A/09/172
December 2009

Recommended Best Practice for the Analysis of Potassium Content in Potassium Chloride (KCl) Fertilizers

International Fertilizer Industry Association (IFA)

International Fertilizer Industry Association (IFA) - 28, rue Marbeuf - 75008 Paris - France
Tel. +33 1 53 93 05 00 - Fax +33 1 53 93 05 45/47 - ifa@fertilizer.org - www.fertilizer.org

This best practice recommendation was researched and prepared by the IFA Working Group on the Harmonization of Fertilizer Sampling and Methods of Analysis, which consists of representatives from the global fertilizer industry. This document is available to the general public and is a reference document for the international trade of fertilizer products. It should not be considered to be an international standard; nor does this document take precedence over existing national and regional regulations or standards.

This recommendation and its background documents are available to the general public on the IFA web site (www.fertilizer.org), or through written request to the IFA Secretariat.

Contents

Executive Summary

The IFA Method Harmonization Working Group's evaluation of analytical methods used globally for the quality testing of potassium content in potassium chloride (KCl) fertilizers indicates that the ***tetraphenylboron method*****,** in its two variations (gravimetric and titrimetric), is the preferred – or best practice – methodology for use in international fertilizer trade.

The following factors were used in developing this recommendation for the industry:

- The tetraphenylboron method is in wide use in most markets and has been regularly subjected to large-scale inter-laboratory testing;
- This methodology has been proven to be statistically sound, yielding precise and accurate results repeatedly and consistently. It is often the preferred method for many laboratory proficiency programmes;
- The tetraphenylboron method is relatively simple and cost-effective to conduct. It requires laboratory equipment that uses reasonably inexpensive and safe reagents, thus facilitating its quick adoption in global markets.

1. INTRODUCTION

During its first phase of method review, the IFA Method Harmonization Working Group decided to evaluate the methods used to determine potassium content (expressed as K_2O) in potassium chloride (KCl) fertilizers in global markets.

As a result of this research, 26 individual methods were identified as derived from six basic methodologies:

1. Tetraphenylboron (STPB)
2. X-ray spectrometry
3. Flame photometry
4. Atomic absorption spectrometry (AAS)
5. Perchlorate
6. Inductively-coupled plasma optical emission spectrometry (ICP-OES)

The Working Group evaluated these basic methodologies using an established set of criteria in order to ensure an objective assessment process. Subsequently, a method ranking was developed and a recommended best practice was determined, based on the Working Group's deliberations.[1]

2. EVALUATION OF METHODS USED INTERNATIONALLY

2.1 Current status of methodology

The six method areas evaluated are listed in Table 1.

Table 1

Group	Method	Entity or national body
Tetraphenylboron (STPB)	Gravimetric	ISO 5318, STO SPEKS, EN15477: 2009
	Titrimetric	ISO 5310, AOAC 958.02
Flame photometry	Oxalate	AOAC 983.02 a
	Citrate	AOAC 983.02 b
ICP-OES	Citrate	n/a
	Oxalate	n/a
Atomic absorption spectrometry (AAS)	Oxalate	n/a
X-ray spectrometry	Fluorescence	n/a
Perchlorate	Perchlorate	STO SPEKS

It is important to note that the tetraphenylboron, flame photometric and perchlorate methods are the only method groups currently endorsed by a recognized national or regional agency.

2.2 Statistical evaluation

The methods validated by AOAC, ISO, SPEKS and CEN include the calculations for metrological characteristics such as the method's precision (accuracy) indicators, r (intra-laboratory repeatability), R (inter-laboratory reproducibility) and Δ (error or accuracy), which are available from the Magruder and the Saskatchewan Potash Producers Association (SPPA) check sample programmes. For most of the non-validated methods, only data for R and in some cases r exist. For comparative purposes, the six method groups were evaluated according to R data only. R values for these and other methods, ranked from lowest to highest, are provided in Annex 1.

<u>Tetraphenylboron (STPB)</u>

It should be noted that the mathematical calculations of the metrological characteristics used in North America and those used according to metrological standards ISO 5725 are different. In 2008, VNII Halurgy (the Russian Research Institute of Halurgy in Saint Petersburg) initiated a study to compare the precision indicators of the two variations of the tetraphenylboron method (gravimetric and

[1] For more details on the method evaluation criteria, method ranking process, and Working Group deliberations, please visit the Harmonization web pages at www.fertilizer.org.

titrimetic). The study included a statistics and measurements programme to determine the metrological indicators r, R and Δ of the SPPA titrimetric tetraphenylboron method, based on ISO 5725 section 1-6 (for KCl 95%-98%).[2]

The results shown in Table 2 suggest that the methods are comparable.

