AN APPLICATION REPORT FROM
SPECTRO ANALYTICAL INSTRUMENTS

ICP-OES 157

SPECTROGREEN

Analysis of Animal Feed by ICP-OES With Dual Side-On Plasma Observation

Introduction

Animal feed is the basis for meat production and thus key element of the human food chain. Safe food is necessary for healthy livestock animals as well as for pets. Raw materials such as protein-rich soybean or rapeseed meal are used to produce compound feed which is adapted to the needs of different species and their varying life stages or the specific requirements for example in animal fattening, dairy farming or even for the use of animals in sports.

To ensure the quality of animal feed, several regulations are in place to control the supply chain of those products. Regulations such as the European directive 2002/32/EC [1] on undesirable substances in animal feed or the US FDA CFR 21.I.E 500-599 [2] cover the aspects of additives in feed, labeling as well as standards for sampling and analysis.

The Asian-Pacific region is the largest producer of animal feed, followed by Europe and North America with poultry feed having the largest share among the different branches.

The production of high-quality products requires the monitoring of both matrix and trace elements. This report describes the principal methodology for the analysis of soybean meal and a poultry feed. Reference materials as examples for raw material and compound feed products were analyzed. Typical detection limits and the performance achieved with the SPECTROGREEN DSOI are demonstrated.

The SPECTRO GREEN with dual side-on plasma observation offers a simple, fast, accurate, precise and cost-efficient method for the analysis of animal feed after microwave assisted digestion.
This report describes the principal methodology for the analysis of animal feed. It presents typical detection limits for a wide range of elements and studies the accuracy using two reference materials and a spike recovery.

Experimental

Instrumentation

All measurements were performed with the SPECTROGREEN ICP with dual side-on plasma observation. It enables an average factor 2 enhanced sensitivity compared to single radial plasma observation and a comparable sensitivity to vertical torch dual view systems, while eliminating typical axial view interferences. In addition, it offers a high matrix compatibility, linear dynamic range and precision without the need to change the plasma observation mode during analysis.
The SPECTROGREEN features a Paschen-Runge spectrometer mount, employing the proprietary Optimized Rowland Circle Alignment (ORCA) technique. Consisting of two hollow section cast shells, optimized small volume and 15 linear CMOS detectors, the wavelength range between 165 and 770 nm can be analyzed, allowing complete spectrum capture within 3 s. Due to the unique reprocessing capabilities of the system, a new measurement is not required even if additional elements or lines are to be determined at a later point in time.
The optic is hermetically sealed and filled with argon, continuously circulated through a filter, which absorbs oxygen, water vapor and other species. High optical transmission in the UV is achieved, allowing the determination of non-metals as well as the use of prominent and interference free lines in this region.
An air-cooled, 27.12 MHz, free running type LDMOS ICP-generator is installed, which ensures excellent stability of the forward power even in the case of rapidly changing sample loads.
All relevant ICP operating parameters are software controlled, allowing easy selection of the optimum operating conditions.
For sample introduction, a SeaSpray nebulizer and a cyclonic spray chamber were used. The ICP operating conditions are given in Table 1.

Plasma Power	1150 W
Observation Mode	Dual-Side-On
Coolant flow	12 L/min
Auxiliary flow	0.8 L/min
Nebulizer flow	0.9 L/min
Plasma Torch	Quartz, fixed, 1.8 mm Injector tube
Spray Chamber	Cyclonic
Nebulizer	SeaSpray
Sample aspiration rate	2 mL/min
Replicate read time	42 s per replicate

Table 1 : Typical ICP-OES operating conditions

Sample Preparation

0.5 g of solid sample material was digested with 8 mL HNO_3 [3] and 2 ml H_2O_2 [4] using the Milestone Ethos UP (Milestone, Italy) microwave system. After digestion, the samples were diluted with deionized water to a final volume of 25 ml.

Calibration

For calibration, commercially available multielement [5] and single element solutions [6] were used, acidified with 20% v/v HNO_3 [3] and diluted by weight with deionized water to the concentrations given in Table 2.

