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Simultaneous ICP Atomic Emission Spectrometer ICPE™-9820

Application News

Determination of Elemental Composition of Animal Feed by ICP-OES According to EN 15621

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User Benefits

- Simultaneous analysis over a wide range of concentrations from low to high by combined use of high sensitivity axial view, and radial view for high concentration elements, using ICPE™-9820.
- High throughput, accurate and reliable method to measure the nutrients and toxic composition in animal feeds.

■ Overview

In this work, a fast and robust ICP-OES method was developed for measuring the concentration of 22 elements (As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, No, P, Pb, S, Se, Sr, V and Zn) in different types of animal feeds on Shimadzu ICPE-9820. The sample preparation and analysis were performed in accordance with the European Standard EN15621.

■ Introduction

With growing demand for animal feed globally, providing nutritious, well-balanced and quality feed is essential in the industry for both feed suppliers and consumers. The feed suppliers need to efficiently utilize available resources and choose the most suitable feed for their animals, based on analysis information of elemental content [1-2]. In addition, the presence of harmful heavy metals and contaminants in animal feed due to environmental pollution or feed processing would also affect animal health and thus adversely impact on human health.

Among various techniques for elemental composition analysis, ICP-OES (Figure 1), is one of the most preferred analytical methods due to its high sensitivity, low detection limits, multi-elemental capability and high matrix tolerance. In this application, an ICP-OES method was developed and optimized following the EN15621 [3] guidelines for methods of sampling and analysis for animal feeding stuffs. The ICP method was evaluated and applied to analyse the essential and toxic elemental composition of different commercial animal feed samples.

Fig. 1 ICPE™-9820

■ Experimental

Sample preparation

Eight solid animal feed samples were analysed in this application, including three categories of three dog feeds, three cat feeds and two rabbit feeds. 1.0 g of dried feed sample was taken from a plastic zip-lock package and weighed using an analytical balance. The feed sample was placed into a microwave vessel with mixed 6 mL of HNO_3 and 1 mL of H_2O_2. Microwave digestion program was carried out with parameters shown in Table 1. The digested contents were transferred into polypropylene vials and topped up to 100 mL using ultrapure DI water before ICP-OES analysis. Total digestion can be achieved for all animal feed samples after microwave digestion program.

Analytical conditions

The analysis was carried out using Shimadzu ICPE-9820, coupled with mini plasma torch, concentric nebulizer and cyclonic chamber. The detailed instrument configuration and operation parameters for analysis are summarised in Table 2.

Table 1 Microwave digestion program

Step	Time (min)	Power	Temperature (°C)
1	15	1800 W	Ramp to 200
2	15	1800 W	Hold at 200
3	30	Cool down	

Table 2 Instrument configuration and ICP parameters

Parameter	Settings
Torch	Mini Torch
Nebulizer	Concentric Type
Chamber	Cyclonic Type
Peristaltic Pump	Inside
Radio Frequency Power (kW)	1.20
Plasma Gas (L/min)	10.0
Auxiliary Gas (L/min)	0.60
Carrier Gas (L/min)	0.60
Exposure time (s)	15
Sensitivity	Wide Range
View Direction	Axial/Radial
Solvent Rinse Time (s)	10 (low), 0 (high)
Sample Rinse Time (s)	15 (low), 0 (high)

Calibration curves

Concentrated nitric acid (65%), hydrogen peroxide (30%) used were in trace metal grade. Ultrapure water was from the Milli-Q water-purification system. External calibration standards were prepared by mixing single elemental stocks from Merck and Sigma-Aldrich.

Calibration standards were prepared in a matrix of 1% HNO3 (Table 3) based on the concentrations found in the feed samples. Yttrium was used as internal standard at concentration of 1 mg/L. Two separated calibration standard sets were prepared to minimize chemical incompatibility.

Table 3. Calibration standards concentration (mg/L)

Element	Set 1			
	Std.1	Std.2	Std.3	Std.4
As	0.08	0.4	0.8	2
B	0.08	0.4	0.8	2
Cd	0.08	0.4	0.8	2
Co	0.08	0.4	0.8	2
Cr	0.08	0.4	0.8	2
Cu	0.08	0.4	0.8	2
Mn	0.4	2	4	10
Mo	0.08	0.4	0.8	2
Ni	0.08	0.4	0.8	2
S	20	100	200	500
Se	0.08	0.4	0.8	2
V	0.08	0.4	0.8	2

Element	Set 2			
	Std.1	Std.2	Std.3	Std.4
Ba	0.08	0.4	0.8	2
Ca	20	100	200	500
Fe	0.4	2	4	10
K	20	100	200	500
Mg	4	20	40	100
Na	20	100	200	500
P	20	100	200	500
Pb	0.08	0.4	0.8	2
Sr	0.08	0.4	0.8	2
Zn	0.4	2	4	10

■ Results and Discussion

Calibration linearity and detection limits

All calibration curves showed good linearity with r>0.9995 (Table 4). LODs and LOQs were calculated as 3 times and 10 times standard deviation of 10 measurements of calibration blank. The low LODs and LOQs indicates method capability to quantify trace level elements.

