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Fertilizers and soil conditioners — Determination of water-soluble potassium content — Potassium tetraphenylborate gravimetric method

Matières fertilisantes — Dosage de la teneur en potassium — Méthode gravimétrique au tétraphénylborate de potassium

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Foreword

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

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

Fertilizers and soil conditioners — Determination of water-soluble potassium content — Potassium tetraphenylborate gravimetric method

1 Scope

This International Standard specifies a gravimetric method for the determination of the water-soluble potassium content of test solutions of fertilizers. It is suitable for use in arbitration and for reference purposes.

This International Standard is applicable to those fertilizers containing more than 1,0 % K_2O or equivalent amount of K content.

2 Normative references

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

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

ISO 5317, *Fertilizers — Determination of water-soluble potassium content — Preparation of the test solution*

3 Principle

Precipitation of potassium ions present in an aliquot portion of the test solution (previously treated with bromine water and activated charcoal if cyanamide and/or organic materials are present) by sodium tetraphenylborate in a weakly alkaline medium in the presence of disodium ethylenediamine-tetraacetatedihydrate (EDTA disodium salt) to eliminate interference by ammonium ions and other metal cations.

Filtration of the precipitate, drying and weighing.

4 Reagents

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

During the analysis, use only reagents of recognized analytical grade, and water conforming to grade 3 of ISO 3696:1987

4.1 Sodium tetraphenylborate, approximately 15 g/L solution.

Dissolve 7,5 g of sodium tetraphenylborate [$NaB(C_6H_5)_4$] in 480 ml of water. Add 2 ml of the sodium hydroxide solution (4.4) and 20 ml of a 100 gram/litre (g/L) solution of magnesium chloride hexahydrate ($MgCl_2·6H_2O$). Stir for 15 min and filter through the filter paper (5.2).

This solution may be stored in a plastics bottle for not longer than 1 month. Filter immediately before use.

4.2 Sodium tetraphenylborate, wash solution.

Dilute 1 volume of the Sodium tetraphenylborate solution (4.1) with 10 volumes of water.

4.3 EDTA, disodium salt, 40 g/l solution.

Dissolve 4,0 g EDTA disodium salt in water in 100 ml graduated flask. Make up to the volume and mix.

4.4 Sodium hydroxide, 400 g/L solution.

4.5 Phenolphthalein, 5 g/L ethanolic solution.

Dissolve 0,5 g of phenolphthalein in 100 ml of 95 % (volume fraction) ethanol.

4.6 Bromine water, saturated solution, approximately 3,2 % (w/v) bromine; shelf life of less than 6 months.

4.7 Charcoal, activated, which does not adsorb or liberate potassium ions.

5 Apparatus and materials

During the analysis, use only glassware of grade A, and the following:

5.1 Gooch crucibles, having a sintered glass or porcelain disc of porosity grade P 10 or P 16 (pore size index of 4 μm to 16 μm).

5.2 Quantitative filter paper (intermediate speed).

5.3 Drying oven, capable of being controlled at 120°C ± 5°C.

5.4 Usual laboratory equipment, including pipettes, beakers (250 ml), and volumetric flasks, etc.

6 Test solution

Use the clear solution prepared as specified in ISO 5317, also described as follows:

Weigh, to the nearest 0,001 g, 5 g of the prepared test sample to form the test portion. Transfer the test portion to the flask with 400 ml of water. Bring to a boil and continue to boil for 30 min. Cool the contents of the flask and transfer to the volumetric flask. Dilute to the mark, mix well and filter into a dry beaker. Discard the first 50 ml of filtrate.

7 Procedure

7.1 Aliquot portion of test solution

7.1.1 Procedure in the presence of cyanamide and/or organic materials

Preparation of the test solution as specified in ISO 5317.

Transfer, by means of a pipette, an aliquot portion, V1, of the test solution (Clause 6), containing 50 mg to 100 mg of potassium oxide (K_2O), preferably about 80 mg, to a 250 ml beaker. Add 5 ml of the bromine water (4.6) and boil the solution until all the bromine has been removed and then, if necessary, to reduce the volume to less than 100 ml. Allow the solution to cool to ambient temperature and transfer it to a

100 ml volumetric flask. Add about 0,5 g of the activated charcoal (4.7) and shake vigorously. Dilute with distilled water to the mark and mix well.

