

Multi-Element Analysis of Trace Metals in Animal Feed using ICP-OES

A fast, simple, and low cost method, using an Agilent 5110 VDV ICP-OES, suitable for high throughput labs



Authors

Peter Riles, Agilent
Technologies, Melbourne,
Australia

Introduction

Trace metals testing is important to ensure the quality and safety of processed animal feeds. Typically, manufacturers analyze raw materials, monitor the manufacturing process, and carry out final product quality assurance/quality control (QA/QC) testing. If the final product fails to meet its trace metal specifications, further testing can be undertaken to identify the source of contamination.

This application has been developed to meet the market need for the determination of trace elements in animal feed products. Typical instrument parameters for boron, calcium, copper, potassium, magnesium, manganese, phosphorous and zinc are specified in the AOAC International 985.01 Metals and Other Metals in Plants and Pet Foods standard (3). Recommendations from the AOAC method have been used where applicable.

In this study, 23 elements were determined in five animal feed certified reference materials (CRMs) using an Agilent 5110 VDV ICP-OES with AVS 7.

Experimental

Instrumentation

An Agilent 5110 vertical dual view (VDV) was fitted with the optional AVS 7 switching valve. The 5110 uses an Easy-fit torch that, once inserted, automatically aligns with the instrument's optics, and automatically connects all gases. The torch removes operator-to-operator variability when setting up the instrument and allows for fast startup. Mass flow controllers are used on all torch gases to provide excellent plasma stability and reproducible results over extended periods.

The fully integrated AVS 7 switching valve features a two position, seven port valve, and a high speed positive displacement pump (PDP) to rapidly fill the sample loop. Controlled bubble injection reduces sample uptake, stabilization times, and rinse delays to deliver the highest analytical precision. The PDP is reliable and requires less maintenance than the typical vacuum pump found on other valve systems. The AVS 7 is simple to set up and operate, as it is fully integrated within the ICP-OES hardware and controlled through the Agilent ICP Expert software. The valve system automatically delivers the sample to the nebulizer.

Analysis times and argon consumption per sample are given in Table 1 (average time of 15 analyses). When calculating the argon consumption, all gas flows within the instrument were considered to ensure that an accurate representation of argon consumption was calculated. The total includes all optic-purge and cooling functions that use gases.

Table 1. Analysis time and argon use for the 5110 VDV ICP-OES with AVS 7.

Parameter	5110 VDV ICP-OES
Analysis time per sample (s)	64
Argon use per sample (L)	24

Application parameters and viewing modes were selected during method development to achieve optimum performance. Table 2 outlines the wavelengths, background correction selected, and viewing modes for all elements analyzed in this study, including the respective internal standard. Major elements were analyzed radially, while trace elements were analyzed axially. AOAC 985.01 method recommends typical instrument parameters for some elements. These recommendations were considered. However, alternate wavelengths were selected for boron, calcium, copper, magnesium, and zinc to maximize the linear dynamic range.

Yttrium and bismuth were used for internal standardization, both at 10 mg/L. Yttrium was used to correct ionic state wavelengths, and bismuth used to correct atomic state wavelengths. A few exceptions are due to easily ionizable element (EIE) effects on ionic lines where Bi proved a more suitable internal standard. This approach was used as EIEs, particularly potassium and calcium, cause enhancement of the signal for soft analytical lines, e.g. copper 327.395 nm and bismuth 223.061 nm. Bismuth corrects well for this enhancement, as it reacts similarly in the plasma.

Table 2. Elements, wavelengths, background selection, internal standards, and viewing mode settings.

