	0,025	0,024	0,025
Reproducibility standard deviation s_R	0,046	0,045	0,049	0,037

A.9.6 Dependence of precision on general mean, m

An examination of the data in Table A.48 does not indicate any dependence and average values can be used.

A.9.7 Final values of precision

The precision (expressed in the mass fraction) of the mass fraction of water measurement method should be quoted as follows:

— repeatability standard deviation: s_r = 0,024

— reproducibility standard deviation: s_R = 0,044

The conclusion above was determined from a uniform-level experiment involving nine laboratories, no outliers and stragglers have been reported.

A.10 Conclusion

We have accomplished the interlaboratory testing on determination of total nitrogen, 1DDR (Titrimetric method after distillation), 7DDR (Titrimetric method after distillation), 1DDR (Refractometer method), 7DDR (Refractometer method), sulfur, mass fraction of biuret, and water in sulfur coated urea, based on this Annex.

We have recruited 11 laboratories around the world to participate in our ring tests, and have received data from 10 laboratories in total.

Statistic work on the precision of test results has been accomplished based on ISO 5725-2.

Based on our statistic results, six outliers and 12 stragglers have been found within all those original test values, no specific outlying laboratories was reported. We believed that all those outlier and stragglers was caused by random errors.

The final precision value revealed by statistic work could be used to determine the repeatability standard deviation and reproducibility standard deviation of our test method.

Meanwhile, the final precision value shows that the test method described in this International Standard was reliable because a good consistency has been shown between the reported test values from all the participating laboratories.

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