Filter the solution and use a pipette to transfer 50 ml of the filtrate into a 250 ml beaker.

7.1.2 Procedure in the absence of cyanamide and/or organic materials

Transfer, by means of a pipette an aliquot portion, V1, of the test solution (Clause 6) containing 25 to 50 mg (preferably 40 mg) of K_2O to a 250 ml beaker and adjust the volume to approximately 50 ml by dilution or evaporation.

NOTE   If the content of fertilizer sample cannot be specified, use the procedure described in 7.1.1.

7.2 Determination

Further treat the aliquot portion of the test solution (7.1) as follows.

Add 20 ml of the EDTA solution (4.3) and 3 to 5 drops of the phenolphthalein solution (4.5). Add, drop by drop, the sodium hydroxide solution (4.4) until a pink colour appears and then add 1 ml of the sodium hydroxide solution in excess.

Slightly boil for 15 min.

The solution should remain pink. If it does not, add 1 to 3 drops of the phenolphthalein solution (4.6) and, if necessary, restore the pink colour by adding, drop by drop, the sodium hydroxide solution. (4.5).

Remove the beaker from the steam bath and immediately add, drop by drop, while stirring, 30 mL of the tetraphenylborate solution (4.1).

Continue stirring for 1 min then cool rapidly to ambient temperature in running water and allow to stand for 15 min.

Weigh the filter crucible (5.1) previously dried in the oven (5.3) controlled at 120 ± 5 °C, and cooled in a desiccator and then weighed to the nearest 0,000 1 g.

Decant the supernatant liquid through the crucible. Rinse the beaker and precipitate 3 to 5 times with a total of about 40 ml of the wash solution (4.2), followed by 5 ml of water.

Dry the crucible and precipitate in the oven (5.3) controlled at 120 ± 5 °C for 90 minutes, allow to cool in a desiccator and weigh to the nearest 0,000 1 g.

7.3 Blank test

Carry out a blank test at the same time as the determination.

7.4 Periodic quality control

Carry out a quality control test periodically as the determination using K_2SO_4 standard material.

8 Expression of results

8.1 Calculation

The potassium content, expressed as a percentage by mass as potassium (K) or as potassium oxide (K_2O), is given by Formula (1) and Formula (2).

a)   if cyanamide and/or organic materials are present

$$\frac{\left[(m_2 - m_1) - (m_4 - m_3)\right] \times f \times V_0 \times 200}{m_0 \times V_1} \tag{1}$$

b) if cyanamide and/or organic materials are absent

$$\frac{\left[(m_2 - m_1) - (m_4 - m_3)\right] \times f \times V_0 \times 100}{m_0 \times V_1} \qquad (2)$$

where

m_0 is the mass, in grams, of the test portion;

m_1 is the mass, in grams, of the filter crucible;

m_2 is the mass, in grams, of the crucible and precipitate;

m_3 is the mass, in grams, of the crucible used for the blank test;

m_4 is the mass, in grams, of the crucible used for the blank test and the corresponding precipitate;

V_0 is the volume, in millilitres, of the test portion (volume in which the test portion was dissolved;

V_1 is the volume, in millilitres, of the aliquot portion of the test portion taken for the determination;

f is a factor which, if the potassium content is expressed as potassium (K), is equal to 0,1091 or if the potassium content is expressed as potassium oxide (K_2O), is equal to 0.,1314.

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

Repeatability limit r: 0,19 %

8.2.3 Reproducibility, R

Reproducibility limit R: 0,006 2 m + 0,305 2, in which m represented the concentration of K_2O.

9 Test report

The test report shall contain at least the following information:

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

b) test method used with reference to this International Standard (i.e. ISO 17319);

c) test results obtained;

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

e) date when the analysis was finished;

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

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

Annex A
(informative)

Report of Method Accuracy

A.1 Overview

Review of ISO standard on determination of potassium content in fertilizer

The current effective ISO standard on determination of potassium content in fertilizer is ISO 5310:1986. ISO 5310:1986 specifies a titrimetric method (volumetric method) for the determination of the potassium content of fertilizers.

