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Rapid Multi-Elemental Analysis of Fertilizers using the Agilent 5110 VDV ICP-OES

Accurate determination of 21 elements in under one minute

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Introduction

Successful, high-yield crop production often depends on the application of fertilizers to ensure that the correct quantity of nutrients is available to plants during the growth cycle. Excess amounts of some nutrients can also be detrimental to plant health, therefore monitoring the quantity of nutrients in fertilizers is essential. Elemental analysis techniques provide valuable information on fertilizer quality. This information helps to determine the correct quantity of fertilizer to apply to satisfy the nutrient requirements necessary for optimal crop yield. However, elemental analysis of fertilizers can be challenging due to the broad concentration range of analytes present in samples. The presence of high concentrations of major nutrient elements and significantly lower concentrations of trace elements can cause difficulty in obtaining reliable results. Depending on the analytical technique used, and the analytical working range of the technique, laboratories are often required to perform multiple dilutions to obtain analysis for all elements. When analyzing samples by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES),

the number of analytes present can cause spectral overlaps from other elements and molecular species that can be difficult to remove. Obtaining reproducible results can be challenging due to the complex nature and variability between fertilizer samples. The Agilent 5110 Vertical Dual View (VDV) ICP-OES can be used for the accurate and precise elemental determination of complex samples, while ensuring the demands of high-throughput agricultural laboratories are met.

Several regulated methods relate to the assessment of the nutrient requirements or test heavy metals in different types of fertilizers by ICP-OES. For example, AOAC 2017.02 (2006.03) and SUIP #25 Heavy Metal Rule, EN 233/2012 (EN 2003/2003) (1, 2). Depending on the regulated method, sample preparation involves either digestion or extraction.

In this study, 21 nutrient and trace elements were determined in fertilizers according to AOAC 2017.02 (2006.03). All elements, including Al, As, B, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, V, and Zn, were analyzed using the Agilent 5110 VDV ICP-OES fitted with the Advanced Valve System (AVS 7) seven-port switching valve.

Experimental

Instrumentation

The 5110 VDV ICP-OES fitted with the AVS 7 accessory and SPS 4 autosampler is ideal for the fast, accurate, and precise analysis of fertilizer samples. The 5110 features the Easy-fit torch that minimizes variability by automatically aligning the torch, enabling reproducible performance regardless of the operator. It also reduces variability between instruments. The vertical torch orientation ensures robust measurements over extended periods for a range of samples, with less cleaning, less downtime, and fewer replacement torches. The solid-state radio frequency (SSRF) system featured on the 5110 provides a reliable, robust, and maintenance free plasma suitable for handling complex samples. The system can rapidly adjust to changes in the plasma conditions arising from the varying composition of different types of fertilizers. Speed of sample analysis is an important factor in the cost-per-sample calculations faced by high-throughput, routine analysis labs. The fully integrated AVS 7 switching valve decreases sample uptake time and total run time. Fast analysis times allow labs to generate results quicker, as well as reducing running costs. For example, argon consumption is significantly reduced with the AVS 7. The fast, efficient analysis provided by the switching valve also extends the lifetime of consumables, further reducing operating costs.

The Vista Chip II detector features a wide linear dynamic range allowing for both major and trace elements to be analyzed from a single sample preparation method,

eliminating the need to perform multiple dilutions. Fertilizers often contain several elements that are subject to spectral interferences. The continuous wavelength coverage of the Vista Chip II from 167 to 785 nm, ensures a suitable, interference-free line can be found. Also, there is no time penalty when adding additional wavelengths to the analysis. ICP Expert software utilizes the unique Fitted Background Correction (FBC) technique that models the background to each analyte peak (3). The variation in analytes present in fertilizer samples can be automatically corrected to remove complex background structures without the need for user intervention. Unlike off-peak background correction, where the analyst needs to set a suitable background point.

Coupling the powerful ICP Expert software with the Vista Chip II detector, enables the 5110 ICP-OES to quickly screen samples, in addition to providing quantitative analysis. IntelliQuant is a unique acquisition mode that identifies analytes in a sample from an additional fast scan and provides semiquantitative results for elements not included in the calibration standards (4).

