SPECTRO REPORT

APPLICATION REPORT 77
SPECTROFLAME MODULA S

THE SIMULTANEOUS DETERMINATION OF MAJOR AND TRACE ELEMENTS IN FERTILIZERS

S. Pethig, P. Heitland and K. Krengel-Rothensee
SPECTRO Analytical Instruments GmbH, Kleve, Germany

ABSTRACT

The simultaneous determination of nitrogen (N), of additional major elements (P, K, Mg, S, Ca) and trace impurities (Cd, Cu, Mo, Al, Fe, Mn, Zn) is described in this application report. For the determination of nitrogen in fertilizers a special adapter for the torch has been developed by SPECTRO to minimize the diffusion of atmospheric nitrogen into the plasma. For changing a sample, the peristaltic pump of the spectrometer has to be switched off to prevent ambient air from being pumped into the plasma. At a weight of 20 g fertilizer in 1 L solution, the detection limit for nitrogen (N I 174.530 nm) is about 0.04% calculated to the solid sample.

1. INTRODUCTION

Fertilizers are produced in large amounts and have to be carefully controlled. The determination of the major and trace elements in the fertilizers has become an important application for ICP spectrometry.

The major elements are N, P, K, Ca, S and Mg. For the determination of N, which is normally present in the form of nitrate or ammonium, special conditions are required because atmospheric nitrogen influences the determination of nitrogen in the solution.

The sample preparation, calibration and analysis of fertilizers, including the determination of nitrogen, is described in this application report.

2. EXPERIMENTAL

2.1 Instrumental Parameters

All measurements were performed with a SPECTROFLAME MODULA S (Side-on observation). The instrument description and the instrument conditions are shown in Table 1 and Table 2.

The optical systems of the SPECTROFLAME ICP series which are used in the UV/VUV range are installed in a vacuum resistant tank which is filled with high purity nitrogen. This nitrogen is cleaned continuously by pumping the gas through a gas cleaning system. Because of this cleaning a continuous high light transparency in the UV/VUV area is possible. The gas cleaning system also protects the optical systems against contamination.

For the determination of nitrogen a special N_2 adapter developed by SPECTRO was used to prevent diffusion of nitrogen from the surrounding air. If the adapter is not installed, the diffusion of nitrogen from the surrounding air will lead to higher nitrogen intensities in the blank solution.

The optimum instrument conditions for the simultaneous determination of the major and trace elements are given in Table 2. For the determination of all elements the background correction was used. The integration time is defined as 10 s for all elements.

Table 1: Installed Optical Systems in the SPECTROFLAME MODULA S

Optic	Wavelength Range (nm)	Grating (grooves/mm)	Gas
UV-Monochromator	160 to 460	2400	Nitrogen
2 Polychromators	210 to 460	3600	Air
1 Polychromator	270 to 790	1800	Air
1 Monochromator	210 to 460	2400	Air

Table 2: ICP operating conditions for the SPECTROFLAME MODULA S

Sample Introduction	
Torch	fixed torch (SPECTRO)
N_2Adapter	SPECTRO
Peristaltic Pump	sample flow 2 mL/min
Nebulizer	Crossflow (SPECTRO)
Spray Chamber	Glass, Scott type (SPECTRO)
Nebulizer Pressure	3 bar
Coolant Gas Flow	13 L/min
Auxiliary Gas Flow	0.5 L/min
Nebulizer Gas Flow	1.2 L/min
Generator	free running, 27.12 MHz

2.2 Line Selection

The wavelengths used for the single elements are shown in Table 3.