The principle of ISO 5310:1986 is as follows:

— Prepare a test solution as specified in ISO 5317 or ISO 7407;

— Precipitate the potassium ions present in an aliquot portion of the test solution (previously treated with bromine water and activated charcoal if cyanamide and/or organic materials presented) by excess amount of sodium tetraphenylborate (NaTPB) in a weakly alkaline medium;

— Filter and determine the unreacted NaTPB by back-titration with cetyltrimethylammonium bromide (CTAB) solution, using thiazol yellow (Titan yellow) as the indicator.

As a kind of volumetric method, this method would be expected to have an increased possibility of deviation when it is used for analyzing high concentration potassium samples due to the higher dilution ratio.

Abolished ISO standard: ISO 5318:1983 (withdrawn in 2008).

ISO 5318:1983 specifies a gravimetric method for the determination of the potassium content of a test solutions of fertilizers. It is suitable for use in arbitration and for reference purposes.

The principle of ISO 5318:1983 is as follows:

— Preparation of a test solution as specified in ISO 5317;

— Precipitation of potassium ion present in an aliquot portion of the test solution (previously treated with bromine water and activated charcoal if cyanamide and/or organic materials presented) by NaTPB in a weakly alkaline medium in the presence of ethylene diaminetetraacetic acid (EDTA) disodium salt and formaldehyde (HCHO) to eliminate the possible interference by ammonium ions;

— Filtration of the precipitate, drying and weighing.

The method mentioned in ISO 5318:1983 was proposed by Ford in 1956 and it is one of the classic methods for determination of potassium content. It has been recognized as the official method for determination of potassium content by AOAC (Association of Official Analytical Chemists, US), CEN (ComiteEuropeen de Normalization, EU), and SAC (Standardization Administration of the People's Republic of China).

This method calls for precise concentration control of the concentration of alkali (NaOH) solution, it may have an increase of the possibility of deviation by badly control of the concentration of alkali (NaOH) solution. Since the reaction between formaldehyde with ammonium ion (NH_4^+) is reversible:

$$6\,HCHO + 4\,NH_4Cl + 4\,NaOH \Leftrightarrow (CH_2)_6\,N_4 + 4\,NaCl + 10\,H_2O \tag{A.1}$$
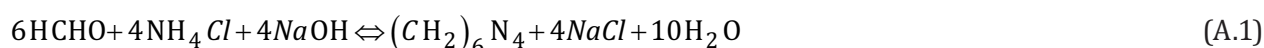
This reaction will form hexamethylenetetramine, namely, urotropin.

In this reversible reaction, the ammonium ion (NH_4^+) can be well screened under the concentration of NaOH higher than 0,05 mol/L; Otherwise, namely, when the concentration of NaOH is lower than 0,05 mol/L, Formula (A.1) will turn back to its left side to form more ammonium ions (NH_4^+), which may lead to an unexpected precipitation of ammonium tetraphenylborate (NH_4TPB) in the solution, by the combination of sodium tetraphenylborate (NaTPB) with ammonium ions (NH_4^+).

On the other hand, in order to maskall the ammonium ions (NH_4^+) under the alkali condition, some other cations such as Ca(II), Mg(II), Fe(III) will form precipitation of hydroxide and/or phosphate, so ethylene diaminetetraacetic acid (EDTA) is needed here to mask all the other cations may exist in the solution. Data has shown that the Fe(III) in the solution will form precipitation of iron hydroxide under the concentration of NaOH higher than 0,16 mol/L.

Considering all the restrictions mentioned above, the standard ISO 5318:1983 has a strict requirement on alkali (NaOH) concentration which should be controlled between 0,05 mol/L~0,16 mol/L, otherwise, there will be significant deviation on test results.

On the other hand, from the EH&S point of view, there exists a common view that formaldehyde (HCHO) is definitely not an environment-friendly substance. HCHO will undergo a polymerization process under a long period of reservation; it calls for a pretreatment process of filtrating before taken as the reagent, these processes will cause tears of the operators. As a Group I carcinogenic substance (see MSDS sheet of HCHO aq. from Sigma-Aldrich), formaldehyde causes sensitization to eyes, skin as well as respiratory tract. All these shortcomings will definitely do harm to the health of operators, and bring about difficulty to this method practically.

China's effort towards solving existing problems

In order to solve those as-mentioned problems, we have established a method which can eliminate the interference of ammonium ion (NH_4^+) without adding formaldehyde. The test for determining the accuracy and precision of our newly-established method can be found as follows and also in our international ring test report (Annex to the CD2).