Different operator skill levels can be addressed, and routine analysis is simplified with ICP Expert Applet software. ICP Expert Applet mode is a simplified user-interface that allows users to confidently run an analysis with minimal training. The operator simply needs to walk up to the instrument, light the plasma, and click run.

The instrument and method parameters for the 5110 VDV ICP-OES are given in Table 1 with the AVS 7 settings given in Table 2.

Table 1. 5110 VDV ICP-OES instrument and method parameters.

Parameter	Setting	
Viewing mode	Axial	Radial
Read time (s)	5	3
Replicates	Standards = 5 Samples = 3	
Sample uptake delay (s)	0	
Stabilization time (s)	8	0
Rinse time (s)	0	
Pump speed (rpm)	12	
RF power (kW)	1.3	
Aux flow (L/min)	1.0	
Plasma flow (L/min)	12.0	
Nebulizer flow (L/min)	0.70	
Viewing height (mm)	-	8
Nebulizer	Seaspray concentric glass	

Table 1 continues…

Parameter	Setting
Spray chamber	Double-pass glass cyclonic
Torch	Easy-fit demountable VDV, 1.8 mm i.d injector
Sample pump tubing	White/White
Internal standard tubing	Black/Black
Waste pump tubing	Blue/Blue
Background correction	Fitted
Internal standard	Yttrium 5 ppm

Table 2. AVS 7 settings.

Parameter	Setting
Valve uptake delay (s)	8.0
Pump rate - uptake (mL/min)	35.0
Pump rate - inject (mL/min)	9.0
Sample loop volume (mL)	1.0
Preemptive rinse time (s)	1.0
Bubble inject time (s)	2.0

Sample preparation

A Standard Reference Material (SRM) 695 Trace Elements in Multi-Nutrient Fertilizer (NIST, Gaithersburg MD, USA) and a commercially available trace multi-element fertilizer were bought for analysis. The SRM was dried before sample preparation. Both samples were prepared for analysis according to the microwave digestion method specified in AOAC 2017.02 (an expansion of AOAC 2006.03). An accurately recorded mass of 0.50 g of sample was digested in a mixture of 9 mL HNO_3 and 3 mL HCl. The digest was made up to 100 mL. The final matrix was effectively 12% reverse-aqua-regia (RAR). Digestion of each sample was carried out according to the conditions provided in Table 3, using a Mars 6 Microwave Digestion System (CEM Corporation, NC, USA).

Table 3. Microwave digestion parameters.

Parameter	Setting
Temperature (°C)	200
Power (W)	1030−1800
Ramp time (min)	25
Hold time (min)	20

Standard preparation

Working standards were prepared using Agilent Single Elemental Standards. The concentration ranges of the standards are listed in Table 4. The standards and quality control (QC) solutions were matrix matched to the digested sample using nitric acid (EMSURE, Merck), hydrochloric acid (EMSURE, Merck), and ultrapure 18.2 MΩ Milli-Q water (Millipore).

Multiple wavelengths were selected for each element to show that the recovery of each target element was not affected by interferences that may be present in the fertilizer samples. A linear calibration was obtained for all lines, as indicated by >0.999 correlation coefficients for all elements (Table 4). Automated FBC was used for all wavelengths.

Table 4. Wavelength and working calibration range.

