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SPECTROGREEN

Analysis of Fertilizer and Fertilizer Precursor Materials Using Side-On and Dual Side-On Plasma Observation

Introduction

Soil fertility is observed for a long time. Already thousands of years ago crop productivity was enhanced by the use of minerals and manure. The age of artificial fertilization started in the beginning of the 20th century with the development of the Haber and Oswald process for the production of ammonia and nitric acid.

Fertilizers contain substances enhancing enhance growth, with nitrogen being the most important element also phosphorus and potassium as well as Ca, Mg and S are referred to as macro nutrients. Micro-nutrients are consumed in smaller quantities. Cu, Fe, Mn, Mo, Zn, B, Si, Co and V, are important for the plants metabolism and have a strong impact on the plant despite their low concentrations.

Fertilizers are available as single straight, binary, NPK, multi nutrient and micro-nutrients products in a variety of compositions, in granular and liquid forms.

In addition to the product composition, also the precursor materials, e.g. phosphate rock or recycled metals need to controlled as they may contain unwanted or toxic elements. Those elements also need to be controlled in the final product.

Several ICP methods for the elemental analysis of fertilizer exist:

- EN 16317 Fertilizers and liming materials — Determination of arsenic by inductively coupled plasma-atomic emission spectrometry (ICP-AES) after aqua regia dissolution
- EN 16319 Fertilizers and liming materials — Determination of cadmium, chromium, lead and nickel by inductively coupled plasma-atomic emission spectrometry (ICP-OES) after aqua regia dissolution
- ISO 17318 Fertilizers and soil conditioners — Determination of arsenic, cadmium, chromium, lead and mercury contents (ICP-OES)
- EN 15962 Fertilizers - Determination of the complexed micro-nutrient content and of the complexed fraction of micro-nutrients
- EN 16963 Fertilizers — Determination of boron, cobalt, copper, iron, manganese, molybdenum and zinc using ICP-AES

While ICP-OES, being a trace analytical technique, is mainly used for the analysis of toxic metal and micro-nutrients present in the product at ppm levels and below, as a technique, it is also a very potent method when it comes to the determination of major constituents, making it rather universal.

Experimental

Instrumentation

All measurements were performed with the SPECTROGREEN ICP optical emission spectrometer with single and dual-side-on plasma observation. 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. 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. For sample introduction, a Cross Flow nebulizer and a miniature Scott spray chamber were used. The ICP operating conditions are given in Table 1 and 2.

Calibration and Sample Preparation

1 g of the phosphate rock sample was digested by microwave assisted digestion with 2 mL nitric and 6 mL hydrochloric acid. After dissolution, the samples were diluted to 100 mL using deionized water.

Table 1: Typical ICP operating conditions (phosphate rock)

Power	1100 W
Observation Mode	Dual Side-On
Coolant flow	13 L/min
Auxiliary flow	0.80 L/min
Nebulizer flow	0.83 L/min
Plasma torch	Quartz, fixed, 1.8 mm injector tube
Spray chamber	Scott
Nebulizer	Cross Flow
Sample aspiration rate	2 ml/min
Replicate read time	28 s per replicate

Table 2: Typical ICP operating conditions (solid fertilizer)

Power	1175 W
Observation Mode	Single Radial
Coolant flow	13 L/min
Auxiliary flow	0.80 L/min
Nebulizer flow	0.75 L/min
Plasma torch	Quartz, fixed, 1.8 mm injector tube
Spray chamber	Scott
Nebulizer	Cross Flow
Sample aspiration rate	2 ml/min
Replicate read time	55 s

Table 3: Calibration standards (Phosphate Rock)

Element	Blank [mg/L]	Std 1 [mg/L]	Std 2 [mg/L]	Std 3 [mg/L]
Al, As Au, B, Ba, Cd, Ce, Co, Cr, Cu, Dy, Er, Eu, Gd, Hf, Hg, Ho, La, Li, Lu, Mo, Na, Nd, Ni, Pb, Pm, Pr, Sb, Se, Si, Sm, Sn, Sr, Ta, Tb, Th, Ti, Tm, U, V, Y, Yb, Zn, Zr	0	0.5	1	2
Ca	-	2000	2500	3000
Fe	-	150	250	350
K	0	2.5	5	10
Mg		100	50	-
Mn	0	10	20	-
W	0	0.5	1	-
P	-	1000	1200	1500

1 g of fertilizer sample was digested by microwave with 2 ml nitric and 6 ml hydrochloric acid and diluted to 25ml. For the determination of the major compounds, the samples were further diluted 1:100 in 1% HNO_3.