Element and wavelength (nm)	Background correction method	Internal standard (wavelength nm)	Viewing mode
Al (396.152)	FACT	Bi (223.061)	Radial
As (188.980)	FACT	Bi (223.061)	Axial
B (249.772)	FACT	Bi (223.061)	Axial
Ba (233.527)	Fitted	Bi (223.061)	Axial
Bi (223.061)	Fitted	None	Radial and Axial
Ca (373.690)	Fitted	Y (371.029)	Radial
Cd (226.502)	FACT	Y (371.029)	Axial
Co (228.615)	FACT	Y (371.029)	Axial
Cr (267.716)	Fitted	Y (371.029)	Axial
Cu (327.395)	Fitted	Bi (223.061)	Axial
Fe (238.204)	Fitted	Bi (223.061)	Axial
K (766.491)	Fitted	Bi (223.061)	Radial
Mg (279.078)	Fitted	Bi (223.061)	Radial
Mn (257.610)	Fitted	Y (371.029)	Axial
Mo (202.032)	Fitted	Y (371.029)	Axial
Na (589.592)	Fitted	Bi (223.061)	Radial
Ni (231.604)	FACT	Y (371.029)	Axial
P (214.914)	Fitted	Y (371.029)	Axial
Pb (220.353)	Fitted	Y (371.029)	Axial
S (181.972)	Fitted	Bi (223.061)	Axial
Se (196.026)	Fitted	Bi (223.061)	Axial
Sr (216.596)	FACT	Y (371.029)	Axial
V (292.401)	FACT	Bi (223.061)	Axial
Y (371.029)	Fitted	None	Radial and Axial
Zn (206.200)	Fitted	Bi (223.061)	Axial

Table 3 outlines the 5110 VDV ICP-OES instrument parameters and Table 4 outlines the AVS 7 parameters used for this application. Plasma parameters were adjusted to achieve lower background signals, and improve the intensity

of some elements. To reduce the effects seen from EIEs, the viewing height was set to 14 mm so that measurements could be taken in a cooler zone of the plasma.

Table 3. Instrument parameters.

Parameter	Settings
Replicate read time (s) (Radial/Axial)	5/10
Replicates	3
Sample uptake delay (s)	0
Stabilization time (s)	7
Rinse time (s)	0
Pump speed (rpm)	12
Fast pump during uptake and rinse (rpm)	NA
RF power (kW)	1.4
Aux flow (L/min)	1
Plasma flow (L/min)	12
Nebulizer flow (L/min)	0.9
Viewing height (mm)	14
Nebulizer	SeaSpray
Spray chamber	Double Pass Cyclonic
Torch	Standard 1.8 mm torch
Sample pump tubing	White-White
Internal standard pump tubing	Black-Black
Waste pump tubing	Blue-Blue
Ar/O ₂ addition	No
Ar/O ₂ (%)	NA
Background correction	FACT/Fitted
Viewing mode	VDV

Table 4. AVS 7 switching valve system parameters.

Parameter	Setting
Loop uptake delay (s)	5.0
Uptake pump speed (Refill) (mL/min)	36
Uptake pump speed (Inject) (mL/min)	6
Sample loop size (mL)	1.5
Time in sample (s)	4.5
Bubble inject time (s)	1.0

A combination of automated fitted background correction (FBC) and Fast Automated Curve Fitting Technique (FACT) modeling was used for background correction. An example of fitted background correction is shown in Figure 1. FBC simplifies method development by eliminating the need for the user to manually determine off-peak background correction points (4).

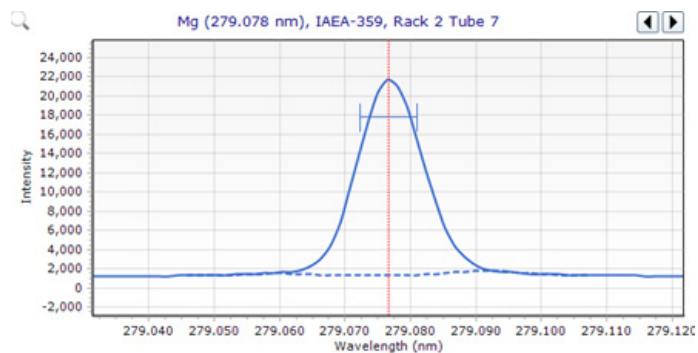


Figure 1. Mg 279.078 nm using Fitted Background Correction.

FACT modeling is used to correct for spectral overlap but equally it can be used to correct for highly complex background structures, where background interferences can have a significant effect. Using FACT can achieve lower detection limits for some elements, compared to other correction techniques (5). An example of FACT correction is illustrated in Figure 2. FACT models the peak as the contribution arising from the analyte of interest. In this example there is no spectral interference from another element but FACT works equally well with or without an interference being present. The outcome in this example is excellent modelling of the analyte peak, and a stable flat background, enabling superior detection limits.