Element and wavelength (nm)	Viewing mode	Background correction	Concentration range (ppm)	Correlation coefficient
Al 308.215	Radial	Fitted	0−100	0.99999
Al 396.152	Radial	Fitted	0−100	1.00000
As 188.980	Axial	Fitted	0−10	0.99998
As 193.696	Axial	Fitted	0−10	0.99997
B 249.678	Axial	Fitted	0−100	1.00000
B 249.772	Axial	Fitted	0−100	1.00000
Ca 315.887	Radial	Fitted	0−1000	1.00000
Ca 317.933	Radial	Fitted	0−1000	1.00000
Cd 214.439	Axial	Fitted	0−10	0.99996
Cd 228.802	Axial	Fitted	0−10	0.99999
Co 228.615	Axial	Fitted	0−10	0.99997
Co 230.786	Axial	Fitted	0−10	1.00000
Cr 205.560	Axial	Fitted	0−10	1.00000
Cr 267.716	Axial	Fitted	0−10	1.00000
Cu 324.754	Radial	Fitted	0−250	0.99998
Cu 327.395	Radial	Fitted	0−250	0.99997
Fe 234.350	Radial	Fitted	0−500	0.99998
Fe 240.489	Radial	Fitted	0−500	0.99997
K 766.491	Radial	Fitted	0−1500	0.99979
Mg 277.983	Axial	Fitted	0−500	0.99998
Mg 279.078	Axial	Fitted	0−500	0.99988
Mn 279.482	Axial	Fitted	0−250	0.99994
Mn 293.931	Axial	Fitted	0−250	0.99991
Mo 202.032	Axial	Fitted	0−10	0.99999
Mo 204.598	Axial	Fitted	0−10	1.00000
Na 588.995	Radial	Fitted	0−100	0.99983
Na 589.592	Radial	Fitted	0−100	0.99999
Ni 216.555	Axial	Fitted	0−10	0.99999

Element and wavelength (nm)	Viewing mode	Background correction	Concentration range (ppm)	Correlation coefficient
Ni 231.604	Axial	Fitted	0−10	0.99999
P 177.434	Radial	Fitted	0−1000	0.99993
P 178.222	Radial	Fitted	0−1000	1.0000
Pb 220.353	Axial	Fitted	0−10	0.99999
S 181.972	Axial	Fitted	0−1000	0.99999
S 180.669	Radial	Fitted	0−1000	1.00000
Se 196.026	Axial	Fitted	0−10	1.00000
V 292.401	Axial	Fitted	0−10	0.99997
V 311.837	Axial	Fitted	0−10	0.99999
Zn 213.857*	Axial	Fitted	0−100	0.99999
Zn 334.502	Axial	Fitted	0−100	0.99997

All linear fit except Zn 213.815, which was calibrated with quadratic fit.

The representative calibration curve in Figure 1, for B 249.772 nm, highlights the wide linear dynamic range of the 5110 ICP-OES, from 0 to 100 ppm. An example of automatic background fitting using FBC is shown in Figure 2. FBC provides accurate correction of background structures allowing the low-level detection of B 249.772 nm.
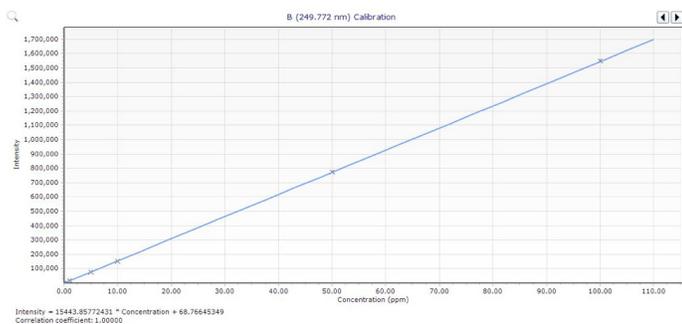

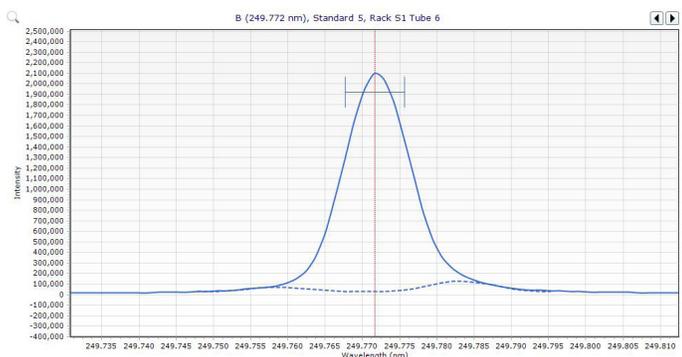**Figure 1.** Calibration curve for B 249.772 nm.

