Application Note

Food and agriculture

Agilent

Trusted Answers

High-Precision Determination of Phosphorus and Potassium in Fertilizers by ICP-OES

Accurate nutrient analysis of fertilizers using an Agilent 5800 ICP-OES and standard bracketing

Author

Ruby Bradford,
Agilent Technologies, Inc.

Introduction

Accurate characterization of fertilizer nutrient content is critical for optimizing plant growth, maximizing yield, and ensuring sustainable agricultural practices. Fertilizers must comply with strict regulatory specifications, particularly for declared NPK (nitrogen–phosphorus–potassium) ratios, which define the relative nutrient content supplied to crops. Even small deviations from the specified ratio can impact plant yield, regulatory compliance, customer confidence in the product, as well as its commercial value.

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) is a well-established technique for multi-element analysis of complex samples, so is ideally suited to meet the precision and accuracy requirements of fertilizer testing.[1,2] However, applications that require very tight tolerances, such as NPK verification, benefit from enhanced calibration approaches as even small deviations from reported values can have large financial implications for the manufacturer.

Using Agilent ICP-OES instruments, standard bracketing calibration based on a *standard–sample–standard* measurement sequence, minimizes the impact of sample-to-sample variability and matrix effects.[3,4] This approach further improves analytical precision and accuracy compared to conventional external calibration, making it a particularly valuable method for analyzing fertilizers with tightly controlled specifications.

In this study, an Agilent 5800 Vertical Dual View (VDV) ICP-OES, equipped with an Agilent SPS 4 autosampler and controlled using Agilent ICP Expert Pro software,[5] was used to determine P and K concentrations and corresponding NPK ratios in a standard reference material (SRM) and two commercially available fertilizers. The standard bracketing method was adapted from ISO methods 11494 and 11495[6,7] and adjusted for fertilizer analysis. The performance of the method, when combined with real-time data processing tools, was evaluated for accuracy and precision.

Experimental

Instrumentation

The Agilent 5800 VDV ICP-OES was configured with the Agilent SPS 4 autosampler, which provided automated sample delivery to the instrument (Figure 1). The 5800 ICP-OES was equipped with an Agilent SeaSpray nebulizer, double-pass cyclonic spray chamber, and one-piece VDV torch with a 1.8 mm internal diameter (ID) injector. All components were controlled by Agilent ICP Expert Pro* software. Instrument operating parameters are listed in Table 1.

Figure 1. Agilent 5800 VDV ICP-OES, Agilent SPS 4 autosampler, and monitor showing Agilent ICP Expert Pro software.

Table 1. Agilent 5800 VDV ICP-OES instrument and method parameters.

Parameter	Setting
Viewing Mode	Radial
Viewing Height (mm)	8
RF Power (kW)	1.3
Nebulizer Flow (L/min)	0.7
Plasma Flow (L/min)	12
Aux Flow (L/min)	1.0
Replicates	3
Rinse Time (s)	30
Read Time (s)	10
Fast Pump Speed (rpm)	30
Stabilization Time (s)	20
Sample Pump Tubing	White/white
Waste Pump Tubing	Blue/blue
Internal Standard	Y 371.029 nm
Background Correction	Fitted
Bracketing Cycles*	5

** Each sample measurement (bracketing cycle) was repeated five times, see Figure 3.*

NPK ratios

NPK ratios are commonly used to describe the major nutrient composition of fertilizers and are used in fertilizer nutrient labeling. The ratio represents the relative amounts of available N, P, and K. P and K are not reported as elemental P and K, but as their oxide equivalents, P_2O_5 and K_2O. Because ICP-OES measures elemental P and K concentration, converting the results to oxide forms for fertilizer labeling requires additional calculations (multiply %P by 2.29 to obtain %P_2O_5 and %K by 1.205 to obtain %K_2O). For example, a potassium dihydrogen phosphate (MKP) fertilizer containing 0% nitrogen, 52% P_2O_5 equivalent, and 35% K_2O equivalent would have an NPK ratio of 0:52:35.

The expected NPK ratios for each of the samples analyzed in this study are listed in Table 2.

Table 2. NPK ratios of the three fertilizer samples analyzed in this study.