Table 4: Calibration standards (solid fertilizer)

Element	Blank [mg/L]	Std 1 [mg/L]	Std 2 [mg/L]	Std 3 [mg/L]
Cd, Cr, Cu, Hg, Mn,Mo, Ni, Pb, Zn	0	0.5	1	2
B, Fe, Mg	0	2.5	5	10
P	0	5	10	20
K	0	10	20	40

Results and Discussion

Table 5 and 6 show the selected wavelengths and the achieved limits of detection (LOD). The limits of detection (LOD) were calculated using the 3σ standard deviation of 10 replicate measurements of the blank sample, the slope of the calibration curve and the applied dilution factor and thus represent the limits of detection in the original, undiluted sample.

Table 5: Typical limits of detection (LOD) in phosphate rock

Element	λ [nm]	LOD 3σ [mg/kg]	Element	λ [nm]	LOD 3σ [mg/kg]	Element	λ [nm]	LOD 3σ [mg/kg]
Al	176.641	0.64	**Ho**	345.600	0.055	**Si**	251.612	1.5
As	189.042	0.2	**K**	766.491	3.1	**Sm**	428.079	1.7
Au	242.795	0.21	**La**	333.749	0.070	**Sn**	189.991	0.51
B	182.641	0.12	**Li**	670.780	0.12	**Sr**	407.771	0.70
Ba	455.404	0.024	**Lu**	261.542	0.025	**Ta**	268.517	1.7
Cd	226.502	0.13	**Mg**	202.647	0.92	**Tb**	350.920	0.37
Co	228.616	0.19	**Mn**	257.611	0.011	**Th**	401.913	1.3
Cr	284.325	0.23	**Mo**	202.095	0.12	**Ti**	334.941	0.020
Cu	219.226	0.38	**Na**	589.592	0.61	**Tm**	346.220	0.083
Dy	353.170	0.14	**Nd**	406.109	0.41	**U**	409.014	3.6
Er	326.478	0.56	**Ni**	231.604	0.077	**V**	311.071	0.23
Eu	420.505	0.25	**Pb**	220.353	0.73	**W**	207.911	0.3
Gd	335.862	0.16	**Pr**	417.939	1.8	**Y**	371.030	0.043
Hf	277.336	0.79	**Sb**	206.833	1.2	**Yb**	328.937	0.014
Hg	194.227	0.24	**Se**	196.090	0.85	**Zn**	213.856	0.029

Compared to the single radial plasma observation, using DSOI a 60% higher sensitivity can be obtained, with limits of detection in the low ppm range in the solid material.

Table 6: Typical limits of detection (LOD) in solid fertilizer

Element	λ [nm]	LOD 3σ [mg/kg]
B	249.677	0.048
Cd	228.802	0.009
Cr	267.716	0.016
Cu	324.754	0.055
Fe	238.204	0.013
Hg	184.95	0.028
K	766.491	1.6
Mg	279.553	0.0008
Mn	257.611	0.0045
Mo	202.095	0.025
Ni	231.604	0.028
P	177.495	0.050
Pb	220.353	0.143
Zn	213.856	0.006

Sample Analyses

For the phosphate rock analyzes using the SPECTROGREEN with DSOI interface, the sample dilution was selected to enable the determination of the trace elements as well as the major components with one single analysis.

The use of the radial observation technique provides advantages in this respect, as it guarantees a much higher linear dynamic range, since self-absorption effects at higher concentration levels are greatly reduced.

