



SPECTROGREEN

Analysis of Soil by ICP-OES with Dual-Side-On Plasma Observation

Introduction

Protecting soil from contamination is an important task for our society. It is a vital resource for growing food and can be considered as non-renewable due to the very slow process of soil formation. Through agriculture, waste treatment or industrial emissions, soil can be contaminated with negative consequences for the food chain and respectively human health.

In Europe, the Council directive 86/278/EEC [1] regulates the soil protection, when sewage sludge is used in agriculture as a fertilizer. It limits the concentration of seven heavy metals to prevent harmful effects on soil, vegetation, animals and man by a ban using the sludge, if the requirements are

not fulfilled. Council directive 1999/31/EEC [2] regulates the impact from landfilling on soil and Directive 2010/75/EU [3] controls industrial emissions. Additionally, in the 7th Environment Action Programme (EAP) of the European Parliament [4], the protection of soil as part of the natural capital is one of the priority action areas, which confirms the importance.

Due to its multi-element determination capability, high linear dynamic range and sensitivity, Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is widely used for the analysis of soil. The application is described in several ICP-OES standard procedures such as ISO 22036 [5]

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The multi-elemental analysis of soil is one of the major applications for ICP-OES. This report demonstrates that the SPECTROGREEN has all the required analytical capabilities in terms of sensitivity, precision and accuracy to perform the analysis of soil.

The SPECTROGREEN with Dual Side-On Interface enables the accurate determination of alkali and earth alkali elements without ionization buffering. Trace elements are detected with high sensitivity without the need of a second plasma view. Instrument parameters and line selection are described. Low detection limits combined with a high analysis speed were achieved. Excellent results were found for spike recovery measurements in soil and for the analysis of a certified reference material.

and US-EPA Method 6010C [6]. The preparation of solid soil samples is described in US-EPA Method 3050B [7] and in the European Standard EN 16174 [8].

This report describes the principle methodology for the analysis of soil. It presents typical detection limits for a wide range of elements as well as studies on precision and accuracy using a QC sample and a certified reference material.

Experimental

Instrumentation

All measurements were performed with the SPECTROGREEN ICP optical emission spectrometer (SPECTRO Analytical Instruments, Kleve, Germany) 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 later 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 Cross Flow nebulizer and a Scott type spray chamber were used. The ICP operating conditions are given in Table 1.

Table 1: Typical ICP operating conditions

	Dual-Side-On Interface
Power	1100 W
Observation Mode	Dual-Side-On
Coolant flow	13.0 L/min
Auxiliary flow	0.80 L/min
Nebulizer flow	0.93 L/min
Plasma Torch	Quartz, fixed, 1.8 mm Injector tube
Spray Chamber	Scott type
Nebulizer	Cross Flow
Sample aspiration rate	2 mL/min
Replicate read time	44 s per replicate





Sample Preparation

Sample preparation was performed according to European Norm EN 16174 [8], which provides two methods for the digestion of aqua regia soluble fractions in sludge, treated biowaste and soil. Method A describes the digestion with thermal heating under reflux conditions, Method B uses microwave heating with temperature control and was chosen for the preparation of the samples in this report. The procedure does not necessarily digest the total sample, but it is suitable for most environmental applications.

For the digestion according to Method B of EN 16174 [8], 0.75 g of the homogenized, dried sample was weighed into a decomposition vessel. 6 mL hydrochloric acid [9] and 2 mL nitric acid [10] were added into the vessel and were mixed with the sample by gently swiveling the vessel. After the first reaction, the vessel was closed, weighed and placed into the microwave. The digestion program consisted of a ramp of 15°C/min to a maximum temperature of 175°C and a dwell time of 10 minutes. After completion, the vessel was cooled to room temperature and weighed again to ensure that the mass lost during digestion was below 10%. Finally, the vessel was opened carefully under a laboratory fume hood. The digested sample was transferred quantitatively to a volumetric flask and was diluted to the nominal volume of 25 mL. Undissolved constituents were separated by filtration using a membrane filter.

Calibration

For calibration, a commercially available multi-element standard [11] and single element standards [12] were used. All calibration standards contained 32% aqua regia [9;10] to match the matrix of the digested samples. Additionally, the common matrix elements of soil, Al, Ca, Fe and P, were added in typical concentration ranges [12]. The composition of each calibration standard is listed in Table 2.