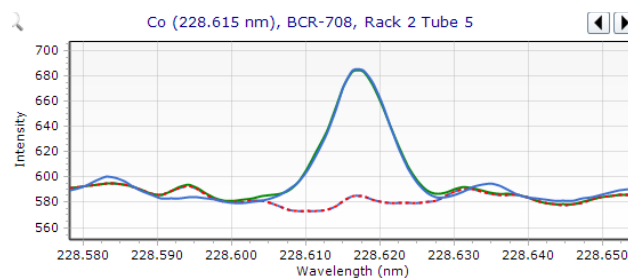


Figure 2. FACT model for Co 228.615 nm.

Linear calibration curves were used for all elements. All elements displayed excellent correlation coefficients of greater than 0.99936 (Table 5). A representative curve for Al 396.152 nm is shown in Figure 3.

Table 5. Calibration parameters and correlation coefficients for all elements.

Element and wavelength (nm)	Concentration range (mg/L)	Correlation coefficient	Calibration fit
Al (396.152 nm)	0–5.5	0.99999	Linear
As (188.980 nm)	0–1.1	0.99971	Linear
B (249.772 nm)	0–5.5	0.99984	Linear
Ba (233.527 nm)	0–2.75	0.99989	Linear
Ca (373.690 nm)	0–550	0.99993	Linear
Cd (226.502 nm)	0–1.1	0.99997	Linear
Co (228.615 nm)	0–5.5	0.99997	Linear
Cr (267.716 nm)	0–5.5	0.99994	Linear
Cu (327.395 nm)	0–5.5	0.99991	Linear
Fe (238.204 nm)	0–27.5	0.99975	Linear
K (766.491 nm)	0–550	0.99995	Linear
Mg (279.078 nm)	0–550	0.99994	Linear
Mn (257.610 nm)	0–11	0.99992	Linear
Mo (202.032 nm)	0–1.1	0.99997	Linear
Na (589.592 nm)	0–55	0.99999	Linear
Ni (231.604 nm)	0–5.5	0.99996	Linear
P (214.914 nm)	0–550	0.99993	Linear
Pb (220.353 nm)	0–2.75	0.99997	Linear
S (181.972 nm)	0–275	0.99999	Linear
Se (196.026 nm)	0–1.1	0.99972	Linear
Sr (216.596 nm)	0–55	0.99987	Linear
V (292.401 nm)	0–5.5	0.99996	Linear
Zn (206.200 nm)	0–27.5	0.99936	Linear

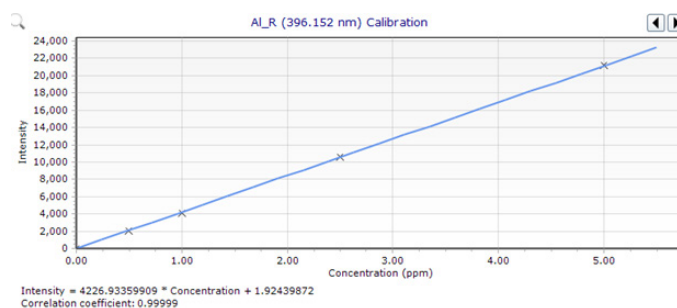


Figure 3. Calibration graph for aluminum 396.152 nm from radial view.

Standards and sample preparation

Varying concentrations of working calibration standards were prepared from single element Agilent ICP-OES Calibration Standards. The standards and QC solution were made by matching the acid concentration to the digested samples using nitric acid and hydrochloric acid (Emsure, Merck), and diluting with 18.2 MΩ Millipore water (Table 6). Solutions were separated into three sets to minimize any chemical incompatibilities, e.g. barium and sulfur may precipitate as barium sulfate if present in the same solution.

Four CRMs were used to validate the method: BCR-708 Dairy Feed (IRMM, Belgium); IAEA-359 Cabbage (International Atomic Energy Agency, Austria); IPE-148 Lucerne (WEPAL, The Netherlands); SOWW-1 Soft winter wheat (NRCC, Canada). The BRAN-1 Corn Bran (NRCC, Canada) CRM was used for a spike recovery test. Due to the concentrations in the CRMs used to validate the application, and to take full advantage of the linear dynamic range of the 5110 ICP-OES, calibration ranges generally exceeded those recommended in AOAC 985.01.