Table 2

ISO 5725 indicators	Titrimetric tetraphenylboron method (SPPA)	Gravimetric tetraphenylboron method, attestation certificate, STO SPEKS
r	0.2	0.4
R	1.2	1.0
Δ	0.8	0.7

The SPPA has also conducted inter-laboratory tests using the volumetric tetraphenylboron method. Forty-two samples were used across ten laboratories, leading to high levels of precision (Annex 4). Other potash enterprises and research centres in Russia and Belorussia have conducted further large-scale inter-laboratory tests using the tetraphenylboron method (Annex 3).

In January 2009, the Comité Européen de Normalisation (CEN) issued a gravimetric STPB method for the determination of water soluble potash in fertilizers. An inter-laboratory test was used to determine the precision of the method, yielding results for r and R similar to those shown for the SPPA and SPEKS methods in Table 2.[3]

Flame photometric method

The flame photometric analysis method is widely used in agri-chemistry worldwide, especially for quality testing of NPK compound fertilizers. The precision characteristics demonstrated in the Magruder check sample programme clearly indicate that this method is less precise than the tetraphenylboron method.

AAS, ICP-OES

The findings of the Magruder check sample programme carried out in North America show that this method is less precise than the tetraphenylboron method group.

X-ray spectrometry and perchlorate

No precision and accuracy data were available for these method groups.

Summary of Statistical Evaluation

As mentioned above, the methods validated by AOAC, ISO, SPEKS and CEN include the calculations for metrological characteristics such as r (intra-laboratory repeatability), R (inter-laboratory reproducibility) and Δ (error or accuracy). These data are available from each organization.

The data clearly demonstrate that the precision characteristics of the tetraphenylboron method outperform the other analysis methods.

2.3 Evaluation of the correctness of results obtained

All method types included regular checks for the correctness of the results obtained, based on check samples and inter-laboratory tests.

2.4 Scope/applicability

By definition, the matrix for fertilizer-grade potassium chloride is limited to 99% soluble chlorides and 0-1% water-insoluble compounds such as anhydrite, dolomite, smectite and iron oxide.

[2] More detailed findings concerning potash testing can be reviewed at www.magrudercheck sample.org.

[3] Actual values can be found in the official CEN publication and on the official web site http://www.cen.eu/cenorm/homepage.htm.

2.5 SHE evaluation matrix

Group	Method	Safety risk*	Environ-mental risk**
STPB	Gravimetric	low	low
	Titrimetric	low, high when using formaldehyde	low, high when using formalde-hyde
Flame photometry	Oxalate/ citrate	high, compressed gas high, explosion	low
ICP-OES	Oxalate/ citrate	moderate, compressed gas moderate, asphyxiation	low
Atomic absorption spectro-metry	Oxalate	high, compressed gas high, explosion	low
X-ray spectro-metry	Fluores-cence	moderate, asphyxiation moderate, ionizing radiation	low
Perchlorate		high, oxidizer	high, can be toxic

* Safety: moderate to high risks require additional engineering controls and safety procedures

** Environmental: includes reagents and waste

Perchlorate method

The perchlorate method has a major drawback, which is the application of a toxic reagent, chloric acid, resulting in the formation of oxidants (perchlorates). For environmental and health reasons, the use of this method is not recommended.

Safety precautions

Safety is an extremely important aspect of all laboratory activities. Therefore, due consideration should be given to safety in laboratory procedures covering applications such as wet chemistry, flame atomic absorption and ICP spectrophotometers. The high and moderate risk conditions identified in the SHE matrix can be significantly reduced, while having accurate, documented routines in place as well as properly trained laboratory personnel. Modern technology often has the advantage of additional built-in safety features.

Sound safety techniques should, in principle, be applied for all lab procedures and equipment. Where properly applied, they provide a safe means to handle toxic chemicals such as formaldehyde. Newer atomic absorption instruments are now available with built-in features to further improve safety, such as gas leak detectors and blow out seals if the gases are mixed incorrectly. In the case of ICP and inert gas leaks, gas sensors can protect atmospheric air, which in turn protects the workers.

2.6 Use and general acceptance

All of the methods studied have wide-ranging use and acceptance. The STPB method is the most broadly applied, as it is practised in all but one of the world's potash-producing countries. It is also used in most of the countries and regions that are major potash consumers.