During a long-term of practices, we have confirmed that the potassium content determined without adding formaldehyde after heating in alkali condition is almost the same as the one with formaldehyde added, even though there is a large amount of ammonium ion (NH_4^+) existing in the sample. A preliminary speculation is that ammonium ion (NH_4^+) may form ammonia (NH_3) in alkali solution and then be totally evaporated under constant heating.

$$NH_4^+ + OH^- \xrightarrow{\quad heating \quad} NH_3 \uparrow + H_2O \tag{A.2}$$

A.2 Detailed Accuracy Test

A.2.1 Test methods of ISO 17319

A.2.1.1 Principle

Heating the test solution in an alkaline medium (NaOH) to eliminate the interference of ammonium ion (NH_4^+), adding disodium ethylenediamine-tetraacetate dehydrate (EDTA, disodium salt) to eliminate interference of other metal cations, then precipitation of potassium ions in an aliquot portion of the test solution by sodium tetraphenylborate in an alkaline medium to get potassium tetraphenylborate precipitate. Filtration of the potassium tetraphenylborate precipitate, drying and weighing.

A.2.1.2 Test methods

The procedures are basically the same as the one specified in ISO 5318, the key difference here is no formaldehyde will be added in the test solution.

A.2.2   Results and Discussion

A.2.2.1   Test samples

Sixteen typical samples of potassium sulfate from China, USA and Germany, 5 different formulas of compound fertilizers, 1 organic-inorganic compound fertilizer, 2 standard reference materials of potassium chloride and potassium sulfate have been selected as test samples, which are of different specifications and prepared by various technique to guarantee a wide range of representatives of the samples.

A.2.2.2   Comparative test by 2 analysis methods of potassium sulfate (K_2SO_4) sample (with vs. without HCHO)

In order to validate the practicability of our test methods without HCHO, we carried out comparative test by 2 analysis methods of potassium sulfate (K_2SO_4) sample (with vs. without HCHO), the test results are as follows (Table A.1):

Table A.1 — Results of K_2O concentrations with and without HCHO, in the unit of %

No. of sample	With HCHO	Without HCHO	Difference between two methods	No. of sample	With HCHO	Without HCHO	Difference between two methods
001	51,53	51,40	0,13	009	52,16	52,15	0,01
002	50,83	51,07	−0,24	010	49,52	49,72	−0,20
003	51,69	51,85	−0,16	011	28,65	28,92	−0,27
004	48,60	48,79	−0,19	012	50,92	51,04	−0,12
005	51,46	51,19	0,27	013	51,70	51,46	0,24
006	50,92	50,99	−0,07	014	50,94	50,98	−0,04
007	48,20	48,20	0,00	015	37,28	37,50	−0,22
008	46,24	46,24	0,00	016	26,42	26,28	0,14

Table A.1 has shown clearly that the absolute difference between the two methods is between 0,00 % approximately 0,27 %, which lies in the range of absolute difference between parallel tests specified in ISO 5318 (no more than 0,39 %), which indicates that the test results of the two methods (with vs. without HCHO) are highly comparative.

To further validate that there is no significant difference between the two methods (with vs. without HCHO), we have chosen No.001 sample to carry out 5 parallel tests by two methods (with vs. without HCHO), the results are as follows (Table A.2):

Table A.2 — Replicated 5 test results of K_2O concentrations of sample 001: methods with/without HCHO, in the unit of %

No. of sample	with HCHO					without HCHO				
001	52,45	52,40	52,24	52,04	52,28	52,41	52,37	52,31	52,22	52,08

Data from Table A.2 are taken for F-tests, variations of both the two set of data from the two methods (with vs. without HCHO) are compared firstly.

$$n_1=5, \qquad f_1=4, \qquad s_1=0{,}160$$

$$n_2=5, \qquad f_2=4 \qquad s_2=0{,}132$$

$$\therefore F_{calculation}=s_1^2/s_2^2=1{,}47$$

Referring to the one side numerical table of F-value (with confidence coefficient = 95 %), we found $F_{critical}$ = 6,39. Since $F_{calculation}$ = 1,47 < $F_{critical}$ = 6,39, it indicates that the variations of both the two sets of data have no significant difference, which also means the precision of both the two methods have no significant difference.