Table 7: Analysis of trace elements in phosphate rock

Element	Sample 1 [%]	Sample 2 [%]	Sample 3 [%]	Element	Sample 1 [%]	Sample 2 [%]	Sample 3 [%]	Element	Sample 1 [%]	Sample 2 [%]	Sample 3 [%]
Al	0.98	0.49	0.37	**Hg**	<LOD	<LOD	<LOD	**Se**	<LOD	<LOD	0.0002
As	0.003	0.003	0.003	**Ho**	0.0008	0.0009	0.0009	**Si**	0.39	0.67	0.64
Au	0.001	0.001	0.001	**K**	0.24	0.22	0.18	**Sm**	0.003	0.004	0.004
B	0.005	0.004	0.004	**La**	0.016	0.019	0.019	**Sn**	<LOD	<LOD	<LOD
Ba	0.013	0.011	0.010	**Li**	0.0002	0.0002	0.0002	**Sr**	0.14	0.15	0.16
Ca	27.6	32.5	32.5	**Lu**	0.0003	0.0003	0.0003	**Ta**	<LOD	<LOD	<LOD
Cd	0.0002	0.0002	0.0002	**Mg**	0.72	0.27	0.33	**Tb**	0.0004	0.005	0.005
Co	0.002	0.001	0.001	**Mn**	0.14	0.13	0.13	**Th**	0.001	0.001	0.001
Cr	0.004	0.003	0.003	**Mo**	0.0009	0.0008	0.0009	**Ti**	0.014	0.011	0.009
Cu	0.002	0.001	0.001	**Na**	0.58	0.68	0.65	**Tm**	0.0002	0.0002	0.0002
Dy	0.004	0.004	0.004	**Nd**	0.017	0.019	0.020	**U**	0.002	0.002	0.003
Er	0.002	0.003	0.003	**Ni**	0.003	0.003	0.003	**V**	0.006	0.005	0.005
Eu	0.001	0.001	0.001	**P**	5.26	7.08	7.06	**W**	0.0001	<LOD	0.0001
Fe	3.34	2.71	2.71	**Pb**	0.0027	0.0025	0.0023	**Y**	0.023	0.028	0.027
Gd	0.003	0.004	0.004	**Pr**	0.004	0.005	0.005	**Yb**	0.002	0.002	0.0002
Hf	<LOD	<LOD	<LOD	**Sb**	<LOD	<LOD	<LOD	**Zn**	0.012	0.009	0.011

Table 8: Analysis of major elements in phosphate rock

Element	Sample 1 [%]	Sample 2 [%]	Sample 3 [%]	Element	Sample 1 [%]	Sample 2 [%]	Sample 3 [%]
Al_2O_3	1.85	0.94	0.71	MnO	0.18	0.17	0.17
CaO	38.6	45.4	45.5	Na_2O	0.78	0.92	0.88
Fe_2O_3	4.77	3.87	3.88	P_2O_5	12.1	16.2	16.2
K_2O	0.29	0.26	0.22	SiO_2	0.84	1.44	1.37
MgO	1.23	0.44	0.54				

Table 9: Analysis of major and minor elements in solid fertilizer after digestion

Element	Sample 1 [mg/kg]	Sample 2 [mg/kg]	Sample 3 [mg/kg]	Element	Sample 1 [mg/kg]	Sample 2 [mg/kg]	Sample 3 [mg/kg]
B	9273	16.5	379	**Mg**	16.2	632	19493
Cd	< LOD	< LOD	< LOD	**Mn**	628	52.6	1323
Cr	1.6	16.2	1.6	**Mo**	1.3	2.24	11.9
Cu	0.58	4.82	219	**Ni**	0.54	25.5	1.98
Fe	332	7293	1429	**P**	41084	208	5.22
Hg	0.2	0.41	0.56	**Pb**	0.4	4.5	0.35
K	76957	310	414	**Zn**	525	10.3	593

For the analyzes of solid fertilizer a different approach was used. A lower dilution was used to obtain lower detection limits for the analysis of trace elements. For the determination of the major elements, the samples were further diluted 100 times.

Conclusion

The measurements show that the SPECTROGREEN with dual and single side on plasma observation are the perfect instruments for the analysis of fertilizer and fertilizer precursor products. Both techniques benefit from the fact that they provide high matrix tolerance, freedom from matrix effects and offer a high linear dynamic rage, required for the precise determination of major constituents.

The use of the DSOI provides an up to factor two higher sensitivity and thus enables an optimization of the dilution. This simplifies the preparation of calibration standards and enables the measurement of traces, minors and majors in one analysis run.

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