2.7 Time requirement

There is no indication of the time required to carry out tests for the methods listed in Annex 1. It is necessary to make parallel tests for r (repeatability) to demonstrate an admissible difference (in absolute percentage) in values of parallel tests. For some methods, the measurements are conducted automatically, while the sample preparation is done manually. Within this context, the methods cannot be appropriately evaluated according to this criterion.

2.8-9. Complexity and cost

Method complexity and cost are determined by a number of factors which include the upfront capital investment, the labour and raw material costs, the number of tests and duration of testing, and the qualification requirements for laboratory analysts. Since these factors vary widely from laboratory to laboratory, the methods cannot be appropriately evaluated according to this criterion.

2.10. Dynamic range

In general, it has been determined that the calibration curves, dilutions and sensitivity are appropriate for the nutrient level.

3. BEST PRACTICE RECOMMENDATION

The IFA Method Harmonization Working Group's evaluation of the methodologies to determine potassium content provides the following insights:

1. Of the six basic analytical methodologies, the tetraphenylboron method (both gravimetric and titrimetric variations) can be recommended as the preferred, or best practice, method for determining potassium content.
2. The tetraphenylboron method is widely used around the world and has well-known ring test data. Between 2003 and 2008, large-scale inter-laboratory testing of the gravimetric and titrimetric variations was conducted in North America, Russia, Belorussia and Europe. These ring test results have provided sufficient and objective evidence that these variations are appropriate and preferred control methods. Additional ring test data for validation of the method are not required for the STPB methodology.
3. The IFA Method Harmonization Working Group considered that if there were no serious safety, environmental, health or cost issues, the "status of methodology" and the "statistical evaluation" criteria would be given the greatest importance during the method ranking.
4. If the STPB gravimetric and titrimetric variations are not in current use in a particular market, it is recommended that an independent control organization qualified to conduct the STPB analysis should be contracted to conduct the analytical work.
5. The STPB methods were enforced as international standards ISO 5318 and CEN EN 15477 (gravimetric) and ISO 5310 (titrimetric). The tetraphenylboron method's status is the highest compared to the other five basic methods.
6. The IFA Method Harmonization Working Group recommends that all laboratories follow the IFA Laboratory Quality Assurance Guidelines to ensure consistent and reliable results.

Annex 1

Statistical results from the Magruder inter-laboratory tests on high-grade potash samples ≥ 60% K_2O from 2003 to 2008

Sample number	**200804**		**200512**		**200310**		**200306**		**Average standard deviation R**
Method used	**# of labs**	**Std. dev. R**	**# of labs**	**Std. dev. R**	**# of labs**	**Std. dev. R**	**# of labs**	**Std. dev. R**	
STPB Oxalate	15	0.34	17	0.44	21	0.52	21	0.67	0.51
Flame photometric Oxalate	4	1.12	4	1.34	6	0.28	6	0.43	0.71
Flame photometric Citrate	8	0.78	7	1.19	6	1.10	6	0.82	0.97
ICP-OES Citrate	9	0.86	4	1.16	7	1.49	6	0.71	1.04
ICP-OES Oxalate	6	1.15	5	1.56	7	0.67	6	0.98	1.05
AAS Oxalate	9	0.99	12	2.02	12	1.57	12	1.09	1.45
X-ray spectrometry	No data available								
Perchlorate	No data available								

Annex 2

Summary Table of Methods to Determine the K_2O Content of Potash Supplied in Various Countries

