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Evaluation of Commonly Used Methods for the Analysis of Acid-Soluble Phosphate in Internationally Traded Inorganic Fertilizers

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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.

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Abstract

Several methodologies are used throughout the world to determine phosphate concentration (measured as PO_4 and expressed as % P_2O_5) in fertilizers. Concentrated phosphate materials, including diammonium phosphate (DAP) and monoammonium phosphate (MAP), are traded in large volumes (millions of metric tons) internationally. The International Fertilizer Association (IFA) identified a need to assess the methods currently being used to measure the phosphate content for suitability (scope), accuracy and repeatability. Even small discrepancies in the expressed P_2O_5 content can have a major financial impact on buyers and sellers as contracts are settled and import regulations are imposed.

The IFA's Technical Committee selected a working group to address issues dealing with harmonization of fertilizer sampling and analytical methodologies. The working group identified phosphate content in DAP and MAP fertilizers as a major concern for commerce. The working group initiated a method screening and comparison project to assess method performance and to determine which methods, if any, could be considered best practice methods and, therefore, be deemed acceptable for use by the industry.

In order to systematically review the acceptability of methods for consideration, the task force developed an assessment protocol outlined in a white paper involving three steps: 1) compile all known relevant methods practiced in global fertilizer trade; 2) review and evaluate methods based upon specific evaluation criteria and 3) compare the methods that most closely fit the evaluation criteria by multi-laboratory analysis of unknown materials for accuracy and repeatability.

Six methods were evaluated for analysis of total phosphate in concentrated phosphate products. From these methods, four were determined to be acceptable as best practice methods. The study members proposed three of the methods, while a fourth method was commonly used amongst the participating laboratories. This publication is a summary of the method comparison process and statistical evaluation of analysis of total phosphate content in concentrated phosphate fertilizers.

Evaluation of Commonly Used Methods for the Analysis of Acid-Soluble Phosphate in Internationally Traded Inorganic Fertilizers

1. Introduction

Under the authorization of the International Fertilizer Association's (IFA's) Technical Committee, a working group was formed to address issues dealing with harmonization of fertilizer sampling and analytical methodologies. With the acceleration of global fertilizer trade, IFA's diverse membership has experienced an increasing number of contractual disputes due to the variable use of methods and procedures to sample and analyze international product shipments.

In a member-driven initiative, a broad-based task force was formed in 2007 to address this matter. Company representatives from key global producers, traders and inspection companies participate in the task force.

Method variability and inaccuracies often impact IFA members as well as others throughout the international fertilizer community. Lack of internationally accepted or standardized fertilizer sampling and analytical methods is seen as a leading cause for non-representative, inaccurate or highly variable sample results. Initial discussions of the group included identification of drivers for IFA action, a vision or set of goals for the group and a list of short-term action items. Among the priority goals, four primary action items were identified, namely: 1) to prioritize products and key parameters and to evaluate related methods for their applicability, statistical performance and degree of validation using acceptable criteria; 2) to develop a list of recommended voluntary best practice methods based on a balanced, structured, and collaborative assessment process; 3) to publish a listing of IFA recommended sampling, sample preparation and analytical methods that can be referenced in international trade; and 4) to identify and promote IFA member participation in standards setting organizations such as AOAC International or International Organization for Standardization (ISO) to develop and recommend methods for comparison and validation.

These criteria were applied to assessment of methodologies to analyze phosphate in concentrated phosphate materials, which was identified among the high priority action items. This action item was further delineated to assessment of methods for total (acid soluble) and soluble (in several different extraction solutions) or "available" phosphate. This paper focuses on the first of these two objectives and is the culmination of the initial assessment of total phosphate methods commonly used throughout the world.

With a view toward structuring a fair review process, 13 selection and ranking criteria were identified as metrics for the review and selection process prior to selection. Based on the criteria above, three candidate methods were chosen for study following a literature search and evaluation by the group. Participating laboratories were also allowed to submit data for methods they consider viable and that were commonly used by them. Data for three additional methods were considered.

Study samples were selected based on several criteria and were tested for homogeneity. Selection factors included: inclusion of reference materials, geographic region of source materials, analyte concentration and contaminant levels.

Participating laboratories were chosen based on their ability to utilize at least one of the three candidate methods, their geographic location and their ability to show proficiency by testing four practice samples supplied to the entire group of candidate laboratories. 45 laboratories were invited to participate in the study. 26 of the invited laboratories were able to participate in the study, with 17 laboratories reporting acceptable data. 7 laboratories reported acceptable data for two methods; so 24 sets of data were used in the evaluation.

2. Materials and Methods

2.1 Identifying and Engaging Representative Stakeholders

Under the authorization of the IFA's Technical Committee, a need was identified to address issues dealing with Harmonization of Fertilizer Sampling and Analytical Methodologies.

Based upon the aforementioned evaluation criteria, methodologies designed to analyze phosphate in concentrated phosphate materials were given a top priority. Fertilizer phosphate analysis was further broken down to assess methods for total (concentrated mineral acid soluble) and soluble (in several different extraction solutions), often referred to as available (or citrate soluble) phosphate. IFA represents most of the international fertilizer producing companies, so the working group also invited independent contract laboratories as well as regulatory laboratories to ensure assessment by a broad base of experts with experience in the analysis of fertilizers. There were two areas of concentration for the outreach, namely, to identify expert reviewers to evaluate protocols and to assess the data and identify candidate laboratories that would represent the industry in a balanced way. The reviewers became the Phosphate Working Group, a subgroup of the Steering Committee. The end result was an invitation list of 45 candidate laboratories. As a result of these invitations, 31 laboratories accepted and were sent practice samples. The 26 laboratories listed in Table 1 successfully demonstrated proficiency based upon their reported data from the practice samples. Proficiency on practice samples was determined by the ability to analyze at least two of the four samples within $\pm 1\%$ P₂O₅ and the two remaining samples within $\pm 2\%$ P₂O₅ of the known, theoretical, or homogeneity value.