Figure 2. Automatic FBC for B 249.772 nm.

Results and Discussion

Detection limits

The Method Detection Limits (MDLs) given in Table 5 are the average of six analytical runs, analyzed on two instruments, on different days. The method detection limits (MDLs) are based on 3 sigma of 10 replicate measurements of the method blank samples (12% RAR).

Table 5. MDLs for all elements based on the sample weight of 0.50 g in 100 mL per the AOAC 2017.02 method.

Element	Viewing mode	MDL (mg/kg)
Al 396.152	Radial	5.42
As 188.980	Axial	2.59
B 249.772	Axial	0.81
Ca 317.933	Radial	9.64
Cd 214.439	Axial	0.12
Co 228.615	Axial	0.29
Cr 267.716	Axial	0.18
Cu 327.395	Radial	1.27
Fe 234.350	Radial	2.72
K 766.491	Radial	24.67
Mg 279.078	Axial	2.31
Mn 293.931	Axial	0.16
Mo 202.032	Axial	0.51
Na 589.592	Radial	3.98
Ni 216.555	Axial	0.56
P 177.434	Radial	9.67
Pb 220.353	Axial	1.73
S 181.972	Axial	5.53
Se 196.026	Axial	3.68
V 292.401	Axial	0.12
Zn 213.857	Axial	0.73

Sample analysis

The fertilizer SRM was analyzed six times using the Agilent 5110 VDV ICP-OES. The results in Table 6 show the mean measured concentration in the SRM digest and the mean recoveries of the elements compared to the certified values. The results for all elements were within ±10% of the certified or reference values, demonstrating the precision and accuracy of the 5110. Only Al wasn't completely digested

under the sample preparation conditions specified in AOAC 2017.02. A stronger acid such as hydrofluoric acid (HF) would be necessary for complete digestion of Al. A spike recovery test was carried out to validate the results obtained using the 5110 for all elements, including Al (displayed in Table 7).

Table 6. Averaged results (n=6) for the analysis of SRM 695 Trace Elements in Multi-Nutrient Fertilizer. The elements are grouped as listed in the certificate of analysis.

Element and wavelength (nm)	Measured value	Certified value	Recovery, %
Major and minor elements (%)			
Ca 317.933	2.26	2.26	100
Cu 327.395	0.123	0.123	100
Fe 234.350	3.85	3.99	97
K 766.491	10.75	11.65	92
Mg 279.078	1.72	1.79	96
Mn 293.931	0.298	0.305	98
Na 589.592	0.375	0.405	93
S 181.972	4.94	–	–
Zn 213.857	0.327	0.325	101
Trace elements (mg/kg)			
As 188.980	190	200	95
Cd 214.439	16.8	16.9	99
Co 228.615	59.4	65.3	91
Cr 267.716	225	244	92
Mo 202.032	19.1	20.0	96
Ni 216.555	127	135	94
Pb 220.353	258	273	95
V 292.401	113	122	93
Reference values (%)			
Al 396.152*	0.51	0.61	84
B 249.772	0.11	0.11	99
P 177.434	7.28	7.20	101
Reference values (mg/kg)			
Se 196.026	<MDL	2.10	-

* The AOAC 2017.02 method digestion parameters were inefficient for the complete digestion of Al, resulting in the lower than expected recovery. Spike recoveries in Table 7 demonstrate excellent recovery of Al on the 5110 VDV ICP-OES.

Four sub-sample digests of the commercial fertilizer and spiked digests were analyzed in three runs on two instruments on different days. The quantitative sample analysis results and spiked sample recoveries for all 21 elements are shown in Table 7. All spike recoveries were within ±10% of the expected concentration, validating the 5110 VDV ICP-OES method.

Due to the wide range of elements present in fertilizer samples, spectral interferences can occur, which can be challenging for analysts. For example, P 213.618 nm can suffer spectral overlap in the presence of Cu at 213.598 nm. In these instances, the user has access to full wavelength coverage of the Vista Chip II and can select wavelengths free of interferences. The results in Table 7 show good agreement between the concentration measurements for multiple wavelengths of the same element (within ±10%).