Combined standard deviation, s, can be calculated as follows:

$$s = \sqrt{\frac{\Sigma\left(x_{i1} - \overline{x}_1\right)^2 + \Sigma\left(x_{i2} - \overline{x}_2\right)^2}{n_1 + n_2 - 2}} = 0,206 \tag{A.4}$$

Then we use *t*-tests on the two sets of data from the two methods (with vs. without HCHO), to verify if there is any systematic difference between the two sets of data:

$$t_{calculation} = \frac{|x_1 - x_2|}{s} \cdot \sqrt{\frac{n_1 - n_2}{n_1 + n_2}} = 0,03, P = 0,90, f = 8 \tag{A.5}$$

Referring to the two side numerical table of $t_{a,f}$-value, we found $t_{0.10,8}$ = 1,86, since $t_{calculation}$ = 0 03 < $t_{0.10,8}$ = 1 86, it indicates that there is no significant difference between the data from both methods (with vs. without HCHO).

All the statistical work here illustrates that both the two methods (with vs. without HCHO) are equally effective for the determination of the potassium content of potassium sulfate (K_2SO_4) sample. Both methods share a high quality of accuracy and precision. We will show more details on applying our new method (without HCHO) below.

A.2.2.3 Precision test of the new method (without HCHO) of potassium sulfate (K_2SO_4) sample

To further validate the precision of the new method (without HCHO), we choose 3 representative samples to carry out 5 parallel tests, and a Dixon test was carried out to validate the precision of data from the new method (without HCHO). The results are as follows (see Table A.3).

Table A.3 has shown clearly that the range of data from parallel tests is between 0,11 % approximately 0,33 %, which lies in the range of absolute difference between parallel tests specified in ISO 5318 (no more than 0,39 %) and shows a good quality of precision of the new method (without HCHO).

Referring to the numerical table of $Q_{(0.05,5)}$-value, we found $Q_{(0.05,5)}$ = 0,642 since $Q_{calculation}$ < $Q_{(0.05,5)}$ = 0,642, we also found a good quality of precision of the new method (without HCHO).

Table A.3 — Precision test results of the new method (without HCHO)

No. of sample	Test results (%)		Arithmetic average (%)	Range (%)	Data for Dixon tests	Standard Deviation (%)
008	46,21 46,31 46,39	46,24 46,10	46,25	0,29	Q_1 = 0,379 Q_5 = 0,276 $Q_{(0.05,5)}$ = 0,642	0,11
009	52,41 52,31 52,08	52,37 52,22	52,28	0,33	Q_1 = 0,424 Q_5 = 0,121 $Q_{(0.05,5)}$ = 0,642	0,13
015	37,29 37,34 37,62	37,62 37,37	37,45	0,33	Q_1 = 0,151 Q_5 = 0 $Q_{(0.05,5)}$ = 0,642	0,16

A.2.2.4 Potassium oxide content of potassium sulfate (K₂SO₄) sample by new test method (without HCHO) (see Table A.5)

The parallel differences lie between 0,02 % and 0,38 %, all within the allowable deviation and indicate the good parallelism of the new method (without HCHO).

Table A.4 — The K₂O content of the sample, in the unit of %

No. of sample	Replicate results		Average	parallel differ-ence	No. of sample	Replicate results		Average	parallel differ-ence
001	51,47	51,32	51,40	0,15	009	52,22	52,08	52,15	0,14
002	51,01	51,13	51,07	0,12	010	49,71	49,74	49,72	0,03
003	51,98	51,72	51,85	0,26	011	28,86	28,97	28,92	0,11
004	48,78	48,80	48,79	0,02	012	51,11	50,98	51,04	0,13
005	51,10	51,28	51,19	0,18	013	51,43	51,48	51,46	0,05
006	51,07	50,91	50,99	0,16	014	50,88	51,08	50,98	0,20
007	48,01	48,39	48,20	0,38	015	37,37	37,62	37,50	0,25
008	46,10	46,39	46,24	0,29	016	26,39	26,16	26,28	0,23

A.2.2.5 The applicability of the new method (without HCHO) — Test on compound fertilizer and organic-inorganic compound fertilizer

To verify the method's applicability of different fertilizers, we choose compound fertilizer (fertilizer with the most complicated compositions) and organic-inorganic compound fertilizer to be the test sample to verify the practicability and accuracy of our new method (without HCHO).