Invited Company	Location
BASF Antwerpen NV	Antwerpen, Belgium
Central Inst. for Supervising & Testing in Ag.	Praha, Czech Republic
CF Industries (now Mosaic Fertilizer, LLC)	Plant City, FL, USA
Foskor Ltd.	Phalaborwa, South Africa
IFDC	Muscle Shoals, AL, USA
Incitec Pivot	Queensland, Australia
Inspectorate	Klaipedo, Lithuania
Intertek	St. Rose, LA, USA
Intertek	Odessa, Ukraine
J.R. Simplot	Pocatello, ID, USA
Jordan Phosphate Mines Company	Amman Jordan
Lovochemie a.s.	Lovosice, Czech Republic
Mosaic	Mulberry, FL, USA
Mosaic	Riverview, FL, USA
National Center Testing Fertilizer	Shanghai, China
OCP	Casablanca, Morocco
OCP	El Jadida, Morocco
OCP Maroc Phosphore	Safi, Morocco
PCS	Aurora, NC, USA
Voskresensk Mineral Fert. JSC (VMU)	Moscow, Russia
Plante direktoratets Laboratorium	Lyngby, Denmark
SGS	St. Rose, LA, USA
Thornton Labs	Tampa, FL, USA
Uralchem, LLC	Moscow, Russia
Uralchem, LLC Voskresensk	Moscow, Russia
Yara Norge AS	Porsgrunn, Norway

Table 1. Participating laboratories receiving unknown samples.

Due to sample delivery and other scheduling issues, only 22 laboratories were able to report data from the various methods. Data were collected and statistically evaluated to identify laboratories that demonstrated high proficiency when analyzing unknown samples. Only data from highly proficient laboratories were used to determine method performance, accuracy and repeatability. After the data were reviewed, 22 sets of data were collected from 17 high performing laboratories. It should be noted that seven of the 17 high performing laboratories that were within 1% P_2O_5 , with RSD-R values below 1.5 and greater than 80% of their HorRat-R values below 1.5 for the reference samples were considered to be high performing laboratories.

Great care was taken to accurately assess specific key steps in the procedures and equipment used by participating laboratories. Each participating laboratory was required to complete a questionnaire, provided in **Appendix I** and state that they used one of the proposed methods noted with no modifications. If minor modifications were made, then laboratories were still encouraged to participate and to note the changes or modifications they used.

2.2 Developing Method Evaluation Criteria

The steering committee developed a set of criteria used for method selection and evaluation. The Phosphate Working Group used these criteria to screen and select candidate methods. With a goal of structuring a balanced and fair review process, the following 13 criteria listed in **Table 2** were chosen in advance to guide the review and selection process. The objective of this study was to compare methods for suitability (scope), accuracy and repeatability (1), not to compare or assess laboratory performance other than using proficient laboratories and their data for method comparisons.

No.	Variable	Criteria
1	Method source	Has method been validated by a recognized entity (e.g. AOAC, EN, GOST, ISO)?
2	Use and general acceptance	Is the method widely used in commerce and/or has economic significance?
3	Availability and quality of references	Are data and references accessible?
4	Statistical evaluation of data	r (repeatability), R (reproducibility), Δ (bias; Ref. 1)
5	Performance	Check sample/round robin testing or known standard data
6	Scope of validation studies	What matrices/samples were studied?
7	Complexity	What instruments, equipment and expertise are needed?
8	Chemistry	Grouping the methods by similar chemistries for evaluation
9	Sample size and preparation	Is it appropriate for the materials tested?
10	Dynamic range	Are calibration curves, dilutions and sensitivities
11	Time	Time required - can method be run efficiently in-mass or
12	Health/environmental	Safety and environmental impact of reagents
13	Cost and availability	Instrument, equipment, reagents cost and availability

 Table 2. Criteria used for method selection.

2.3 Identifying Candidate Methods

Based on all of the criteria above, and following an extensive literature search and evaluation by the group, three candidate total phosphate methods were proposed for laboratory study. These three primary methods are listed in **Table 3**.

Additionally, participating laboratories were allowed to submit data for methods they considered viable and commonly used. These methods that were not identified by the team are listed in **Table 4**.

ID	Method	Technique
а	EN 15956 Digestion/EN15959 Analysis	Nitric/sulfuric acids digestion
b	GOST - 20851.2-75 1.b	Nitric/hydrochloric acid digestion spectrophotometric detection (Ref. 4)
С	AOAC 962.02/AFPC-XI 3.B	1-1 Hydrochloric digestion gravimetric detection (Refs. 5, 6)

Table 3. Total phosphate methods identified by selection criteria.

Table 4. Additional methods proposed by participating laboratories.

ID	Method	Technique
d	AOAC 978.01	Nitric/hydrochloric acid digestion automated spectrophotometric detection (Ref. 7)
е	AFPC-XI 3.D	2-1 Hydrochloric acid digestion
f	XRF spectrometry internal company method	XRF spectrometry pressed powder

Data were collected for all six methods listed in **Tables 3 and 4**. Each method is identified by a lower case italic letter (*a-e*) throughout the remainder of the text and tables. The complete list of methods that were researched is shown in **Appendix II**.

The six methods evaluated are further described below as:

- Method a European Normalization (EN) 15956 Fertilizers Extraction of phosphorus soluble in mineral acids – September 2011 (2) followed by EN 15959 – Fertilizers – Determination of extracted phosphorus – November 2011 (3).
- Method b GOST 20851.2-75 Method for determination of phosphates in mineral fertilizers – Nitric or hydrochloric acid digestions with differential spectrophotometric detection (4; translation by SGS, Geneva, Switzerland).
- Method c AOAC 962.02 (5)/Association of Fertilizer and Phosphate Chemists (AFPC) – XI 3.B (6; methods were deemed to be essentially the same) – Total Phosphorous in Fertilizers – Gravimetric quinolinium molybdophosphate method with 1-1 hydrochloric acid digestion.
- Method *d* AOAC 978.01 Total Phosphorous in Fertilizers Automated spectrophotometric method – Nitric/hydrochloric acids digestion (7) with automated spectrophotometric detection of molybdovanadophosphate (8).
- Method *e* Internally developed method using X-ray fluorescence spectrometry of pressed powder; method supplied by Jordan Phosphate Mines Co., Amman, Jordan.