Table 3: Selected Wavelengths

Element	Wavelength (nm)
Al	308.315
Ca	317.933
Cd	226.502
Cu	324.754
Fe	259.940
K	766.491
Mg	279.079
Mn	257.610
Mo	281.615
N	174.520
P	177.500
S	182.040
Zn	213.856

2.3 Sample Preparation

20 g of the sample material was treated with 500 mL deionized water and 10 mL of concentrated hydrochloric acid. The solution was warmed to a temperature of 80°C and mixed by a magnetic stirrer for 30 minutes. The insoluble residue was then separated by filtration and the filtrate was filled to a volume of 1000 mL after cooling. The elements of interest present in the residue exist in forms which are not bioavailable to the plants, therefore the residue was eliminated for the additional measurements. If it is not necessary to detect nitrogen, a weight of 10 g/L with the same acid concentration is sufficient.

2.4 Calibration

For the calibration the following fertilizers with known concentrations were used:

- NPK Fertilizer 1 (NPK: Nitrogen, Phosphorus, Potassium)
- NPK Fertilizer 2
- NPK Fertilizer 3
- NPK Fertilizer 4

The concentration of the major elements in the calibration standards are shown in Table 4. Table 5 shows the concentrations of the trace elements in additional standards. A matrix matched solution was used as a blank (40 mL concentrated hydrochloric acid in 1000 mL deionized water).

Two different fertilizer samples with known concentrations were used for the analysis:

- Sample 1 : NPK Fertilizer containing 20.2 % N
- Sample 2 : NPK Fertilizer containing 12.2 % N

If nitrogen is to be determined the peristaltic pump of the spectrometer should be switched off while changing samples to prevent the entry of atmospheric air.

Table 4: Calibration Standards for the Determination of the Major Elements

Element/ Oxide	NPK 1 (%)	NPK 2 (%)	NPK 3 (%)	NPK 4 (%)
N	12.91	15.04	19.9	23.91
P_2O_5	9.13	5.33	20.1	8.13
K_2O	16.25	20.53		8.18
MgO	4	2.26	0.24	0.28
SO_4	18.21	24.21	5	2
CaO	3.89	2.17	10.94	5

Table 5: Calibration Standards for the Determination of the Trace Elements

Element	Standard 1 (mg/kg)	Standard 2 (mg/kg)	Standard 3 (g/kg)	Standard 4 (g/kg)	Standard 5 (g/kg)
Cd	0	50			
Cu	0	50			
Mo	0	50			
Al			3. 68	4.47	5.97
Fe			4.60	6.40	8.65
Mn			0.048	0.066	0.091
Zn			0.135	0.175	0.225

3. RESULTS AND DISCUSSION

In Table 6 the detection limits of the determined elements with a weight of 10 g/L of the fertilizer are shown. The detection limit of nitrogen (at a weight of 20 g/L of the fertilizer) is about 0.04% calculated to the solid sample.

In Tables 7 and 8 the results for the determination of one of the major elements, nitrogen, in Samples 1 and 2 respectively are shown. To test the reproducibility of the results the calibration and measurement of the samples was repeated on successive days. A good correspondence between the nominal and actual nitrogen values is shown. The relative standard deviation between the nominal and actual values range from 0.03-0.16 %.

The precision of the major and the trace elements is typically less than 1%. With the use of an internal standard the precision of the determination can be improved [1].

Table 6: Detection Limits (3σ) of the elements in fertilizers detected with the SPECTROFLAME MODULA S (Weight and final volume are given in the description of sample preparation)

Element	Wavelength (nm)	Detection Limit (mg/kg in the solid sample)
Al	308.315	0.15
Ca	317.933	0.4
Cd	226.502	0.3
Cu	324.754	0.35
Fe	259.940	0.32
K	766.491	6
Mg	279.079	4.5
Mn	257.610	0.08
Mo	281.615	0.28
N	174.520	400
P	177.500	3
S	182.040	3
Zn	213.856	0.6

Table 7: Results of the Determination of Nitrogen in Fertilizer Sample 1 with the SPECTROFLAME MODULA S