	Ag, As, B, Ba, Be, Cd, Co, Cu, Cr, Hg, Li, Mn, Ni, Pb, Sb, Se, Si, Sn, Sr, Tl, V, Zn	Al, Fe	Na	Mg	P	Ca, K
Calibration range [mg/L]	0 - 2	0 -15	0 - 25	0 -75	0 - 150	0 - 500

Table 2: Calibration Standard concentration ranges

Element	λ [nm]	LOD (3σ) [mg/kg]
Ag	328.068	0.07
Al	396.152	0.3
As	193.759	0.1
B	249.773	0.02
Ba	455.404	0.008
Be	313.042	0.002
Ca	183.801	0.06
Cd	214.438	0.007
Co	228.616	0.03
Cr	267.716	0.03
Cu	324.754	0.06
Fe	238.204	0.02
Hg	184.950	0.02
K	766.491	1.6
Li	670.780	0.06
Mg	285.213	0.01
Mn	257.611	0.004
Mo	202.095	0.02
Na	589.952	0.4
Ni	221.648	0.03
P	177.495	0.04
Pb	220.353	0.2
Sb	206.833	0.1
Se	196.090	0.2
Si	251.612	0.07
Sn	189.991	0.04
Sr	407.771	0.002
Tl	190.864	0.1
V	311.071	0.06
Zn	213.856	0.007

Table 3: Typical limits of detection (LOD) for the selected lines with dual side-on plasma observation. LODs in the solid material were calculated using a dilution factor of 50.

Results and Discussion

Table 3 shows the selected wavelengths and the limits of detection (LOD) achieved. The LODs were calculated according to the equation [7]:

$$\mathbf{LOD = 3\ RSD_b\ c/100*SBR}$$

Where:

RSD_b – relative standard deviation of 10 replicates of the blank [%]
c – concentration of the standard
SBR – signal to background ratio

The practical detection limits are dependent on the actual dilution of the solid sample material. The detection limits presented in table 3 were calculated with a dilution factor of 50.

Dependent on element and emission line, the typical relative short-time precision of the blank sample was found in the range between 0.2 and 0.8%

Accuracy

The accuracy and precision of the method were investigated by analyzing two feed reference materials. Soybean meal (CRM SBM S 124122) [8] and poultry feed (LGC7173) [9] were chosen as typical representatives for animal feed.

The materials were digested according to the described procedure and analyzed using the developed method. A comparison of the measured values with the certified values can be found in Tables 4 and 5 (next page).

Element	Measured Concentration [g/kg]	Certified Value	Recovery [%]
Ca	19.5	17.8	110
Cu	15.1	14.0	108
Fe	0.16	0.15	107
K	7.59	7.48	101
Mg	2.09	2.04	102
Mn	0.095	0.09	106
Na	1.19	1.18	101
P	6.86	6.59	104
Zn	0.078	0.078	100

Table 4: Recovery of the poultry feed reference material (LGC 7173)

In the directive 2002/32/EC [1], undesirable substances in animal feed are regulated. Maximum allowed concentrations are given for arsenic with 2 mg/kg, cadmium with 0.5 mg/kg and lead with 5 mg/kg.
These concentrations were spiked to the poultry feed reference material to test the recovery of these elements at the limiting value. The results displayed in table 6 show an excellent recovery of the spiked concentrations.

Element	Measured Sample Conc. [mg/kg]	Measured Sample + Spike Conc. [mg/kg]	Measured Spike Conc. [mg/kg]	Given Spike Conc. [mg/kg]	Spike Recovery [%]
As	0.4	2.5	2.1	2.0	105
Cd	0.2	0.7	0.5	0.5	102
Pb	0.4	5.1	4.7	5.0	95

Table 6: Spike recovery of regulated elements in animal feed according to 2002/32/EC

Element		Measured Concentrations	Certified Value	Recovery [%]
Matrix Elements				
Al	[g/kg]	0.69	0.63	109
Ca	[g/kg]	4.6	4.4	104
Fe	[g/kg]	0.54	0.5	107
K	[g/kg]	23.3	23.3	105
Mg	[g/kg]	3.6	3.6	109
Na	[g/kg]	0.60	0.59	104
P	[g/kg]	7.6	6.9	110
Trace Elements				
F	[mg/kg]	< LOD	< 0.005	-
As	[mg/kg]	< LOD	< 0.005	-
Ba	[mg/kg]	7.7	7.1	108
Be	[mg/kg]	0.06	0.06*	-
Cd	[mg/kg]	0.05	0.05*	-
Co	[mg/kg]	0.71	0.66	108
Cr	[mg/kg]	2.8	2.6	108
Cu	[mg/kg]	17.9	16.8	107
Mn	[mg/kg]	50.4	45.9	110
Mo	[mg/kg]	4.4	4*	-
Ni	[mg/kg]	4.4	4.3	102
Pb	[mg/kg]	2.2	2.4	92
Sb	[mg/kg]	< LOD	< 0.005	-
Se	[mg/kg]	< LOD	< 0.005	-
Sr	[mg/kg]	6.4	6.2	103
Tl	[mg/kg]	< LOD	< 0.005	-
Zn	[mg/kg]	66	62	106