2.4 Test Sample Selection and Preparation

After careful consideration, 10 materials were selected for sample preparation (five were duplicated) and are listed in **Table 5**. Three materials, Samples 4, 6 and 9, are reference materials. Results from these samples were compared to the certified/consensus results from the suppliers. This information was used to assess accuracy of the methods employed in the study. The 15 unknowns are summarized in **Table 5**.

Table 5. List of test samples used along with their certified (known) or established (in homogeneity testing) values for total phosphate content.

No.	Grade N-P-K ^a	Source material	Target $P_2O_5, \%^b$	Known (K) or homogeneity value (H) SD, % ^c
1	18-46-0	DAP, high Cl ^d from central Florida	46	H 46.24 ± 0.09
2	11-52-0	High CI ^d MAP from Louisiana	53	H 53.88 ± 0.14
3	0-46-0	Moroccan TSP	47	H 47.63 ± 0.10
4	13-61-0	H.J. Baker analytical grade MAP (>99.9%) ^e	61	H 61.86 ± 0.09
5	0-32-0	Moroccan rock	29.5	H 29.40 ± 0.10
6	0-32-0	Florida rock (AFPC Rock Check #22) [*]	33	K 33.06 ± 0.17
7	0-39-0	Russian apatite rock	39	H 39.28 ± 0.16
8	15-15-15	BASF compound N-P-K	15	H 15.09 ± 0.04
9	14-16-14	NIST 695 N-P-K blend (NIST reference data) ⁹	16	K 16.50 ± 0.23
10	15-42-0	Chinese DAP	41	H 41.09 ± 0.27
11	18-46-0	DAP, high Cl ^d from central Florida (Duplicate #1)	46	H 46.24 ± 0.09
12	11-52-0	High CI ^d MAP from Louisiana (Duplicate #2)	53	H 53.88 ± 0.14
13	0-32-0	Moroccan rock (Duplicate #5)	29.5	H 29.40 ± 0.10
14	0-39-0	Russian apatite rock (Duplicate #7)	39	H 39.28 ± 0.16
15	15-15-15	BASF compound N-P-K (Duplicate #8)	15	H 15.09 ± 0.04

^a Grade is the nitrogen, available phosphate, and soluble potash guarantees of the product.

^b Target is the expected total phosphate value based on homogeneity testing.

^c Homogeneity values are based on AFPC data in **Table 6**.

^d CI = Citrate insoluble phosphate.

^e H.J. Baker Specification for analytical grade ammonium phosphate-monobasic, 99.9%, catalog. http://hjbaker.com/cropnutrition/

^{*f*} AFPC Certificate Check–22 Certificate. http://www.afpc.net/ checkrock22.html (accessed April 25, 2014)

^g NIST SRM 695 Certificate of Analysis. http://www-s.nist.gov/srmors/quickSearch.cfm

Criteria used in the sample selection process including samples with established or certified values, different geographic regions of rock source and dynamic concentration ranging from 15 to 61% P_2O_5 . These unknown test materials were distributed as blind duplicates. Additionally, each laboratory was asked to run each sample in duplicate (but on different days) to assess both interlaboratory and intralaboratory precision.

The sample preparation and homogeneity process consisted of ensuring preground powdered samples were screened with an ASTM 40 (425 µm sieve opening), grinding granule and crystal samples using a micropulverizer fitted with a screen size of 0.027 in slots and screening the ground portion through the sieve per AOAC method preparation guidelines (9). A minimum of 40 aliquots for each material were prepared using 50 mL plastic digestion bottles with a minimum of 25 g/bottle. Ten bottles were chosen randomly and tested for homogeneity. The 10 samples were then returned to the inventory. Homogeneity testing was completed according to International Union of Pure and Applied Chemistry (IUPAC) guidelines (10) using two accepted methods of analysis. Results presented in **Table 6** satisfy requirements for sufficient homogeneity.