Quantitative results of animal feed samples

Quantitative results of the 22 elemental compositions in eight animal feed samples were measured and summarised in Table 5. Toxic elements such as As, Cd and Pb were either not detected or in low concentrations.

Table 4: Elements, wavelengths, correlation coefficients(r), LODs and LOQs (Unit in mg/L)

Element	Wavelength (nm)	View Mode	r	LOD	LOQ
As	193.759	Axial	0.99994	0.018	0.07
B	249.773	Axial	0.99999	0.001	0.003
Ba	230.424	Axial	0.99996	0.0008	0.003
Ca	315.887	Radial	0.99978	0.014	0.05
Cd	226.502	Axial	1.00000	0.0004	0.0013
Co	238.892	Axial	0.99994	0.0015	0.005
Cr	267.716	Axial	1.00000	0.001	0.004
Cu	324.754	Axial	1.00000	0.0008	0.003
Fe	238.204	Axial	0.99999	0.0006	0.002
K	766.490	Radial	0.99942	0.4	1.2
Mg	285.213	Radial	0.99954	0.005	0.015
Mn	259.373	Axial	0.99999	0.0003	0.0009
Mo	202.030	Axial	0.99996	0.0019	0.007
Na	589.592	Radial	0.99999	0.04	0.11
Ni	231.604	Axial	1.00000	0.001	0.004
P	213.618	Axial	0.99992	0.007	0.03
Pb	220.353	Axial	1.00000	0.004	0.01
S	180.731	Axial	0.99997	0.04	0.13
Se	203.985	Axial	0.99984	0.03	0.08
Sr	216.596	Axial	0.99999	0.0016	0.006
V	292.402	Axial	0.99999	0.0005	0.0016
Zn	202.548	Axial	0.99997	0.001	0.004

Table 5. Quantitative results of different animal samples and MDLs (mg/kg)

Element	Cat 1	Cat 2	Cat 3	Dog 1	Dog 2	Dog 3	Rabbit 1	Rabbit 2	MDL[b]
As	N.D. [a]	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	7
B	1.9	3.1	11.1	5.3	1.2	10.1	12.4	14.5	0.3
Ba	1.8	2.2	11.7	<MDL[c]	1.6	0.8	5.1	9.8	0.3
Ca	10000	7410	16000	123	1590	555	6500	13600	5
Cd	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.2	0.13
Co	N.D.	N.D.	<MDL	N.D.	N.D.	N.D.	N.D.	N.D.	0.5
Cr	0.4	0.4	2.3	<MDL	<MDL	<MDL	0.83	2.3	0.4
Cu	3.7	3.7	11.9	2.0	2.8	3.0	15.9	9.2	0.3
Fe	62.2	73.8	540	22.8	39.7	19.6	232	321	0.2
K	7580	4320	9610	11700	4340	6800	7680	9390	120
Mg	818	1170	1450	1360	727	1230	1380	2450	1.5
Mn	10.5	8.8	74.2	1.2	18.3	4.1	86.9	52.4	0.09
Mo	1.0	0.9	1.5	1.6	1.0	1.2	1.3	1.4	0.7
Na	13700	6160	5850	3810	9000	6030	738	1990	11
Ni	N.D.	N.D.	1.3	N.D.	N.D.	0.6	2.1	0.8	0.4
P	10500	7960	10100	6710	4930	3790	3080	5110	3
Pb	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1
S	4640	4390	5940	7750	4280	4200	2160	3390	13
Se	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	8
Sr	6.1	19.3	55.9	1.4	1.8	3.1	8.9	37.4	0.6
V	N.D.	N.D.	2.2	N.D.	N.D.	N.D.	0.4	1.5	0.16
Zn	32	52.4	264	23.7	21.7	16.5	66.8	62.7	0.4

a, N.D.: not detected
b, MDL: method detection limits are calculated by LOQ x Dilution Factor (DF).
c, <MDL: method detection limits

Recovery and Precision

Method accuracy was evaluated by spike recovery test. The spike concentrations for different elements, as shown in Table 6, were determined by concentrations found in animal feed samples.

Spike recovery of 83-115% was achieved in various sample matrix demonstrating the robustness of the ICP-OES method to handle animal feed samples. Good precision was obtained with %RSD within 3% attained for all analytes.