The CRMs were prepared for microwave digestion (CEM) by weighing approximately 0.5 g of reference material into a sealable PTFE test tube and adding 2 mL of concentrated HNO₃ and 2 mL of concentrated HCl. Digestion of each sample was carried out according to the conditions provided in Table 7. Samples were diluted to 50 mL with 18.2 MΩ Millipore water. AOAC 985.01 suggests a dry ashing procedure for sample preparation. However, due to potential loss of volatile metals from dry ashing, as well as ease-of-use, microwave digestion was used for sample preparation.

Table 6. Concentrations and segregation of working calibration solutions and QC solution.

Element	Std 1 (mg/L)	Std 2 (mg/L)	Std 3 (mg/L)	Std 4 (mg/L)	Std 5 (mg/L)	Std 6 (mg/L)	Std 7 (mg/L)	Std 8 (mg/L)	Std 9 (mg/L)	Std 10 (mg/L)	Std 11 (mg/L)	Std 12 (mg/L)	QC Std (mg/L)
Al	0.5	1	2.5	5									1.25
As	0.1	0.2	0.5	1									0.25
B	0.5	1	2.5	5									1.25
Ba					0.5	1	2.5						1.25
Ca					50	100	250	500					125
Cd	0.1	0.2	0.5	1									0.25
Co	0.5	1	2.5	5									1.25
Cr	0.5	1	2.5	5									1.25
Cu	0.5	1	2.5	5									1.25
Fe					5	10	25						12.5
K									50	100	250	500	125
Mg					50	100	250	500					125
Mn	1	2	5	10									2.5
Mo	0.1	0.2	0.5	1									1.25
Na									5	10	25	50	12.5
Ni	0.5	1	2.5	5									1.25
P									50	100	250	500	125
Pb					0.25	0.5	1.25	2.5					1.25
S	50	100	250										125
Se	0.1	0.2	0.5	1									1.25
Sr					5	10	25	50					12.5
V	0.5	1	2.5	5									1.25
Zn					5	10	25						12.5

Table 7. Microwave digestion parameters.

Parameter	Value
Temperature (°C)	200
Ramp time (min)	20
Hold time (min)	15

An aliquot of each reference material was used to determine the moisture content of the material. This moisture content was used to correct the results after analysis. The reference materials used in this study contained between 4 and 10% moisture, as detailed in Table 8.

Table 8. Moisture content of CRMs used.

CRM	Moisture content (%)
SOWW-1	9.5
IPE-148	8.0
BRAN-1	7.1
BCR-708	4.0
IAEA-359	5.9

Results and Discussion

MDLs and LOQs

Detection limits were determined by analyzing various blank samples and calculating the standard deviation. Blanks were analyzed on two instruments over three days, and 60 method blank sample results were used to determine the Method Detection Limit (MDLs) (3 sigma of the blanks). The Limit of Quantitation (LOQ) (10 sigma of the blanks) was also calculated for each element. The data given in Table 9 was calculated based on the sample preparation (0.50 g sample in final volume of 50 mL) procedure.

Table 9. MDLs and LOQs for all elements.

Element and wavelength (nm)	MDL (mg/kg)	LOQ (mg/kg)
Al 396.152	0.381	1.27
As 188.980	0.717	2.39
B 249.772	0.063	0.21
Ba 233.527	0.023	0.08
Ca 373.690	0.830	2.77
Cd 226.502	0.022	0.07
Co 228.615	0.055	0.18
Cr 267.716	0.076	0.25
Cu 327.395	0.035	0.12
Fe 238.204	0.065	0.22
K 766.491	4.33	14.4
Mg 279.078	2.40	8.0
Mn 257.610	0.011	0.04
Mo 202.032	0.115	0.38
Na 589.592	0.791	2.64
Ni 231.604	0.265	0.88
P 214.914	2.74	9.1
Pb 220.353	0.817	2.72
S 181.972	1.38	4.6
Se 196.026	0.810	2.70
Sr 216.596	0.086	0.29
V 292.401	0.052	0.17
Zn 206.200	0.240	0.80

Spike recovery test

A digested sample of the corn bran BRAN-1 CRM was spiked with a low concentration of each analyte to determine the recoveries of the elements. All recoveries were within $\pm 10\%$ of the expected concentration, as shown in Table 10.