Unknown	nown Replicate No.															
No.	Sample	Source	Method	1	2	3	4	5	6	7	8	9	10	Average	SD	RSD, %
7 & 14 ^a	Russian	Apatite	AFPC	39.28	39.41	39.25	39.34	39.10	38.94	39.30	39.40	39.43	39.39	39.28	0.16	0.40
7 & 14 ^a	Russian	Apatite	AOAC	39.14	39.28	39.12	39.38	39.24	39.05	39.16	39.37	39.38	39.26	39.24	0.12	0.30
6 ^a	Florida rock	Check 22	AFPC	33.17	33.18	33.09	33.13	33.13	33.14	32.96	33.21	33.04	32.99	33.10	0.08	0.25
6 ^a	Florida rock	Check 22	AOAC	33.12	33.11	33.09	33.03	33.17	32.99	33.16	33.14	33.16	33.16	33.11	0.06	0.18
1 & 11	Florida DAP	High CI	AFPC	46.27	46.25	46.28	46.35	46.36	46.22	46.31	46.16	46.23	46.12	46.26	0.08	0.17
1 & 11	Florida DAP	High CI	AOAC	46.14	46.16	46.07	46.23	46.26	46.17	46.3	46.14	46.37	46.3	46.21	0.09	0.20
4 ^b	Reagent MAP	H.J. Baker	AFPC	61.82	61.71	61.94	61.84	61.84	61.71	61.74	61.88	61.84	61.76	61.81	0.08	0.12
4 ^b	Reagent MAP	H.J. Baker	AOAC	61.75	61.88	61.94	61.86	61.95	61.83	61.92	62.05	62.05	61.9	61.91	0.09	0.15
8 & 15	BASF	15-15-15	AFPC	15.17	15.18	15.16	15.16	15.15	15.24	15.12	15.2	15.22	15.11	15.17	0.04	0.27
8 & 15	BASF	15-15-15	AOAC	14.98	14.98	14.98	14.99	14.99	15.07	15.01	15.06	15.05	14.98	15.01	0.04	0.24
5 & 13 ^a	Moroccan	Rock	AFPC	29.31	29.22	29.12	29.3	29.33	29.22	29.23	29.25	29.3	29.25	29.25	0.06	0.21
5 & 13 ^a	Moroccan	Rock	AOAC	29.67	29.75	29.6	29.65	29.51	29.55	29.43	29.33	29.66	29.41	29.56	0.13	0.45
3	Moroccan	GTSP	AFPC	47.76	47.79	47.75	47.61	47.93	47.76	47.7	47.94	47.68	47.76	47.77	0.10	0.21
3	Moroccan	GTSP	AOAC	47.35	47.45	47.52	47.55	47.53	47.48	47.59	47.27	47.53	47.56	47.48	0.10	0.21
2 & 12	Louisiana MAP	High CI	AFPC	53.84	54.01	53.8	54.18	54.16	53.86	53.85	53.67	53.97	53.95	53.93	0.16	0.29
2 & 12	Louisiana MAP	High CI	AOAC	53.67	53.89	53.81	53.94	54.03	53.77	53.7	53.6	53.91	53.86	53.82	0.13	0.25
10 ^c	Chinese	DAP	AFPC	41.53	41.44	41.42	41.29	41.37	41.54	41.44	41.48	41.43	41.53	41.45	0.08	0.19

Table 6. Homogeneity data as determined by AFPC (XI 3.D–ICP OES) and AOAC (978.01 automated spectrophotometric) methods, P₂O₅ %.

^a Samples No. 7 and No. 14 (Russian Apatite), No. 6 (Florida rock), and Nos. 5 and 13 (Moroccan rock) are expressed in terms of P₂O₅ versus the normal BPL for rock analysis to aid in comparison of data.

^b Sample No. 4 is dried analytical grade ammonium phosphate-monobasic, 99.9% from H.J. Baker (14).

^c Sample No. 10 is limited in quantity, allowing only for one set of analysis by the AFPC method. Sample No. 9 is NIST SRM 695 with previously established homogeneity data.

2.5 Sample Distribution and Data Collection

From the initial invitations, 31 laboratories responded positively. Record forms were sent for collecting information regarding the method used and critical contact information for the responding laboratories. Twenty-six laboratories responded with appropriate information and a commitment to complete the study. All 26 laboratories received four practice samples. Practice and unknown samples were sent separately to make sure the addresses and customs information were adequate and to ensure the samples were delivered in a timely manner. Each laboratory was asked to complete and report analysis on the practice samples before proceeding with the unknown samples. Practice sample data were reviewed, and in some cases assistance was offered to bring analysis into alignment with expected values, prior to the laboratory being cleared to proceed with the unknown samples. All 26 laboratories provided acceptable practice sample data. Acceptability was determined by the laboratory being within $1\% P_2O_5$ on at least two of the four samples and at least $2\% P_2O_5$ on the two remaining samples.

Each lab was asked to run 30 analysis; 15 on two separate days. The 15 unknowns sent to laboratories included 10 materials with 5 of them prepared in duplicate. This provided data to assess interlaboratory and intralaboratory precision. All 26 participating labs reported data for one or more method.

2.6 Statistical Analysis

Participating laboratories were chosen based on their ability to apply at least one of the three candidate methods and to show proficiency by testing practice samples supplied to the candidate laboratories. Twenty-six of the invited laboratories participated in analysis of the unknowns, with 17 reporting statistically acceptable data. Seven of the 17 laboratories reported data on two methods, so 24 sets of data met the criteria for acceptability. In addition to precision for the reference materials, means and deviations and calculation of RSD, Predicted Relative Standard Deviation (PRSD) and HorRat values (11) were included in the selection of laboratories that performed at a high level of proficiency. Specifically, in our assessment, methods with RSD-R values below 1.5 and with greater than 80% of their HorRat-R values below 1.5 for the unknown samples were considered to be the best practice methods.

The evaluation of data and statistical treatment is for the purpose of selecting only proficient laboratories and assessing the candidate methods, not to evaluate individual laboratory performance. Because of the large number of different laboratories, samples and methods, a display of the statistics from the entire data set is difficult. Thus the data is displayed in Tables 7 through 15 with a capitalized letter indicating laboratory code followed by a lower case letter indicating method code: (a = EN 15956 and 15959 (gravimetric); b = GOST20851.2-75 1.b (spectrophotometric); c = AOAC INTERNATIONAL 962.02/AFPC-XI 3.B (gravimetric); = AOAC INTERNATIONAL 978.01/AFPC-XI 3.B d (automated spectrophotometric). For example, Bb would represent Laboratory B results using the GOST 2085102-45 1.b spectrophotometric method. Overall method performance in **Tables 7** through **15** are based on the average of duplicates and compared against the known values of the material or the grand average of the remaining unknown materials.