Table 6: Spike recovery results, RSD% (n=3) and spiked concentrations

Element	Spiked Conc. (mg/L)	Cat 1		Dog 1		Rabbit 1	
		Recovery	%RSD	Recovery	%RSD	Recovery	%RSD
As	0.2	99%	2.17	92%	0.19	100%	2.37
B	0.2	95%	0.51	94%	0.28	94%	0.38
Ba	0.2	85%	0.44	85%	0.63	86%	0.82
Ca	50	91%	0.13	94%	0.34	88%	0.30
Cd	0.2	90%	0.77	90%	0.39	91%	0.35
Co	0.2	88%	0.60	88%	0.39	89%	0.17
Cr	0.2	95%	0.70	93%	0.32	94%	0.34
Cu	0.2	91%	0.22	89%	0.18	93%	0.24
Fe	1.0	85%	0.53	85%	1.09	94%	0.18
K	50	97%	0.77	110%	0.40	115%	0.50
Mg	10	91%	1.34	92%	0.36	87%	0.42
Mn	1.0	86%	0.42	86%	0.33	87%	0.46
Mo	0.2	99%	0.57	98%	0.57	98%	0.43
Na	50	94%	1.27	97%	0.72	104%	0.58
Ni	0.2	85%	1.03	86%	0.21	85%	0.44
P	50	85%	0.32	87%	0.62	85%	0.26
Pb	0.2	87%	1.11	87%	0.83	86%	0.88
S	50	101%	0.72	100%	0.74	97%	0.24
Se	0.2	107%	2.87	103%	2.14	106%	2.28
Sr	0.2	86%	0.22	87%	0.14	87%	1.12
V	0.2	99%	0.65	98%	0.31	98%	0.28
Zn	1.0	86%	0.55	83%	0.19	84%	0.15

Long term stability

Method long term stability was assessed by analysing a calibration standard continuously. The measurement was taken at every 30-minute interval and the values were normalised to t=0. Figure 2 shows the stability of 22 elements over 2.5 hours with all normalised recovery values within 0.8 - 1.2. The stability of internal standard Y was normalised and plotted. Figure 3 shows the stability of internal standard Y over 4 hours, to monitor the instrument drift. Throughout the 4 hours, the intensities drift was less than 5%, demonstrating the excellent system stability of the ICP-OES.

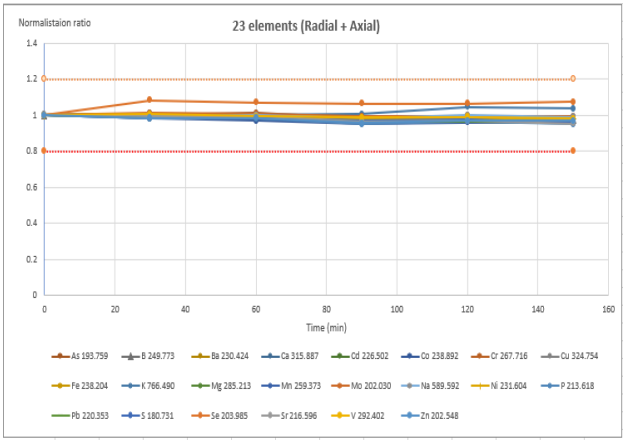

Fig. 2 Recovery of 22 elements over 2.5 hours

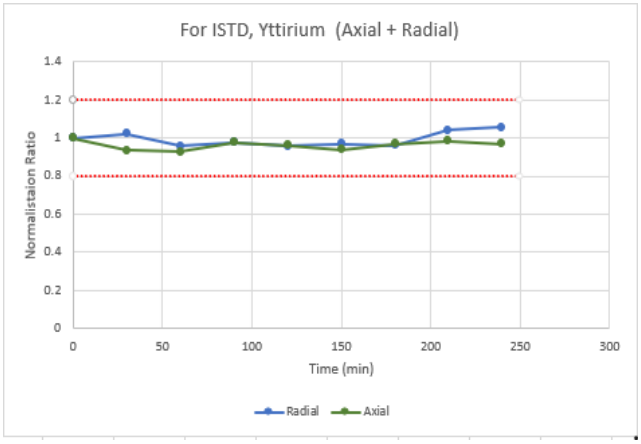

Fig. 3 Stability of internal standard Y over 4 hours

■ Conclusion

In this study, an ICP-OES method was developed and applied to analyse 22 elemental composition in animal feeds after microwave digestion on Shimadzu ICPE-9820 adhering to the EN15621 guidelines. Either axial and radial view mode was used for elements of different characters and concentration ranges.

Good calibration linearity, repeatability, stability and low method quantification limits were obtained demonstrating the capability of Shimadzu ICPE-9820 in animal feed analysis. Satisfactory recovery rates of 83% to 115% were achieved in different sample matrices of animal feeds. The optimized ICP-OES method provides a high throughput, accurate and reliable method to measuring the nutrients and toxic composition in animal feeds.

■ References

1. De Jonge, L.H. & Jackson, F.S. 2013. The feed analysis laboratory: Establishment and quality control. Setting up a feed analysis laboratory, and implementing a quality assurance system compliant with ISO/IEC 17025:2005. H.P.S. Makkar, ed. Animal Production and Health Guidelines No. 15. Rome, FAO.

2. Da Costa, S.S.L., Pereira, A.C.L., Passos, E.A., Alves, J.D.P.H., Garcia, C.A.B. and Araujo, R.G.O., 2013. Multivariate optimization of an analytical method for the analysis of dog and cat foods by ICP OES. *Talanta*, *108*, p.157-164.

3. European Standard EN 15621, EN 15621:2017 E, European Committee for Standardization (CEN), 2017.

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