	Sample 1 Nominal (%)	Sample 1 Actual (%)	Deviation (%)
Average	12.2	12.29	0.09
Std.Dev.Abs.		0.03	
Std.Dev.Rel.		0.3	
Average	12.2	12.34	0.14
Std.Dev.Abs.		0.05	
Std.Dev.Rel.		0.4	
Average	12.2	12.15	0.05
Std.Dev.Abs.		0.2	
Std.Dev.Rel.		1.3	
Average	12.2	12.01	0.19
Std.Dev.Abs		0.05	
Std.Dev.Rel		0.5	
Average	12.2	12.17	0.03
Std.Dev.Abs.		0.06	
Std.Dev.Rel.		0.5	

Table 8: Results of the Determination of Nitrogen in Fertilizer Sample 2 with the SPECTROFLAME MODULA S

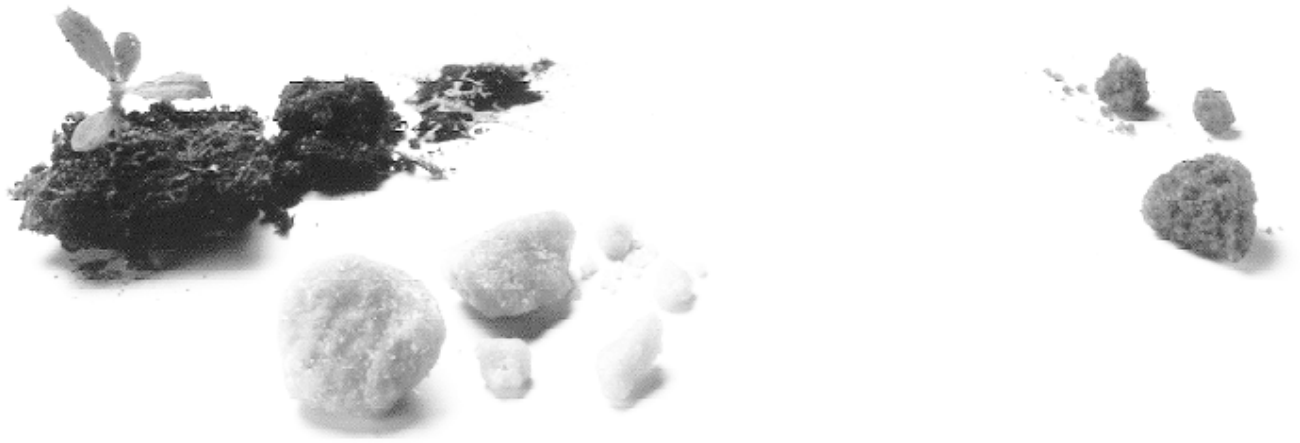
	Sample 2 Nominal (%)	Sample 2 Actual (%)	Deviation (%)
Average	20.2	20.34	0.14
Std.Dev.Abs.		0.12	
Std.Dev.Rel.		0.6	
Average	20.2	20.04	0.16
Std.Dev.Abs.		0.3	
Std.Dev.Rel.		1.0	
Average	20.2	20.06	0.14
Std.Dev.Abs.		0.4	
Std.Dev.Rel.		1.2	
Average	20.2	20.31	0.11
Std.Dev.Abs.		0.06	
Std.Dev.Rel.		0.3	
Average	20.2	20.1	0.1
Std.Dev.Abs.		0.3	
Std.Dev.Rel.		1.0	

4. CONCLUSION

With the SPECTROFLAME MODULA S the rapid simultaneous detection of nitrogen as well as the other major and minor elements present in fertilizers is possible. The detection of nitrogen requires a special torch adapter to prevent the entry of atmospheric air in the plasma which will produce incorrect results. A suitable wavelength for nitrogen determination lies in the VUV range at 174.52 nm. The precision is typically less than 1% relative standard deviation.

5. Literature

[1] SPECTRO Application Sheet 91, Internal Standard



SPECTRO Analytical Instruments • Boschstraße 10 • D-47533 Kleve • Germany • Tel.: +49-(0)2821/892-0 • Fax: +49-(0)2821/23144 • Telex 811734 sptro d • http://www.spectro-ai.com