		P ₂ O ₅ %	
ID ^a	No. 4 Analytical grade MAP	No. 6 AFPC Check 22	No. 9 NIST N-P-K blend
Aa	61.38	33.21	16.62
Bb	61.84	33.18	16.59
Cd	62.00	33.10	16.58
Db	61.63	33.13	16.59
Fd	61.17	32.92	16.50
Gd	61.58	33.05	16.53
На	62.07	33.21	16.75
Hb	61.67	33.70	16.73
Jb	61.94	33.32	16.43
Kc	62.31	33.31	16.66
Kd	62.12	33.13	16.73
Lc	61.82	33.19	33.06 ^b
Nb	61.56	33.00	16.50
Od	61.47	32.88	15.53
Pd	61.93	33.27	16.74
Qc	61.73	33.03	16.48
Ra	61.60	33.00	16.44
Rd	61.80	32.94	16.45
Та	61.28	32.32	16.51
Ua	61.81	32.83	16.80
Vd	61.91	33.09	16.95
Vc	61.76	33.04	16.64
Yd	61.69	32.99	16.66
Zd	61.64	32.85	16.48
Zc	61.87	33.13	16.54
Certified	61.86	33.06	16.50
Average	61.742	33.073	16.573
SD	0.252	0.233	0.255
RSD-R, %	0.408	0.703	1.541
PRSD-R, %	1.077	1.183	1.313
HorRat-R	0.38	0.59	1.17

Table 7. Results for known materials (analytical grade MAP, AFPC Check No. 22, NIST SRIVE)

^a Data are displayed with a capitalized letter indicating laboratory code followed by a lower case italic letter indicating method code.

^b Identified as an outlier and excluded from calculations.

Table 8. EN method data for the known reference materials.

	P ₂ O ₅ %								
ID ^a	No. 4 Analytical grade MAP	No. 6 AFPC Check 22	No. 9 NIST N-P-K blend						
Aa	61.38	33.21	16.62						
Ha	62.07	33.21	16.75						
Ra	61.60	33.00	16.44						
Та	61.28	32.32	16.51						
Ua	61.81	32.83	16.80						
Established	61.86	33.06	16.50						
Average	61.626	32.911	16.621						
SD	0.287	0.329	0.136						
RSD-R, %	0.465	0.998	0.816						
PRSD-R, %	1.077	1.183	1.313						
HorRat-R	0.43	0.84	0.62						

^a Data are displayed with a capitalized letter indicating laboratory code followed by a lower case italic letter indicating method code.

		P ₂ O ₅ %	
ID ^a	No. 4 Analytical grade MAP	No. 6 AFPC Check 22	No. 9 NIST N-P-K blend
Bb	61.84	33.18	16.59
Db	61.63	33.13	16.59
Hb	61.67	33.70	16.73
Jb	61.94	33.32	16.43
Nb	61.56	33.00	16.50
Established	61.86	33.06	16.50
Average	61.727	33.264	16.566
SD	0.143	0.240	0.101
RSD-R, %	0.231	0.722	0.613
PRSD-R, %	1.077	1.183	1.313
HorRat-R	0.21	0.61	0.47

Table 9. GOST method data for the known reference materials.

^a Data are displayed with a capitalized letter indicating laboratory code followed by a lower case italic letter indicating method code.

		P ₂ O ₅ %								
ID ^a	No. 4 Analytical grade MAP	No. 6 AFPC Check 22	No. 9 NIST N-P-K blend							
Kc	62.31	33.31	16.66							
Lc	61.82	33.19	33.06 ^b							
Qc	61.73	33.03	16.48							
Vc	61.76	33.04	16.64							
Zc	61.87	33.13	16.54							
Established	61.86	33.06	16.50							
Average	61.896	33.136	16.578							
SD	0.212	0.105	0.074							
RSD-R, %	0.343	0.317	0.448							
PRSD-R, %	1.077	1.183	1.313							
HorRat-R	0.32	0.27	0.34							

Table 10. AOAC and AFPC gravimetric data for the known reference materials.

^a Data are displayed with a capitalized letter indicating laboratory code followed by a lower case italic letter indicating method code.

^b Identified as an outlier and excluded from calculations.

		P ₂ O ₅ %	
ID ^a	No. 4 Analytical grade MAP	No. 6 AFPC Check 22	No. 9 NIST N-P-K blend
Cd	62.00	33.10	16.58
Fd	61.17	32.92	16.50
Gd	61.58	33.05	16.53
Kd	62.12	33.13	16.73
Od	61.47	32.88	15.53
Pd	61.93	33.27	16.74
Rd	61.80	32.94	16.45
Vd	61.91	33.09	16.95
Yd	61.69	32.99	16.66
Zd	61.64	32.85	16.48
Established	61.86	33.06	16.50
Average	61.73	33.02	16.51
SD	0.268	0.124	0.359
RSD-R, %	0.434	0.375	2.173
PRSD-R, %	1.077	1.183	1.313
HorRat-R	0.40	0.32	1.65

Table 11. AOAC/AFPC spectrophotometric method data for the known reference materials.

^a Data are displayed with a capitalized letter indicating laboratory code followed by a lower case italic letter indicating method code.

Table 12. Data from the EN 15956 dige	stion and EN15959	gravimetric analysis	s methods.
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				P ₂ 0	D₅ %						
-		La	ooratory o	ode					-		
Sample ID	Aa	На	Ra	Та	Ua	Est. ^a	v ^b	σ	RSD-R, %	PRSD-R, %	HorRat-R
1	46.11	46.56	45.98	45.79	46.10	46.24	46.11	0.25	0.55	1.13	0.49
2	53.68	54.20	53.54	53.53	53.68	53.88	53.73	0.25	0.46	1.10	0.42
3	47.85	47.85	47.63	47.42	47.64	47.62	47.68	0.16	0.34	1.12	0.30
4	61.38	62.07	61.60	61.28	61.81	61.86	61.63	0.29	0.47	1.08	0.43
5	29.66	29.82	29.54	29.18	29.47	29.40	29.53	0.21	0.72	1.20	0.60
6	33.21	33.21	33.00	32.32	32.83	33.06	32.91	0.33	1.00	1.18	0.84
7	39.47	39.33	38.73	38.83	39.14	39.28	39.10	0.28	0.73	1.15	0.63
8	14.96	14.95	14.87	14.77	14.91	15.09	14.89	0.07	0.47	1.33	0.35
9	16.62	16.75	16.44	16.51	16.80	16.50	16.62	0.14	0.82	1.31	0.62
10	41.52	41.30	41.46	41.16	41.17	41.09	41.32	0.15	0.36	1.15	0.32
11	46.26	46.49	46.63	46.19	46.46	46.24	46.40	0.16	0.34	1.13	0.30
12	54.02	53.45	53.27	53.71	53.96	53.88	53.68	0.29	0.54	1.10	0.49
13	31.18 ^d	29.80	29.45	29.51	29.16	29.40	29.48	0.23	0.77	1.20	0.64
14	39.77	39.15	38.76	38.73	39.53	39.28	39.19	0.41	1.05	1.15	0.91
15	14.99	15.00	14.94	14.83	14.92	15.09	14.94	0.06	0.41	1.33	0.31

^a Est. = Established value based on supplier information or the value established as the average from the homogeneity study - $% P_2O_5$.