Sample	NPK Ratio
KCl	0:0:63
DAP* ($(NH_4)_2HPO_4$)	18:54:0
MKP (KH_2PO_4)	0:52:35

**Represents pure DAP (most commercially available DAP fertilizers contain additives that affect the NPK ratio)*

**Standard bracketing requires Agilent ICP Expert Pro version 7.8 or later*

Sample preparation

The three samples selected for analysis were NIST SRM 999c potassium chloride (KCl; Gaithersburg, MD, USA)[8] and two commercially available fertilizers: diammonium hydrogen phosphate ($(NH_4)_2HPO_4$; DAP) and potassium dihydrogen phosphate (KH_2PO_4; MKP). KCl and DAP are single-nutrient chemical fertilizers for K and P, respectively, and MKP contains both nutrients.

As there currently is no standard bracketing method for fertilizer analysis, the method was adapted from ISO 13494 and 13495 for the determination of platinum and palladium in jewelry alloys.[6,7] As part of the requirements for standard bracketing, an internal standard (IS) solution must be gravimetrically added to all standards and samples at a consistent, recorded mass. To satisfy this requirement, a 6 mg/L yttrium IS solution was prepared in 5% (v/v) nitric acid (HNO_3) and used consistently for the preparation of both calibration standards and samples.

To prepare the samples for analysis, a representative portion of the sample (0.125 g) was accurately weighed and transferred into a 250 mL volumetric flask. A 25 g aliquot of the IS solution was added to the flask. Approximately 100 mL of de-ionized water was then added, followed by the careful addition of 12.5 mL of concentrated HNO_3. The solution was diluted to volume with de-ionized water and thoroughly mixed. All masses were recorded to enable gravimetric correction during data processing for improved analytical accuracy.

The resulting solution contained a final HNO_3 concentration of 5% (v/v) and represented an overall sample dilution factor of 2000×.

Standard preparation

Standards were prepared within or close to ±5% of the expected sample concentration for effective bracketing. Expected concentrations were estimated based on sample composition and dilution factor. For example, assuming ~52% elemental K in KCl (which can be calculated from the reported NPK K_2O ratio), the 2000× diluted solution corresponds to 0.026% or 260 mg/L elemental K. Standards were therefore prepared at 250 and 270 mg/L. The standard concentrations prepared for each sample are shown in Table 3.

Certified Agilent 10,000 mg/L stock solutions were used to prepare all standards. Concentrations were calculated based on the certificate of analysis (CoA) values. A mass-corrected aliquot of 10,000 mg/L calibration stock solution was weighed and added to a 250 mL volumetric flask, followed by 25 g of the 6 mg/L IS solution. Approximately 100 mL of de-ionized water was then added, followed by the careful addition of 12.5 mL of concentrated HNO_3. The solution was diluted to volume with de-ionized water and thoroughly mixed. Like with the samples, all masses were recorded for input into the software (Figure 2).

Table 3. The low and high standard concentrations per element for each sample.

		Concentration (mg/L)	
		K	P
KCl 999c SRM	Low standard	250	0
	High standard	270	0
DAP	Low standard	0	110
	High standard	0	125
MKP	Low standard	140	110
	High standard	160	125

Number of standards 2

Solution Label	K	Y	Final
	g	g	g
Nominal ISTD Weight		25.0000	
Standard 1	0.0625	25.0495	250.0000
Standard 2	0.0675	25.0680	250.0000

Figure 2. Example of standard value inputs for KCl, including calculated masses of K*, Y solution, and final/total mass**.

**The K and P concentrations can be converted to equivalent metal mass (g) by consulting the CoA.*

***Final (g) can be interchanged with Final (mL), assuming this is kept consistent and volumetric flasks are calibrated.*

Exceptional precision and accuracy

Compared to results obtained using conventional external calibration methods, the standard bracketing approach significantly improves precision and accuracy by compensating for short- and long-term instrumental fluctuations. This performance is of particular importance for fertilizer evaluation as small deviations from required NPK labeling can cause misapplication and reduced crop yield as well as potential non-compliance with regulatory labeling requirements. By continuously correcting signal response via alternating standard and sample measurements (Figure 3), alongside internal standard correction (Y 371.029 nm), the method delivers excellent precision and robustness during extended analytical runs. A comparison of external calibration and standard bracketing has been previously demonstrated in another application note[3] following the same ISO methods for precious metals.