Table 7. Fertilizer sample spike recovery analysis.

Element and wavelength (nm)	Measured sample concentration (mg/L)	Spike concentration (mg/L)	Measured spiked sample (mg/L)	Recovery (%)
Major and minor elements				
Al 308.215	0.344	2.03	2.38	100
Al 396.152	0.258	2.01	2.30	101
B 249.678	7.15	4.01	11.3	104
B 249.772	7.37	4.16	11.7	105
Ca 315.887	411	101	506	94
Ca 317.933	412	102	510	96
Cu 324.754	75.3	20.1	95.0	98
Cu 327.395	76.1	20.2	96.3	100
Fe 234.350	179	100	275	97
Fe 240.489	180	100	274	94
K 766.491	0.502	10.1	11.1	105
Mg 277.983	287	98.3	389	104
Mg 279.078	293	99.0	397	106
Mn 279.482	163	51.1	217	106
Mn 293.931	149	49.8	194	91
Na 588.995	27.8	20.2	47.6	98
Na 589.592	27.9	19.9	48.9	105
P 177.434	0.27	10.4	10.8	103
P 178.222	0.12	10.4	10.6	101

Element and wavelength (nm)	Measured sample concentration (mg/L)	Spike concentration (mg/L)	Measured spiked sample (mg/L)	Recovery (%)
Major and minor elements				
S 181.972	600	99.8	701	100
S 180.669	610	99.6	713	102
Zn 213.857	46.4	10.2	56.1	96
Zn 334.502	46.5	9.85	56.7	103
Trace elements				
As 188.980	0.043	0.510	0.543	98
As 193.696	0.026	0.502	0.520	98
Cd 214.439	0.011	0.102	0.109	97
Cd 228.802	0.008	0.103	0.113	102
Co 228.615	0.149	0.097	0.242	96
Co 230.786	0.157	0.104	0.254	94
Cr 205.560	0.023	0.099	0.119	97
Cr 267.716	0.038	0.106	0.144	100
Mo 202.032	0.001	0.100	0.098	97
Mo 204.598	0.004	0.102	0.104	98
Ni 216.555	0.487	0.205	0.679	94
Ni 221.648	0.466	0.195	0.647	93
Pb 220.353	0.035	0.49	0.51	97
Se 196.026	0.076	1.01	1.08	100
V 292.401	0.008	0.100	0.112	104
V 311.837	0.004	0.092	0.096	100

Long-term stability

A total of 478 spiked fertilizer samples were analyzed over a 6.5-hour period without recalibration (Figure 3). Excellent stability is shown for all elements, with relative standard deviation (RSDs) for all elements between 1.0 and 3.4%. The robust SSRF and the vertically orientated torch ensure that excellent repeatable performance is achieved, sample to sample, hour after hour.
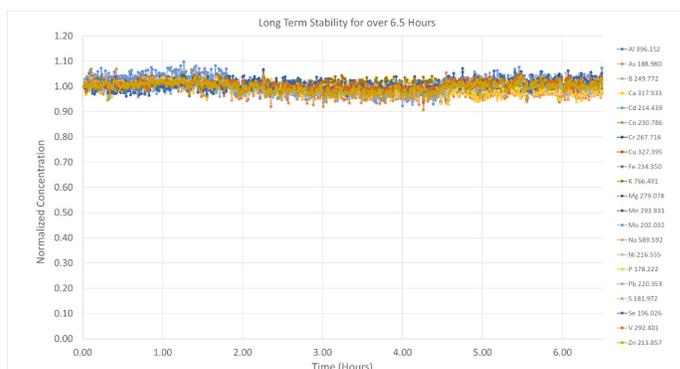

Figure 3. Normalized concentration of 21 elements in 478 spiked fertilizer samples analyzed repeatedly over 6.5 hours.