^b v = Average of the data reported by highly proficient laboratories - % P_2O_5 .

 c σ = Standard deviation based on the reported data by highly proficient laboratories.

^d Outlier; data excluded from calculations.

Table 13. Data from GOST 20851.2-75 1.b s	spectrophotometric method.
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				P ₂ C	D ₅ %						
		Lat	poratory o	ode							
Sample ID	Bb	Db	Hb	Jb	Wb	Est. ^a	v ^b	σ	RSD-R, %	PRSD-R, %	HorRat-R
1	46.373	46.170	46.475	46.370	46.025	46.24	46.2825	0.1623	0.3508	1.1253	0.3117
2	53.823	53.165	54.110	53.820	53.265	53.88	53.6365	0.3613	0.6737	1.0998	0.6125
3	47.578	47.670	47.600	47.635	47.770	47.62	47.6505	0.0675	0.1417	1.1204	0.1264
4	61.843	61.625	61.670	61.940	61.555	61.86	61.7265	0.1428	0.2313	1.0773	0.2147
5	29.508	29.565	30.500	29.690	29.605	29.40	29.7735	0.3681	1.2362	1.2044	1.0264
6	33.180	33.125	33.700	33.315	33.000	33.06	33.2640	0.2403	0.7225	1.1834	0.6105
7	38.718	39.190	39.470	39.200	39.110	39.28	39.1375	0.2426	0.6200	1.1532	0.5376
8	14.930	14.825	15.125	14.710	14.945	15.09	14.9070	0.1379	0.9248	1.3311	0.6947
9	16.593	16.590	16.725	16.425	16.495	16.50	16.5655	0.1015	0.6125	1.3134	0.4664
10	41.550	41.165	41.390	41.540	41.195	41.09	41.3680	0.1639	0.3962	1.1454	0.3459
11	46.563	46.125	46.250	46.220	46.100	46.24	46.2515	0.1653	0.3575	1.1253	0.3176
12	53.803	53.440	53.580	54.370	53.210	53.88	53.6805	0.3949	0.7356	1.0998	0.6688
13	29.785	29.445	29.700	29.600	29.435	29.40	29.5930	0.1380	0.4664	1.2044	0.3872
14	38.988	39.065	39.030	39.470	38.990	39.28	39.1085	0.1830	0.4679	1.1532	0.4057
15	14.920	14.750	14.715	14.720	14.855	15.09	14.7920	0.0815	0.5511	1.3311	0.4140

^a Est. = Established value based on supplier information or the value established as the average from the homogeneity study - $% P_2O_5$.

^b v = Average of the data reported by highly proficient laboratories - $\% P_2O_5$.

^c σ = Standard deviation based on the reported data by highly proficient laboratories.

P ₂ O ₅ %											
		Lat	poratory o	ode					-		
Sample ID	Kc	Lc	Qc	Vc	Zc	Est. ^a	v ^b	σ	RSD-R, %	PRSD-R, %	HorRat-R
1 2 3 4 5 6 7 8 9 10	46.545 53.890 47.700 62.310 29.745 33.310 39.065 15.040 16.660 42.200	46.875 53.625 47.620 61.820 29.350 33.185 38.04 ^d 15.070 33.06 ^d 41.515	46.290 53.650 47.415 61.730 29.560 33.025 39.120 14.760 16.475 41.235	46.300 53.755 47.330 61.755 29.515 33.035 39.170 14.925 16.635 41.500	46.485 53.930 47.405 61.865 29.570 33.125 39.210 14.830 16.540 41.420	46.24 53.88 47.62 61.86 29.40 33.06 39.28 15.09 16.50 41.09	46.4990 53.7700 47.4940 61.8960 29.5480 33.1360 39.1413 14.9250 16.5775 41.5740	0.2131 0.1230 0.1410 0.2124 0.1263 0.1052 0.0544 0.1187 0.0742 0.3285	0.4582 0.2288 0.2968 0.3432 0.4274 0.3174 0.3174 0.1389 0.7956 0.4476 0.7901	1.1253 1.0998 1.1204 1.0773 1.2044 1.1834 1.1532 1.3311 1.3134 1.1454	0.4072 0.2080 0.2649 0.3185 0.3548 0.2682 0.1204 0.5977 0.3408 0.6898
11 12 13 14 15	46.475 53.755 29.870 39.425 15.065	46.575 53.605 29.870 38.170 15.215	46.385 53.705 29.495 39.225 14.800	46.495 53.930 29.595 39.265 14.980	46.255 53.825 29.500 39.110 14.800	46.24 53.88 29.40 39.28 15.09	46.4370 53.7640 29.6660 39.0390 14.9720	0.1093 0.1097 0.1703 0.4461 0.1593	0.2353 0.2040 0.5742 1.1426 1.0642	1.1253 1.0998 1.2044 1.1532 1.3311	0.2091 0.1854 0.4767 0.9908 0.7994

Table 14. Data from AOAC 962.02/AFPC-XI 3.B gravimetric method.

^a Est. = Established value based on supplier information or the value established as the average from the homogeneity study - % P₂O₅.

^b v = Average of the data reported by highly proficient laboratories - $\% P_2O_5$.

^c σ = Standard deviation based on the reported data by highly proficient laboratories.