Table 10. Recoveries for spiked corn bran BRAN-1 CRM.

Element and wavelength (nm)	Unspiked sample (mg/L)	Spiked sample (mg/L)	Spiked blank (mg/L)	Recovery (%)
Al 396.152	-0.001	0.208	0.203	103
As 188.980	0.003	0.049	0.046	98
B 249.772	0.028	0.233	0.208	99
Ba 233.527	0.021	0.033	0.011	108
Ca 373.690	3.57	8.51	4.98	99
Cd 226.502	0.000	0.049	0.049	100
Co 228.615	0.000	0.204	0.199	102
Cr 267.716	0.001	0.204	0.202	101
Cu 327.395	0.021	0.229	0.200	104
Fe 238.204	0.11	2.131	2.031	99
K 766.491	4.49	9.54	4.82	105
Mg 279.078	6.38	11.16	4.77	100
Mn 257.610	0.022	0.543	0.523	100
Mo 202.032	0.001	0.202	0.199	101
Na 589.592	3.49	5.50	2.00	101
Ni 231.604	0.003	0.199	0.195	100
P 214.914	1.53	6.92	5.46	99
Pb 220.353	-0.001	0.203	0.206	99
S 181.972	7.37	12.66	5.27	100
Se 196.026	0.000	0.217	0.210	103
Sr 216.596	0.041	1.021	0.987	99
V 292.401	-0.002	0.215	0.214	102
Zn 206.200	0.16	1.161	1.021	98

Verification of method

The results from the analysis of four CRMs are given in Table 11. The quantitative recoveries for all certified elements measured above the LOQ in the four CRMs were within $\pm 10\%$ of the certified value, where certified values are provided. All results were corrected for moisture content.

Table 11. Concentration measurements of animal feed CRMs using the 5110 VDV ICP-OES, corrected for moisture content. Blank cells indicate no certified value.

	BCR-708 Dairy Feed			IAEA-359 Cabbage			IPE-148 Lucerne			SOWW-1 Soft Winter Wheat		
	Measured (mg/kg)	Certified (mg/kg)	Recovery (%)	Measured (mg/kg)	Certified (mg/kg)	Recovery (%)	Measured (mg/kg)	Certified (mg/kg)	Recovery (%)	Measured (mg/kg)	Certified (mg/kg)	Recovery (%)
Al	54.9			136			358			2.05		
As	<MDL			<MDL			<LOQ	0.428		<MDL		
B	11.1			30.0			36.2	34.4	105	1.236		
Ba	10.9			11	11	99	10.4	9.51	109	0.948		
Ca	4753	4800	99	19138			23316	22800	102	257	240	107
Cd	<LOQ			0.135			<LOQ	0.0512		<LOQ		
Co	1.14			<LOQ			0.30	0.28	108	<MDL		
Cr	10.7			1.39			0.901	0.886	102	<MDL		
Cu	39.5	37	107	5.52	5.67	97	3.99	4.32	92	1.12		
Fe	192			141	148	95	246	233	105	32.6		
K	11285			34248	32500	105	27640	26200	105	1513	1480	102
Mg	1425	1470	97	2095	2160	97	1609	1640	98	201	214	94
Mn	85.1			32.9	31.9	103	41.4	40.1	103	5.6	5.4	104
Mo	2.15			1.59			<LOQ	0.362		<LOQ		
Na	170			584			198	200	99	14.2		
Ni	7.60			1.23			1.148	1.07	107	<MDL		
P	5022	4700	107	5814			2531	2330	109	1141	1080	106
Pb	<MDL			<LOQ			<LOQ	0.863		<MDL		
S	3364			15312			3077	2950	104	1359	1260	108
Se	<MDL			<MDL			<MDL	0.117		<MDL		
Sr	27.2			50.4	49.2	102	57.1	55.5	103	0.441		
V	2.45			0.336			0.86	0.81	106	<MDL		
Zn	121			39.6	38.6	103	19.4	19.9	98	6.84		

Long-term stability

More than 330 digested samples were run over a 6-hour period without recalibrating. During the run, a QC sample was analyzed every 10 samples—details of the QC solution are given in Table 6. The stability plot in Figure 4 shows the recovery of all elements over the 6-hour period to be within $\pm 10\%$. The relative standard deviation of this data was less than 3% for all elements, indicating excellent robustness and precision over the extended run.