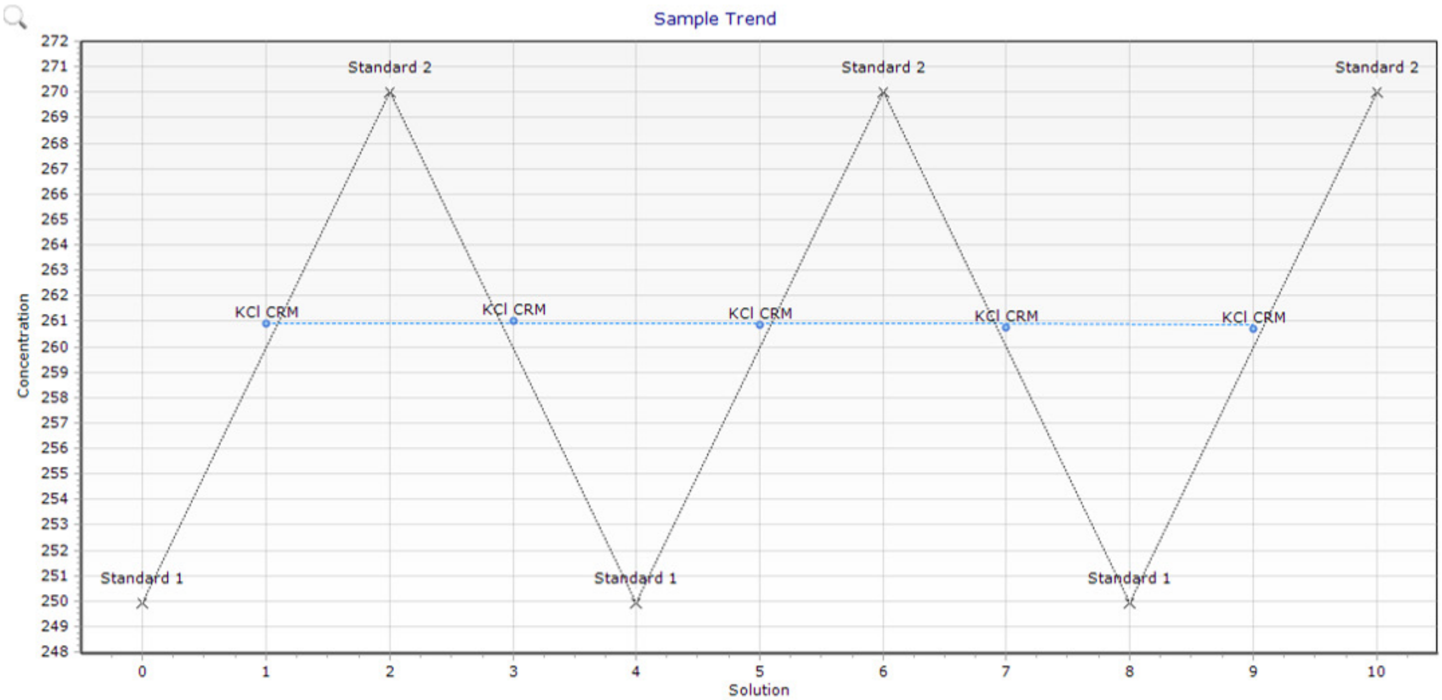

Figure 3. Example of a bracketing sequence, consisting of five bracketing cycles (sample measurements).

Real-time NPK ratio results using custom columns and sample aggregate

The custom column feature in the ICP Expert 7.8 software allows the user to create a results column that can be customized to display real-time calculations without the need for additional conversions or post-analysis processing. For example, users can define custom calculations that automatically convert analytical results (P or K concentrations) into their conventional fertilizer reporting forms P_2O_5 and K_2O, enabling instant calculation of NPK ratios during data acquisition. Automatic conversion eliminates the need for manual post-processing, avoiding transcription errors and improving laboratory efficiency.

The Sample Aggregate (SSUM) QC function further enhances data quality by summarizing results across sequences (including custom columns) and enables further real-time monitoring of key metrics. User-defined thresholds can trigger alerts or stop the run, ensuring data integrity and minimizing rework.