^d Outlier; data excluded from calculations.

							P ₂ O ₅ %									
Sample					Laborat	ory code					_			-		
ID	Cd	Fd	Gd	Kd	Od	Pd	Rd	Vd	Yd	Zd	Est. ^a	v ^b	σ	RSD-R, %	PRSD-R, %	HorRat-R
1	46.22	46.21	46.34	46.55	46.09	46.66	46.29	46.50	46.31	46.27	46.24	46.342	0.165	0.355	1.125	0.316
2	53.82	53.41	53.73	54.02	53.62	53.99	53.65	53.90	53.67	53.50	53.88	53.730	0.191	0.355	1.100	0.323
3	47.51	47.16	47.29	47.62	47.89	47.59	47.42	47.41	47.49	47.28	47.62	47.464	0.197	0.416	1.120	0.371
4	62.00	61.17	61.58	62.12	61.47	61.93	61.73	61.91	61.69	61.64	61.86	61.720	0.267	0.433	1.077	0.401
5	29.47	29.42	29.56	29.55	29.78	29.76	29.56	29.58	29.58	29.28	29.40	29.552	0.141	0.476	1.204	0.395
6	33.10	32.92	33.05	33.13	32.88	33.27	33.03	33.09	32.99	32.85	33.06	33.028	0.121	0.366	1.183	0.309
7	39.33	38.88	39.11	39.19	38.68	39.31	39.12	39.38	39.19	39.09	39.28	39.125	0.201	0.514	1.153	0.446
8	14.98	14.87	14.93	14.83	14.50	15.11	14.76	14.80	15.04	14.88	15.09	14.868	0.162	1.088	1.331	0.817
9	16.58	16.50	16.53	16.73	16.53	16.74	16.48	16.95	16.66	16.48	16.50	16.617	0.145	0.873	1.313	0.665
10	41.44	41.15	41.28	42.08	41.12	41.45	41.24	41.49	41.60	41.32	41.09	41.414	0.265	0.639	1.145	0.558
11	46.12	46.24	46.32	46.37	45.65	46.61	46.39	46.37	46.33	46.17	46.24	46.255	0.239	0.517	1.125	0.460
12	53.73	53.57	53.71	53.90	53.73	53.95	53.71	53.98	53.72	53.66	53.88	53.765	0.126	0.235	1.100	0.214
13	29.47	29.53	29.64	29.56	29.65	29.67	29.50	29.56	29.72	29.35	29.4	29.563	0.105	0.355	1.204	0.295
14	39.27	39.35	39.33	39.14	38.81	39.31	39.23	39.24	39.21	38.92	39.28	39,179	0.171	0.437	1.153	0.379
15	15.03	15.07	15.00	14.94	14.58	15.16	14.80	15.05	15.11	14.81	15.09	14.954	0.167	1.116	1.331	0.838

 Table 15. AOAC 978.01/AFPC spectrophotometric data.

^a Est. = Established value based on supplier information or the value established as the average from the homogeneity study - $% P_2O_5$.

^b v = Average of the data reported by highly proficient laboratories - % P_2O_5 .

^c σ = Standard deviation based on the reported data by highly proficient laboratories.

Fable 16. Overall method con	parisons by proficie	nt laboratories,	, % P ₂ O ₅ .
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Sample ID	All Methods	<i>Method (a)^a EN</i> gravimetric	Deviation	<i>Method (b)^b</i> GOST	Deviation	<i>Method (c)^c</i> AOAC gravimetric	Deviation	<i>Method (d)^d</i> AOAC spectro.	Deviation
1	46.32	46.11	-0.22	46.24	-0.08	46.49	0.17	46.34	0.02
2	53.72	53.73	0.01	53.57	-0.14	53.75	0.03	53.72	-0.00
3	47.56	47.68	0.12	47.67	0.11	47.52	-0.04	47.39	-0.16
4	61.74	61.63	-0.11	61.70	-0.04	61.82	0.09	61.73	-0.01
5	29.58	29.53	-0.05	29.75	0.16	29.59	-0.00	29.49	-0.09
6	33.07	32.91	-0.16	33.22	0.15	33.07	-0.00	33.02	-0.06
7	39.15	39.10	-0.05	39.13	-0.01	39.12	-0.03	39.16	0.02
8	14.91	14.89	-0.02	14.91	-0.00	14.87	-0.05	14.90	-0.01
9	16.57	16.62	0.05	16.55	-0.02	16.38	-0.19	16.63	0.06
10	41.44	41.32	-0.12	41.34	-0.10	41.57	0.13	41.48	0.03
11	46.31	46.40	0.10	46.23	-0.08	46.29	-0.02	46.27	-0.04
12	53.70	53.68	-0.02	53.60	-0.10	53.70	-0.00	53.75	0.05
13	29.57	29.48	-0.09	29.57	-0.00	29.68	0.11	29.55	-0.03
14	39.12	39.19	0.06	39.09	-0.04	38.98	-0.14	39.21	0.08
15	14.93	14.94	0.01	14.80	-0.12	14.89	-0.04	15.00	0.07
Average	37.85	37.81	-0.03	37.82	-0.02	37.85	0.00	37.84	0.00

^a Method *a* = EN 15956.

^b Method b = GOST 20851.2-75.

^c Method c = AOAC **962.02**/Association of Fertilizer and Phosphate Chemists (AFPC)–XI 3.B.

^{*d*} Method d = AOAC **978.01**.

3. Results

As previously indicated, there were three reference materials included in the study to assess accuracy. The data shown in **Table 7** are only from highly proficient laboratories based on performance on the unknown materials.

It is speculated that the reason for the higher RSD-R and HorRat–R values for the No. 9 National Institute of Standards and Technology (NIST) sample is that the phosphate concentration of the material is lower than in typical concentrated products, thus modifications to the weight or calibration solutions were needed to accommodate for the lower concentration.