Rapid full spectrum scan

The results from the fast IntelliQuant semiquantitative scan of the fertilizer SRM sample are shown in Figure 4. In less than an additional 15 seconds, IntelliQuant rapidly scans up to 70 elements. The resulting heat map shows all the elements detected in the scan, as well as their approximate concentration (ppm). IntelliQuant is useful at identifying elements, which are not measured routinely, providing extra quality assurance information. For the fertilizer SRM sample, the scan provided additional semiquantitative elemental information for Ba, Sn, Sr, and Ti.
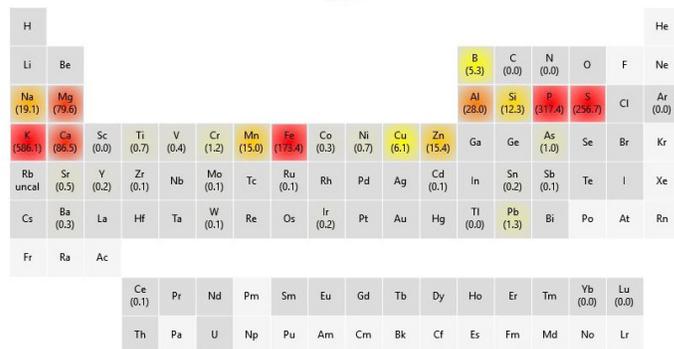

Figure 4. IntelliQuant analysis heat map of the fertilizer SRM.

Sample analysis time

All 21 elements were determined in 49 seconds using the 5110 VDV ICP-OES fitted with the AVS 7. The fast analysis time was due to the high-speed Vista Chip II detector and integrated AVS 7 sampling valve. Total argon consumption per sample was 18.0 L. The calculation considered all gas flows into the instrument to ensure an accurate representation of argon consumption.

For quicker sample analysis speeds, the Agilent 5110 Synchronous Vertical Dual View (SVDV) instrument fitted with the AVS 7 reduces the analysis time to 36 seconds and total argon consumption to 13.2 L per sample. In an 8-hour day, the SVDV instrument fitted with the AVS 7 can enable 213 more samples to be run (Table 8). This higher productivity can be beneficial to high-throughput and commercial labs. The 5110 VDV configuration can be upgraded to operate in SVDV mode.

Table 8. Comparison of analysis times and total argon gas consumption per sample between the 5110 VDV ICP-OES and 5110 SVDV ICP-OES, both fitted with an AVS 7.

Instrument	Sample analysis time (s)	Sample argon consumption (L)	Samples per day*
5110 VDV ICP-OES with AVS 7	49	18.0	587
5110 SVDV ICP-OES with AVS 7	36	13.2	800

*Based on an 8-hour day.

Conclusions

The Agilent 5110 VDV ICP-OES proved suitable for the routine, high throughput analysis of 21 key elements in fertilizers, including major nutrients, minor, and trace elements. Fitted with the AVS 7 switching valve the 5110 VDV ICP-OES, achieved an analysis run time of 49 s with 18 L of total argon consumption per sample.

Following the sample preparation method specified in AOAC 2017.02, the 5110 ICP-OES demonstrated excellent accuracy and precision of SRM material recovery data. The spike recovery test results of a commercial fertilizer confirmed the accuracy of the 5110 for multiple wavelengths across all elements. The robustness of the solid-state radio frequency (SSRF) system and the vertical torch orientation delivered excellent long-term stability during analysis over 6.5 hours.

The Vista Chip II detector allows analysis across a wide dynamic range eliminating the need for multiple dilutions. It also allows access to multiple wavelengths per element, so the user is not limited to wavelengths that may be susceptible to interferences. This feature is especially important for the analysis of complex samples such as fertilizers.

For routine analysis of fertilizers, FBC automatically corrects the background without the analyst needing to intervene. Also, the quick IntelliQuant scan was shown to be a useful way to source additional information for elements not analyzed routinely.

References

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3. Fitted Background Correction (FBC) — Fast Accurate and Fully Automated Background Correction, Agilent Technical Overview, **2016**, 5991-4836EN

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