Methods/ validation criteria	Tetraphenylboron method	Calculation method (by difference)	X-ray spectrometry	Flame photometry	Atomic absorption spectrometry	Perchlorate method	(ICP-OES)
Status of method	**EU:** Regional standard CEN/TS 15477 **EU:** Regional standard – Regulation (EC) 2003/2003 dd. 13 Oct. 2003 relating to fertilizers, Method 4.1 **Russia/Belorussia:** GOST 20851.3-93 (CIS); regional standard STO SPEKS 004-2006 **China:** National standard GB 6549-1996 **Germany:** VDLUFA 5.2.1 **Canada/USA:** SPPA Standard Analytical Procedures. Version 1.1; July 1996. Potassium in KCl. AOAC: Official Methods of Analysis, 1990. 15th edition, 958.02 **USA:** Potassium in KCl. AOAC:Official Methods of Analysis, 1990. 15th edition, 969.04 **Brazil:** ANDA Normative Rules **Jordan:** APC Standard Operating Procedure (based on AOAC 1970) **India:** Fertilizer Control Order 1985 **Chile:** AOAC:958.02	**Russia/Belorussia:** Regional standard STO SPEKS 004-2006 **Canada:** SPPA Standard Analytical Procedures Version 1.1: January 2000 Potassium in White Products **Israel:** Information not available	**Canada:** SPPA Standard Analytical Testing Procedures Version 1.0; November 2006. Potassium by XRF, Practical X-ray Spectrometry, 2nd edition, R. Jenkins & J. L. De Vries; An Introduction to X-ray Spectrometry, R. Jenkins	**Brazil:** ANDA Normative Rules **USA:** AOAC Official Method 983.02 Potassium in Fertilizers Flame Photometric Method (Manual or Automatic) First Action 1983, Final Action 1985 **USA:** AOAC Official Method 955.06 Potassium in Fertilizers Flame Photometric Method First Action 1955 **Malaysia:** Malaysian Standard MS Standard 417, Part 5, 1994 (The Analysis of Fertilizer, Part 5: Method of Determination of Potassium – First Revision). Flame Photometry Method to Determine K_2O in Finished Products	**Chile:** Not available **USA:** AA Oxalate	**Russia/Belo-russia:** Regional standard STO SPEKS 004-2006 **India:** Fertilizer Control Order 1985 **Israel:** Dead Sea Works Ltd. Procedure No. 16.13.47	**USA:** ICP Citrate **Germany:** VDLUFA 5.2.3
				Kenya: National Standard KS			

				350:2007 ICS 65.080 **Israel:** Information not available			
Metrological evaluation of r, R, Δ _	**EU:** EN 15477:2009 – r and R are given for only two concentrations,16% and 24% K_2O **EU:** 2003/2003 – No metrological evaluation is given **Russia/Belorussia:** r, R, Δ are given for the entire range **China:** r is given for one value, 95% KCl **Germany:** r = 0.11%, R = 0.40%, Δ is not given **Canada/USA:** AOAC: 958.02 – r = 0.16%, R = 0.51%, Δ is not given **USA:** AOAC: 969.04: No metrological evaluation is given **Brazil, Chile, India, Jordan:** No metrological evaluation is given	**Russia/Belorussia:** Metrological evaluation is given for all the ranges and components to be measured (NaCl, $MgCl_2.6H_2O$, $CaSO_4$, insoluble residue, H_2O etc.) **Canada:** Metrological evaluation: r ≤ 0.10% K_2O	Metrological evaluation: r ≤ 0.10% K_2O	**Brazil:** No metrological evaluation is given **USA:** AOAC 983.02 – r = 0.41%, R = 0.85%, Δ not given **USA:** AOAC 955.06, **Kenya, Malaysia:** No metrological data is given	**USA:** AA Oxalate r = 0.70%, R = 1.45%, Δ not given	**Russia/Belo-russia:** Metrological evaluation is made **India:** No metrological evaluation is given **Israel:** No metrological evaluation is given	**USA:** Citrate ICP – r = 0.37%, R = 1.04%, Δ not given **Germany:** No metrological evaluation is given
Evaluation of the correctness of the results obtained	**EU:** EN 15477:2009 – Correctness of the results obtained is checked **Russia/Belorussia:** Correctness is checked on the basis of a KCl national standard sample **China, Germany, EU:** 2003/2003 – Correctness of the results obtained is not checked	**Russia and Belorussia:** Correctness is checked on the basis of a KCl national standard **Canada:** Checks on intra- and inter-lab controls	Correctness of the results obtained is to be within 1.5 standard deviations of the given grand mean value	**Brazil, USA**: AOAC 983.02, 955.06, **Malaysia, Kenya:** Correctness of the results obtained is not checked	Unknown	**Russia/Belo-russia:** Correctness is checked on the basis of a KCl national standard sample **India:** Correctness of the results obtained is not checked	**USA:** Unknown **Germany:** Correctness of the results obtained is not checked