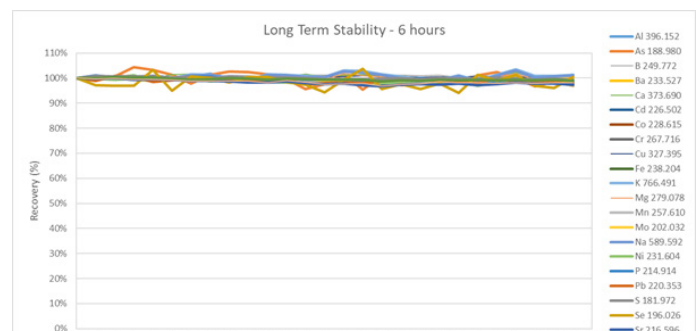


Figure 4. Long-term stability: recovery of a QC sample analyzed every 10 samples over a 6-hour period.

Performance comparison of VDV and SVDV configurations

To compare the vertical dual view (VDV) configuration with the synchronous vertical dual view (SVDV) configuration, the IPE-148 Lucerne CRM was analyzed using an Agilent 5110 SVDV ICP-OES with an AVS 7. The same conditions were used for both instrument-configurations, as detailed in Table 3. The SVDV ICP-OES enables both the axial and radial views of the plasma to be captured in one reading. As shown by the results for IPE-148 CRM in Table 12, over approx. 6 hours, the SVDV instrument can analyze 34% more samples with no sacrifice in accuracy. Compared to VDV, the SVDV configuration can measure samples 25% faster, with a 25% argon gas saving (Table 13). A 5110 VDV ICP-OES can be upgraded onsite to the SVDV configuration if lab productivity demands change.

Table 12. Results from analysis of CRM IPE-148 Lucerne using the 5110 SVDV ICP-OES. Blank cells indicate no certified value.

CRM	IPE-148 Lucerne		
Element	Measured (mg/kg)	Certified (mg/kg)	Recovery (%)
Al	364	-	
As	<MDL	0.428	
B	35.0	34.4	102
Ba	10.0	9.51	106
Ca	23426	22800	103
Cd	<LOQ	0.0512	
Co	0.31	0.28	110
Cr	0.885	0.886	100
Cu	4.29	4.32	99
Fe	242	233	104
K	27812	26200	106
Mg	1617	1640	99
Mn	41.1	40.1	103
Mo	<LOQ	0.362	
Na	193	200	97
Ni	1.107	1.07	103
P	2373	2330	102
Pb	<MDL	0.863	
S	2956	2950	100
Se	<MDL	0.117	
Sr	56.3	55.5	102
V	0.83	0.81	102
Zn	19.6	19.9	98

Table 13. Productivity improvement using the 5110 SVDV ICP-OES.

Parameter	5110 VDV	5110 SVDV	Difference (%)
*Analysis time per sample (s)	64	48	25
Argon use per sample (L)	23.7	17.8	25
Solutions analyzed in approx. 6 hours	335	450	34

*Average time from analysis of 15 samples

Conclusions

Routine measurements of trace elements in animal feed products can be carried out with excellent accuracy and precision using the Agilent 5110 ICP-OES with Advanced Valve System. The AVS 7 increases productivity and maintains excellent precision. The lower-cost Vertical Dual View configuration instrument can accurately measure high concentrations of EIEs as well as other metals with lower concentrations.

Benefits of the 5110 ICP-OES method include:

- FACT correction for highly complex background structures and user-friendly correction of spectral interferences.
- Simple-to-use fitted background correction, which provides excellent correction for complex backgrounds.
- Stable results over extended periods, minimizing the need for recalibration and maximizing sample throughput.
- Accurate and precise results, while maintaining low operating costs with sample analysis times of 64 s and argon consumption of 24 L per sample.

If greater productivity is required, the same analytical method can be run effectively on a Synchronous Vertical Dual View instrument. The 5110 SVDV ICP-OES delivers accurate results in the quickest possible time.

- The SVDV method provides the same accuracy as the VDV method, with approximately 34% increase in sample throughput over six hours.
- The SVDV can reduce argon use per sample analysis by approximately 25%, reducing operating costs.

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Printed in the USA, September 24, 2018
5994-0215EN