A.2.2.5.1 Test samples

Six different compound potassium fertilizer samples with different forms of nitrogen, listed as follows:

Table A.5 — Six different compound potassium fertilizer samples

Sample No.	N:P:K	basic fertilizers
1	6–10–20	ammonium nitrate, thiamine, ammonium phosphate, calcium super-phosphate, potassium sulfate, potassium nitrate
2	7–4-9	Urea, thiamine, ammonium phosphate, potassium chloride
3	12–7-6	Urea, calcium magnesium phosphate, ammonium phosphate, magne-sium potassium sulfate, organic matter (25 %)
4	17–4-5	ammonium chloride, ammonium phosphate, calcium superphosphate, potassium chloride
5	12–8-8	Urea, Ammonium carbonate, ammonium chloride, thiamine, ammonium phosphate, calcium superphosphate, potassium chloride
6	8–8-9	Urea, ammonium chloride, calcium superphosphate, potassium chloride

A.2.2.5.2 Recovery Test

We have chosen potassium chloride (KCl) GR reagent and standard reference material potassium sulfate (K₂SO₄, GBW 06503) for recovery test (with HCHO vs. without HCHO), and study on the recovery rate of KCl in the presence of NH₄⁺.

The test procedures are as follows: weigh a certain amount of KCl, K_2SO_4, NH_4Cl reagent, dilute to 250 mL in a constant volume flask, draw 25 mL filtrate after filtration and operate basically according to ISO 5318. The results are as follows.

Table A.6 — Test of recovery- KCl and K_2SO_4

Sample	Sample weight	NH_4Cl weight (g)	with HCHO			without HCHO		
			precipi-tate	blank	recovery	precipi-tate	blank	recovery
K_2SO_4	0,553 2	/	0,229 4	0,001 6	100,30	0,228 5	0,001 5	99,94
	0,498 9	/	0,206 0	0,001 6	99,78	0,207 4	0,001 5	100,52
KCl	0,489 4	1,118 6	0,250 2	0,004 6	104,52	0,241 4	0,002 5	101,67
	0,507 8	1,118 6	0,260 5	0,004 6	104,96	0,247 9	0,002 5	100,66

K_2O% of standard reference material K_2SO_4

standard reference	Certificate value	with HCHO	without HCHO
K_2SO_4(GBW 06503)	53,95 ± 0,14	53,97	54,08

From the analysis of experimental data for pure reagent KCl and standard reference material K_2SO_4, we can find satisfactory recovery rates with methods both with and without HCHO.

With the existence of NH_4^+, the experimental data for pure reagent KCl by the method with HCHO will show a relatively higher result, the recovery rate will rise by 3 % ca. This phenomenon will also appeal in the experiment on compound fertilizer as shown below.

To validate the accuracy of our new method (with HCHO) for compound fertilizer and organic-inorganic compound fertilizer, we choose 2 compound fertilizers and 1 organic-inorganic compound fertilizer for recovery test:

Table A.7 — Recovery test - compound fertilizer and organic-inorganic compound fertilizer by new method (with HCHO)

Sample	Weight, g	Standard material added, g	precipitate calculated from standard material added, g	Precipitate, g	Precipitate, in practical, g	Recovery standard material, g	Recovery Rate% Recovery rate %
compound fertilizer N-P-K = 20-8-14 (urea, ammonium phosphate, potassium chloride)	1,999 0	0,402 6	0,165 4	0,261 5	0,168 5	0,410 1	101,87
	2,038 7	0,403 3	0165 7	0,263 2	0,168 4	0,409 9	101,63
NOTE 1 Blank experiments precipitation is 0,001 2 g							
NOTE 2 The standard reference material added is pure reagent grade potassium sulfate, with the content of K_2O of 53,98 %.							