When paired with the sample aggregate QC row, the software provides a comprehensive solution for live, at-a-glance data processing. For example, in Figure 5, the custom column (vertical) defined as 'NPK (K) Ratio' converts the averaged results into the equivalent % by mass of K_2O, or the 'K' part of the NPK ratio. Then, the sample aggregate row defined as 'Sample Ave' (horizontal) works to average the results from the preceding sequence. The summarized NPK ratio of the entire sequence is then reported.

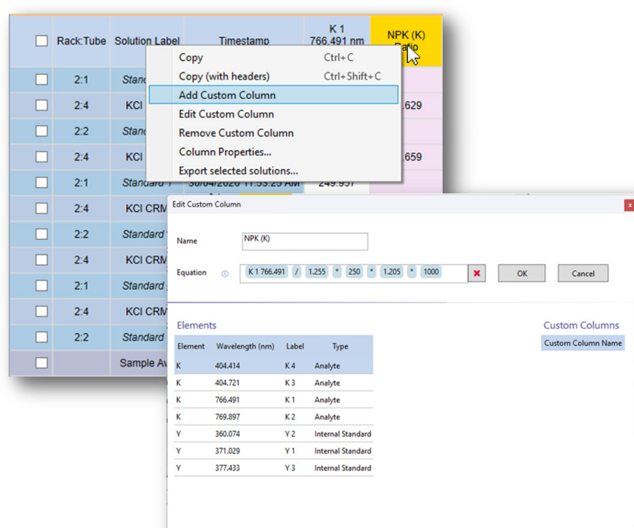

Figure 4. The addition of a custom column allows customizable equations to be displayed as a separate column, summarizing key data points.

	Rack:Tube	Solution Label	Timestamp	K 1 766.491 nm ppm	NPK (K) Ratio
☐	2:1	*Standard 1*	30/04/2026 11:45:41 AM	249.957	
☐	2:4	KCl CRM	30/04/2026 11:47:37 AM	260.913	62.629
☐	2:2	*Standard 2*	30/04/2026 11:49:33 AM	269.999	
☐	2:4	KCl CRM	30/04/2026 11:51:29 AM	261.036	62.659
☐	2:1	*Standard 1*	30/04/2026 11:53:25 AM	249.957	
☐	2:4	KCl CRM	30/04/2026 11:55:21 AM	260.861	62.617
☐	2:2	*Standard 2*	30/04/2026 11:57:17 AM	269.999	
☐	2:4	KCl CRM	30/04/2026 11:59:12 AM	260.784	62.598
☐	2:1	*Standard 1*	30/04/2026 12:01:08 PM	249.957	
☐	2:4	KCl CRM	30/04/2026 12:03:04 PM	260.703	62.579
☐	2:2	*Standard 2*	30/04/2026 12:05:00 PM	269.999	
☐		Sample Ave		260.859	62.617
☐		Sample RSD		0.048	0.048

Figure 5. Sample Aggregate (SSUM – horizontal) and custom column (vertical), work together to summarize data in any way the user requires.

Results and discussion

Sample analysis

Each sample was measured a total of fifteen times (three sequences of five bracketing cycles) using the 5800 VDV ICP-OES standard bracketing method. The aggregated concentration results (mg/kg), RSD, NPK, and error measurements are shown in Tables 4 and 5.

The KCl SRM recoveries were based on a certified K mass fraction of 52.443%, resulting in an expected K_2O mass fraction of 63.194%. All RSD values were below 0.1%, demonstrating the exceptional level of precision that the 5800 ICP-OES bracketing approach provides for fertilizer analysis and NPK ratio determination (Table 4).

The measured NPK values (K_2O and P_2O_5) for all three samples were in excellent agreement with the expected compositions (Table 2), with recoveries between 99 and 102% (Table 5). These results confirm the accuracy and precision of the method for both single-nutrient and mixed fertilizers. The consistency across replicate measurements (RSD <0.1%) highlights the benefit of bracketing for high-precision nutrient analysis of fertilizers.

Table 4. Concentration, precision (RSD), recovery, and error information for the NIST 999c KCl SRM with a theoretical expected K mass fraction value of 63.178%, n=5.