Table 5: Recovery of the soybean meal reference material CRM-SBM S

** non-certified concentration, for information only*

Update on Titanium

On November 25th, 2021 the European Food Safety Agency declared that titanium dioxide can no longer be authorized in additives for animal feed, since no conclusive statement regarding its safe use can be made. [9] Titanium dioxide was typically used as an additive to influence the color, e.g. as an addition to pet food to make it look more appealing to the pet owners.
The concern of the agency is also affecting the use of TiO_2 as an additive for human food (E171), for which it was banned, too.
Also, for the analysis of Ti, ICP-OES is the perfect analytical method, enabling the simultaneous analysis together with all other elements of interest.

To demonstrate this, four pet food additives samples were analyzed for the TiO_2 content. The additive consists of leather whose natural color is not desired and where TiO_2 was used to whiten the product.

Plasma Power	1250 W
Observation Mode	Dual-Side-On
Coolant flow	13 L/min
Auxiliary flow	0.8 L/min
Nebulizer flow	0.85 L/min
Plasma Torch	Quartz, fixed, 2 mm Injector tube
Spray Chamber	Scott
Nebulizer	Cross Flow
Sample aspiration rate	2 mL/min
Replicate read time	22 s per replicate

Table 7 : Used ICP-OES operating conditions

Instrumentation

All measurements were performed with the SPECTROGREEN with dual side-on plasma observation. Instrument parameters as listed in Table 7 were applied for the measurements.

Sample Preparation

0.5 g of solid sample material was digested with 9 mL HNO_3 and 1 ml HF [10] using the Milestone Ethos UP (Milestone, Italy) microwave system. After digestion, the samples were diluted with deionized water to a final volume of 25 ml. Each sample was prepared as a triplicate.

Calibration

For the calibration, a titanium single element standard was used [6]. Calibration standards up to 100 mg/L were prepared (Table 8). All standards were acidified with 50% v/v HNO_3 (Bernd Kraft/ Merck).

The limits of detection (LOD) (Table 9) were calculated using the method previously described [7].

Element	Standard 1 [mg /L]	Standard 2 [mg/L]	Standard 3 [mg/L]	Standard 4 [mg/L]	Standard 5 [mg/L]	Standard 6 [mg/L]
Ti	0	5	10	20	60	100

Table 8: Calibration standards for the calibration of Ti in animal feed

Element	λ [nm]	LOD (3σ) [mg/kg]
Ti	334.187	0.0012
Ti	307.864	0.0021

Table 9: Limits of detection (LOD achieved for two selected Titanium lines)

Results

Titanium concentrations for the four dog food additives samples are shown in table 10. The concentrations are expressed as concentrations in the original solid sample. The titanium dioxide content was calculated from the titanium concentrations.

Sample No.	Digestion No.	Ti [mg/kg]	TiO_2 [%]
1	1	34.3	0.005
	2	36.4	0.006
	3	28.8	0.004
1	**Average**	**33.2**	**0.005**
2	1	6.6	0.001
	2	10.1	0.002
	3	8.13	0.001
2	**Average**	**8.3**	**0.001**
3	1	41.6	0.007
	2	27.6	0.005
	3	32.8	0.005
3	**Average**	**34.0**	**0.006**
4	1	2529	0.422
	2	2894	0.483
	3	3498	0.584
4	**Average**	**2974**	**0.496**

Table 10: TiO_2 result for four dog food additive samples

References

[1] Directive 2002/32/EC of the European Parliament and of the Council of 7 May 2002 on undesirable substances in animal feed

[2] U.S. Food and Drug Administration; Code of Federal Regulations; Title 21, Chapter I, Subchapter E, 500 ff.

[3] HNO_3, suprapure, Bernd Kraft, Duisburg, Germany

[4] H_2O_2 suprapure, Merck, Darmstadt, Germany

[5] Multielement standard solution: 30 elements, Bernd Kraft, Duisburg, Germany

[6] Single element standard, Inorganic Ventures, Christiansburg, VA, USA

[7] P. W. J. M. Boumans, Spectrochim. Acta 46B, 431 (1991)

[7] CRM-SBM-S, 124122, Soybean Meal, High-Purity Standards, Charleston, SC, USA

[8] Poultry Feed – Proximates and elements, LGC7173, LGC Ltd., Teddington, UK

[9] Executive order (EU) 2021/2090 of the commission of 25 November 2021

[10] HF, suprapure, Bernd Kraft, Duisburg

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