Table A.7 *(continued)*

Sample	Weight, g	Standard material added, g	precipitate calculated from standard material added, g	Precipitate, g	Precipitate, in practical, g	Recovery standard material, g	Recovery Rate% Recovery rate %
compound fertilizer N-P-K = 16–16–16 (ammonium phosphate-nitrate, ammonium phosphate, potassium nitrate)	2,023 9	0402 6	0,165 4	0,264 9	0,167 7	0,408 2	101,39
	2,069 3	0,403 3	0,165 7	0,267 0	0,167 7	0,408 2	101,21
organic-inorganic compound fertilizer N-P-K = 12–7-6 [urea, calcium magnesium phosphate, ammonium phosphate, magnesium potassium sulfate, with organic matter (25 %)]	2,321 3	0,352 5	0,144 8	0256 4	0.1421	0345 9	98,14
	2,460 4	0,353 2	0145 1	0,267 3	0,146 3	0,356 1	100,83

NOTE 1 Blank experiments precipitation is 0,001 2 g

NOTE 2 The standard reference material added is pure reagent grade potassium sulfate, with the content of K_2O of 53,98 %.

From Table A.7 we found that the recovery rates (without HCHO method) of different potassium raw material compound fertilizers and organic-inorganic compound fertilizer lie between 98,14 % and 101,87 %, which indicates a high quality of accuracy.

A.2.2.5.3 Comparison between two methods: with vs. without HCHO by 6 samples of various nitrogen forms

Test 6 samples of various nitrogen forms by the above two methods (with vs. without HCHO), and the results are as follows:

Table A.8 — Comparison between two methods: with vs. without HCHO

Sample No.	Method with HCHO		Method without HCHO	
	Measurement value	average	Measurement value	average
1	19,52 19,71	19,62	19,38 19,59	19,48
2	9,44 9,60	9,52	9,09 9,18	9,14
3	5,5 5,48	5,46	5,23 5,32	5,28
4	5,09 5,18	5,14	4,90 4,90	4,90
5	8,52 8,47	8,50	8,30 8,15	8,22
6	9,79 9,81	9,80	9,45 9,49	9,47

From Table A.7 we found that the potassium content value (with HCHO) are generally a little bit higher than the data obtained from our new method (without HCHO). This phenomenon is consistent with the recovery rate of reagent KCl.

A.2.2.6 Lower application limit of the new method (without HCHO)

The principle to determine the lower limit of the new method (without HCHO) is as follows.

Test the blank for 10 times under the same conditions of testing the sample

Calculate the standard deviation of these 10 blank data.

The lower limit of the new method (without HCHO) can be given as 10 times of the calculated standard deviation.

Ten blank experiments precipitation weight:

0,000 5 g, 0,000 4 g, 0 000 0 g, 0,000 3 g, 0,000 2,g, 0,000 4 g, 0,000 2 g, 0,000 3g, 0 000 5 g, and 0,000 3 g.

The standard deviation of these 10 data = 0,000 152 g.

Referring to this International Standard, the repeatability limit is 0,193 %, the reproducibility limit is $2,8*(0,002\ 2m + 0,109)$ in which m represented the concentration of K_2O.

The lower application limit of chemical analysis could be calculated as 10 times of the detection limit.

Calculation on application lower limit is as follows:

$0,015\ 2 \times 0,131\ 4 \times 500 \times 100/(2,0 \times 50) = 1,0\ \%$

So, the new method (without HCHO) is applicable to those fertilizers containing more than 1,0 % K_2O or equivalent amount of K content.

A.3 Conclusion

Based on all the test data above, the method without adding formaldehyde can simplify the testing procedure, avoid the harm to operating person, and reduce the adverse effects on the environment. The accuracy, precision and repeatability etc. are all consistent with the original method (also ref to the ring test report for precision). It can fulfill the potassium determination requirements of all kinds of fertilizers. It is suitable as the candidate to be adopted as an ISO standard.

Annex B
(informative)

Interlaboratory testing

B.1 Overview

The International Laboratories Ring Test of this International Standard has been accomplished from Sep. 2012 to Dec. 2012. There are 14 laboratories participating in the 2 parallel tests on each three samples, including one lab from Iran, one lab from Indonesia, one lab from Canada, and 11 laboratories from China. This international ring test was conducted by Shanghai Research Institute of Chemical Industry, P. R. China, the statistician analysis and final report was prepared by Shanghai Research Institute of Chemical Industry, P. R. China.

The following are the 14 laboratories participating in the 2 parallel tests on each three samples.