	Canada/USA: AOAC: 958.02 – Correctness of the results obtained is to be within 1.5 standard deviations of the given grand mean value **Brazil, Chile, India, Jordan, USA:** 969.04**:** Correctness of the results obtained is not checked					**Israel**: Correctness of the results obtained is not checked	
Scope/ applicability	**EU:** EN 15477:2009, **EU 2003/2003, India**, **Jordan:** 0-99% KCl **Russia/Belorussia:** 92-99% KCl **China:** 95% KCl **Germany:** ~60% K_2O **Canada/USA:** SPPA – 58-63 % K_2O **Canada/USA:** AOAC: 958.02 & 969.04 – 2-63 % K_2O **Chile:** 2-63% K_2O	**Russia and Belorussia:** 92-99% KCl **Canada:** > 62% K_2O	58-62% K_2O	**Brazil, Kenya, Malaysia, USA**: AOAC 983.02, AOAC 955.06: ≤ 63% K_2O	**USA:** 2-63% K_2O	**Russia/ Belorussia:** 92-99% KCl **India:** not given but 95-99% KCl is assumed **Israel:** 96-99% KCl	**USA:** ICP Citrate – 2-63 % K_2O **Germany:** 0.5-63% K_2O
Health/ environmental	Safety requirement for a chemical lab using no extra-toxic reagents	Safety requirement for a chemical lab using no extra-toxic reagents	Safety requirements for a chemical lab. Special safety requirements are needed due to application of X-ray equipment	Safety requirements for a chemical lab using compressed flammable gases	Safety requirements for a chemical lab. Special safety requirements are needed due to application of AAS	Safety requirements for a chemical lab. Special safety requirements are needed due to application of $HClO_4$ (a strong acid) **India:** Application of CH_3OH (poison) is provided for	Safety requirements for a chemical lab applying ICP-OES

Use and general acceptance	Yes	Yes	No	Yes	No	Yes	No
Time	No data	No data	No data	No data	No data	No data	No data
Complexity	Regular chemical method of analysis	Regular chemical method of analysis	Instrumental method of analysis. Complicated (KCl pressing is applied)	Instrumental method of analysis	Instrumental method of analysis. Complicated	Regular chemical method of analysis	Instrumental method of analysis. Complicated
Cost/ availability	Standard lab	Standard lab	Special equipment is required	Special equipment is required	Special equipment is required – an AA spectrophoto-meter. Relatively expensive	Standard lab	Special equipment is required – an optical emission spectrometer with inductively coupled plasma. Relatively expensive
Dynamic range	Appropriate	Appropriate	Appropriate	Appropriate	Appropriate	Appropriate	Appropriate

Annex 3

Ring testing in Russia and Belorussia, 2004-2006: the calculation of error characteristics for the mass fraction measurements of potassium (gravimetric tetraphenylboron method)

Results of computer calculation of the precision characteristics for standard potash samples, 92-98%

Level J	y//	S2r	S2L	S2R	Sr	SR	r	R
1	92.57	0.031278	0.025034	0.056312	0.1769	0.2373	0.5	0.7
2	93.19	0.028703	0.029494	0.058197	0.1694	0.2412	0.5	0.7
3	93.59	0.028185	0.264785	0.292970	0.1679	0.5413	0.5	1.5
4	96.06	0.027970	0.124137	0.1521067	0.1672	0.3900	0.46	1.08
5	98.75	0.015272	0.099708	0.1149800	0.1236	0.3391	0.34	0.94

Homogeneity dispersion according to the Cochran criterion:

							V=5 f=5	
S2r	C calculations =	0.238			S2R	C calculations =	0.434	
	C table =	0.544				C table =	0.544	
	Sr =	0.1621		r = 0.4				
	SR =	0.3673		R = 1.0				

Annex 4

Standard deviation for the 39 potash samples (>60 % K_2O) analyzed in the SPPA Sample Exchange Programme from 2003 to 2008

Sample ID	Std. Dev.	Sample ID	Std. Dev.
K-312	0.249	K-338	0.235
K-313	0.086	K-339	0.192
K-314	0.094	K-340	0.111
K-318	0.098	K-341	0.128
K-319	0.071	K-342	0.200
K-320	0.156	K-343	0.363
K-324	0.346	K-345	0.298
K-325	0.381	K-346	0.201
K-326	0.323	K-347	0.172
K-327	0.205	K-349	0.270
K-328	0.136	K-351	0.184
K-329	0.088	K-352	0.177
K-330	0.199	K-353	0.156
K-331	0.167	K-354	0.094
K-332	0.143	K-355	0.106
K-333	0.181	K-356	0.086
K-334	0.156	K-357	0.138
K-335	0.159	K-358	0.099
K-336	0.280	K-359	0.136
K-337	0.140	**AVG’**	**0.183**

References

1. Magruder Check Sample Programme; North America, www.magrudercheck sample.org; 2003-2008.

2. Saskatchewan Potash Producers Association (SPPA) Round Robin Programme; Saskatchewan Potash Producers Association, Canada; 2003-2008.

3. International Fertilizer Industry Association (IFA) Laboratory Quality Assurance Guidelines; Paris, France; www.fertilizer.org; September 2009.

4. European Committee for Standardization (CEN), http://www.cen.eu/cenorm/homepage.htm; Brussels, Belgium; January 2009.