	KCl 999c SRM						
	Analytical Solution K Concentration (mg/kg)	RSD (%)	Sample K Mass Fraction (%)	K_2O Equivalent (%)	Recovery (%)	Absolute Error (%)	Relative Error (%)
Sequence 1	260.859	0.048	51.964	62.617	99.087	0.577	0.913
Sequence 2	260.725	0.063	51.937	62.584	99.036	0.609	0.964
Sequence 3	260.759	0.089	51.944	62.593	99.049	0.601	0.951
Summary*	260.781	0.022	51.948	62.598	99.057	0.596	0.943

**The Summary row results were calculated by averaging the values from the three sequences of five bracketing cycles, except for 'RSD', which was determined by calculating the relative standard deviation of the sequence results.*

Table 5. NPK ratio, RSD, recovery, and error information for all three samples.

	K 766.491				P 213.618			
Sample	K_2O Equivalent (%)	RSD (%)	Recovery (%)	Relative Error (%)	P_2O_5 Equivalent (%)	RSD (%)	Recovery (%)	Relative Error (%)
KCl SRM	62.598	0.022	99.057	0.943	-	-	-	-
DAP	-	-	-	-	54.789	0.035	102.00	1.97
MKP	34.631	0.021	100.03	0.032	52.616	0.021	100.93	0.930

Conclusion

This study demonstrates the effectiveness of the Agilent 5800 VDV ICP-OES standard bracketing method for high-precision determination of phosphorus and potassium in fertilizers. The method delivered excellent performance, with relative standard deviations below 0.1% and excellent agreement with expected NPK values, with recoveries ranging from 99 to 102%. The combination of gravimetrically prepared standards, internal standard correction, and bracketing calibration minimizes analytical variability and ensures reliable results for fertilizer quality control.

In addition, Agilent ICP Expert Pro software streamlines analysis through real-time calculations and automated quality control tools, improving laboratory efficiency and reducing the risk of reporting errors. This approach provides a robust and practical solution for high throughput fertilizer testing laboratories, enabling precise NPK verification that strengthens regulatory compliance, reduces the risk of mislabeling, and supports accurate product pricing.

References

1. Bradford, R., Determination of 21 Elements in Fertilizers using Autodilution with ICP-OES, Agilent publication, 5994-8647EN
2. Oppedisano, D., Rapid Multi-Elemental Analysis of Fertilizers using the Agilent 5110 VDV ICP-OES, Agilent publication, 5994-0600EN
3. High Precision Analysis of Major Components in Precious Metals by ICP-OES, Agilent publication, 5994-8849EN
4. Integrated Design: Accuracy and Precision of Agilent ICP-OES Instruments, Agilent publication, 5994-8853EN
5. Agilent ICP Expert Software: Powerful software with smart tools for ICP-OES, Agilent publication, 5994-1517EN
6. ISO 11494:2019 Jewellery and precious metals — Determination of platinum in platinum alloys — ICP-OES method using an internal standard element, https://www.iso.org/standard/75285.html
7. ISO 11495:2019 Jewellery and precious metals — Determination of palladium in palladium alloys — ICP-OES method using an internal standard element, https://www.iso.org/standard/75284.html
8. SRM 999c; Potassium Chloride; National Institute of Standards and Technology; U.S. Department of Commerce: Gaithersburg, MD (13 September 2019), https://tsapps.nist.gov/srmext/certificates/999c.pdf

Products used in this application

Agilent products

Easy-fit 1.8 mm one-piece torch for 5000 series VDV/SVDV ICP-OES

Double pass, glass ICP-OES spray chamber, with torque-controlled nebulizer adaptor

SeaSpray concentric glass nebulizer for 5000 series ICP-OES

Peristaltic pump tubing, white/white, 12/pack

Peristaltic pump tubing, blue/blue, 12/pack

Diluent/carrier bottle kit for autosampler (6 L HDPE)

Waste container kit, 10 L with Stay Safe cap and filter

Phosphorus (P) standard, 10,000 µg/mL, in 5% HNO_3, 500 mL

Potassium (K) standard, 10,000 µg/mL, in 5% HNO_3, 500 mL

Yttrium (Y) standard, 10,000 µg/mL, in 5% HNO_3, 500 mL

www.agilent.com/chem/5800icp-oes

DE-015914

Published in the USA, June 29, 2026
5994-9311EN