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

— Potash Corp of Saskatchewan, Canada

— Laboratory of PT. Hanampi Sejahtera Kahuripan, Indonesia

— Soil and water research institute of Iran, Iran

— Jiangsu Province Products Quality Supervising and Testing Institute, China

— Hunan Province Products Quality Supervising and Testing Institute, China

— Shandong Province Products Quality Supervising and Testing Institute, China

— Guizhou Province Products Quality Supervising and Testing Institute, China

— Heilongjiang Province Products Quality Supervising and Testing Institute, China

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

— Shandong Kingenta Ecological Engineering Co. Ltd, Quality Supervising Center, China

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

— Shanghai Entry-Exit Inspection and Quarantine Bureau, China

— China-Arab Fertilizer Co. Ltd, Quality Supervising Center, China

NOTE   The sequence of those laboratories in the list above has no relation with the sequence of data mentioned below.

The test method described in this International Standard was adopted here for determination of potassium contents in the fertilizer samples.

Three different kinds of fertilizer samples were used during the ring test, and each with several mean levels. There are sample A-NPK compound fertilizer(formula: 16-6-20 basic fertilizers include nitric acid; phosphorus ore; liquefied anhydrous ammonia; Monoammonium phosphate and potassium sulfate), sample B-Potassium chloride 62 %, sample C-Organic and inorganic compound fertilizer (formula:8-7-10 organic matter 20 % basic fertilizers include urea; ammonium phosphate; potassium sulfate; humic acids and rape cake). The potassium oxide contents in the fertilizer samples lie in 10 %~60 %.

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

B.2   Statistical analysis of the test results of potassium contents

B.2.1   Original test results

There are 14 laboratories participated in the determination of potassium contents in fertilizers. The test results were listed in Table B.1, with the unit of %.

Table B.1 — Original test results of the determination of potassium contents

Laboratory i	Level j					
	A		B		C	
1	19,90	19,98	62,86	62,70	10,58	10,70
2	19,51	19,62	62,44	62,40	10,42	10,51
3	19,63	19,64	62,54	62,58	10,19	10,18
4	19,51	19,57	62,39	62,54	10,48	10,33
5	19,51	19,53	62,26	62,18	10,48	10,48
6	19,83	19,85	62,40	62,43	10,35	10,34
7	19,72	19,88	61,98	62,12	10,24	10,36
8	19,72	19,73	62,32	62,39	10,41	10,46
9	19,78	19,79	62,44	62,29	10,44	10,54
10	19,53	19,55	61,77	61,87	10,24	10,35
11	19,93	19,74	62,08	62,12	10,53	10,51
12	19,76	19,80	62,61	62,43	10,44	10,43
13	19,69	19,66	62,30	62,25	10,45	10,60
14	19,67	19,65	62,25	62,05	10,23	10,08

B.2.2   Cell means

The cell means of the determination of potassium contents were listed in Table B.2, with the unit of %.

Table B.2 — Cell means of the determination of potassium contents

Laboratory i	Level j		
	A	B	C
1	19,94	62,78	10,64
2	19,565	62,42	10,465
3	19,635	62,56	10,185
4	19,54	62,465	10,405
5	19,52	62,22	10,48
6	19,84	62,415	10,345
7	19,8	62,05	10,3
8	19,725	62,355	10,435
9	19,785	62,365	10,49
10	19,54	61,82	10,295
11	19,835	62,1	10,52
12	19,78	62,52	10,435

Table B.2 *(continued)*

Laboratory i	Level j		
	A	B	C
13	19,675	62,275	10,525
14	19,66	62,15	10,155

B.2.3 Cell absolute differences

The cell absolute differences of the determination of arsenic contents were listed in Table B.3, with the unit of %.

Table B.3 — Cell absolute differences of the determination of potassium contents

Laboratory i	Level j		
	A	B	C
1	0,08	0,16	0,12
2	0,11	0,04	0,09
3	0,01	0,04	0,01
4	0,06	0,15	0,15
5	0,02	0,08	0
6	0,02	0,03	0,01
7	0,16	0,14	0,12
8	0,01	0,07	0,05
9	0,01	0,15	0,1
10	0,02	0,1	0,11
11	0,19	0,04	0,02
12	0,04	0,18	0,01
13	0,03	0,05	0,15
14	0,02	0,02	0,15

B.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.