Data from the EN method(s) – Fertilizers – Extraction of phosphorus soluble in mineral acids followed by EN 15959 – Fertilizers – Determination of extracted phosphorus (**Table 8**) were well within acceptable precision and accuracy limits.

Data from the GOST method for determination of phosphates in mineral fertilizers – Nitric or hydrochloric acid digestions with differential spectrophotometric detection (**Table 9**) were well within acceptable precision and accuracy limits for the reference materials.

Data from the AOAC and AFPC gravimetric method (**Table 10**) were well within acceptable precision and accuracy limits for the reference materials.

Data from the AOAC INTERNATIONAL/AFPC automated spectrophotometric method (**Table 11**) were well within acceptable precision and accuracy limits of the reference materials. In all cases, the candidate methods, as well as the AOAC INTERNATIONAL/AFPC automated spectrophotometric method, demonstrated high levels of accuracy.

Table 12 is a sample-by-sample presentation of laboratories using the EN (*a*) method. **Table 13** is a sample-by-sample presentation of laboratories that used the GOST (*b*) method.

Table 14 is a sample-by-sample presentation of laboratories that used the AOAC INTERNATIONAL/AFPC gravimetric (*c*) method. **Table 15** is a sample-by-sample presentation of laboratories that used the AOAC INTERNATIONAL/AFPC spectrophotometric (*d*) method. **Table 16** provides a summary of method performance on a sample-by-sample basis for the four selected methods. Based upon the data presented in **Tables 12–15** (mean, SD, RSD-R, and HorRat-R), it is apparent there is a high level of agreement among the laboratories using the four methods selected.

4. Conclusions

A summary of the data from the 17 high performing laboratories indicates good agreement and confirms that the methods examined were accurate and reproducible. All four methods met the established RSD-R and Horwitz repeatability goals (RSD-R values below 1.50 and >80% of their HorRat-R values below 1.5), and therefore, are considered acceptable for commerce. The methods found acceptable fall into two broad categories, gravimetric (EN AOAC and INTERNATIONAL) and spectrophotometric (GOST and AOAC INTERNATIONAL). The AOAC INTERNATIONAL spectrophotometric method is automated. allowing for greater throughput. The four methods recommended herein will allow for the flexibility needed in terms of chemistry, equipment, throughput and expense.

References

- (1) Official Methods of Analysis (2012) Appendix D, 19th Ed., Gaithersburg, MD
- (2) Youden, W.T., & Steiner, E.H. (1975) *Statistical Manual of the AOAC*, AOAC INTERNATIONAL, Gaithersburg, MD
- (3) *Fertilizers Extraction of phosphorus soluble in mineral acids*, EN 15956:2011, European Committee for Standardization, Brussels, Belgium
- (4) *Fertilizers Determination of extracted phosphorus*, EN 15959:2011, European Committee for Standardization. Brussels, Belgium
- Mineral fertilizers, Methods for determination of phosphorus, GOST 20851.2-75.
 (1976) Euro-Asian Council for Standardization, Metrology and Certification (EASC), Moscow, Russia
- (6) Official Methods of Analysis (2012) 19th Ed., AOAC INTERNATIONAL, Gaithersburg, MD, Method **962.02**
- (7) Total Phosphorus as P_2O_5 Gravimetric Quimociac Method, AFPC XI 3. B, AFPC Analytical Methods Manual, Bartow, FL
- (8) AFPC ICP OES (Inductively Coupled Plasma-Optical Emission Spectroscopy) (2010) Methods Manual, 10th Ed., Association of Fertilizer and Phosphate Chemists, Bartow, FL
- (9) AOAC/AFPC Automated Spectrophotometric Method (2012) Official Methods of Analysis of AOAC INTERNATIONAL, 19th Ed., Gaithersburg, MD
- (10) IUPAC/CITAC Guide: Selection and use of proficiency testing schemes for a limited number of participants – chemical analytical laboratories (2010) Pure Appl. Chem. 82, 1099–1135

Appendix I Survey Method Information and Input Form

Method Information Input Form – Mineral Acid Soluble P₂O₅ in Fertilizer Materials

Please complete each of the questions below, please free to add additional information as you see fit.

Section I – Laboratory Contact Information

- 1. Organization :
- 2. Contact Name:
- 3. Contact Email: _____

Section II – Method Description & References

If the method used in your laboratory is not performed exactly as written (whether using a reference method or another method), it is very important to note any modifications made in order to document any modifications/improvements made in the method to be considered as a best practice method.

- 4. Please list the name of the method used by your laboratory:
- 5. If the method is not one provided as a reference method where can a written version be obtained?
- 6. Can you provide a written copy of the method used by your laboratory? ______ If so please attach it.
- 7. If you cannot provide an official copy, can you describe the method used? _____ If so please attach it.
- 8. If the method used is one of the reference methods provided please describe any modifications made.

Section III – Specific Digestion Information

- 9. What is the weight of sample used?_____ What is the final sample/solvent ratio? _____
- 10. What acids are used?______ What is the volume of acid used? ______
- 11. What type of heat is used?______What is the temperature range during digestion? ______
- 12. Is there a specific order of solvent additions and times involved?_____ If so please describe the sequence:

Section IV

- 13. Is the determination gravimetric, colorimetric, Spectrophotometric or "other"?
- 14. Describe the instrumentation used for the determination?

15. If calibrations are used please describe the number of points, range, and detection limit:

16. What types of reference materials or known samples are used in the calibration process?

Appendix II Total Phosphate Methods Indentified by Literature Search

Rohm, K. Over the determination of the water-soluble and the entire phosphoric acid in superphosphates. [machine translation]. Chemiker-Zeitung (1906), 30 542-43.

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Kane, Peter F.; Orcutt, Anne L.; Huber, Janet H. Comparison of Traacs 800 autoanalyzer with official methodology for total and available phosphorus in fertilizer. Journal - Association of Official Analytical Chemists (1989), 72(5), 862-71.

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