Table 2: Calibration standards

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]	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]
Ag	0	0.1	0.25	0.5			Mg	200	100.4	51	2	10	
Al	700	600.4	501	402	300	200	Mn	0	0.4	1	2		
As	0	0.4	1	2	20	30	Mo	0	0.4	1	2		
B	0	0.4	1	2			Na	50	10.4	1	2		
Ba	0	0.4	1	2			Ni	0	0.4	1	2		
Be	0	0.4	1	2			P	800	602	205	410	100	50
Ca	1000	1100.4	1301	1502	1800	1400	Pb	0	0.4	1	2	10	
Cd	0	0.4	1	2	0.5	0.1	Sb	0	0.4	1	2		
Co	0	0.4	1	2			Se	0	0.4	1	2		
Cr	0	0.4	1	2	5		Si	0	0.4	1	2		
Cu	0	0.4	1	2	10	20	Sn	0	0.4	1	2		
Fe	400	500.4	601	702	450	550	Sr	0	0.4	1	2		
Hg	0	0.4	1	2			Tl	0	0.4	1	2		
K	0	2	5	10	20	50	V	0	0.4	1	2		
Li	0	0.4	1	2	10		Zn	0	0.4	1	2	10	

Results and Discussion

Table 3 shows the selected wavelengths and the limits of detection (LOD) achieved. The LODs were calculated according to the equation [12]:

$$\text{LOD} = 3 \text{ RSD}_b \text{ c} / 100 \text{ SBR}$$

Where:

- RSD_b: - relative standard deviation of
10 replicates of the blank (in %)
- c: - concentration of the standard
- SBR: - signal to background ratio

The LODs were calculated referring to the dry mass (0.75 g dissolved in 25 mL) and are expressed in mg/kg in the original solid sample.

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Table 3: Typical Limits of Detection (LOD) in solid soil samples

Element	λ [nm]	LOD (3σ) [mg/kg] Dual-Side-On	Element	λ [nm]	LOD (3σ) [mg/kg] Dual-Side-On
Ag	328.068	0.06	Mn	257.611	0.01
As	189.042	0.23	Mo	202.095	0.08
B	249.677	0.05	Ni	221.648	0.05
Ba	455.404	0.01	Pb	220.353	0.4
Be	313.042	0.002	Sb	206.833	0.5
Cd	228.802	0.02	Se	196.090	0.5
Co	228.616	0.04	Sn	189.991	0.14
Cr	267.716	0.04	Sr	407.771	0.007
Cu	324.754	0.06	Tl	190.864	0.4
Hg	184.950	0.08	V	311.071	0.05
K	766.491	1.2	Zn	213.856	0.03
Li	670.780	0.04			

Accuracy and precision

The accuracy and precision of this method were investigated by analyzing a QC standard as a control sample and the reference material BCR 320R.

Table 4 shows the concentrations of the prepared QC standard, the measured concentrations and the recovery of the given concentrations, along with the relative standard deviation (RSD) of five replicate measurements. Excellent recoveries were achieved for all elements as well as good precision with a mean RSD value of 0.4%.

The solid reference material BCR 320R was digested three times using the procedure described above. The measured concentrations and the recoveries of the certified values are presented in table 5. The comparison shows, that the triple determination is in perfect agreement with the given values for all elements. The excellent linearity of the instrument is demonstrated by the good recovery for Mn. Even though the concentration in the reference material was approximately ten times higher than the highest calibration standard, the concentrations were still recovered well.

Table 4: Recovery of QC standard

Element	QC Standard Concentrations [mg/L]	Measured Concentrations [mg/L]	Recovery [%]	RSD [%]
Ag	0.05	0.052	103.0	0.28
Al	350.2	352	100.5	0.62
As	0.20	0.206	103.0	0.22
B	0.20	0.201	100.5	0.19
Ba	0.20	0.202	101.0	0.51
Be	0.20	0.204	102.0	0.44
Ca	1200.2	1217	101.4	0.40
Cd	0.20	0.203	101.5	0.38
Co	0.20	0.205	102.5	0.26
Cr	0.20	0.199	99.5	0.17
Cu	0.20	0.203	101.5	0.26
Fe	450.2	458	101.7	0.20
Hg	0.20	0.206	103.0	0.37
K	11	11.1	101.1	0.25
Li	0.20	0.196	98.0	0.43
Mg	25.2	26.4	104.9	0.41
Mn	0.20	0.206	103.0	0.49
Mo	0.20	0.204	102.0	0.85
Na	5.2	5.46	105.1	0.39
Ni	0.20	0.210	105.0	0.35
P	201	208	103.7	0.38
Pb	0.20	0.200	100.0	0.28
Sb	0.20	0.200	100.0	0.33
Se	0.20	0.202	101.0	0.38
Sn	0.20	0.204	102.0	0.25
Sr	0.20	0.202	101.0	0.48
Tl	0.20	0.199	99.5	0.19
V	0.20	0.204	102.0	0.38
Zn	0.20	0.201	100.5	0.40

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Table 5: Recovery of the reference material BCR 320R (triple determination)

Element	Certified Concentrations [mg/kg]	Measured Concentrations [mg/kg]			Recovery [%]		
		Analysis No. 1	Analysis No. 2	Analysis No. 3	Analysis No. 1	Analysis No. 2	Analysis No. 3
As	21.7 ± 2.0	23.0	22.7	22.8	106.0	104.6	105.1
Cd	2.64 ± 0.18	2.63	2.61	2.59	99.6	98.9	98.1
Co	9.7 ± 0.6	9.45	9.37	9.29	97.4	96.6	95.8
Cu	46.3 ± 2.9	45.4	44.7	44.1	98.1	96.5	95.2
Fe	25700 ± 1300	24500	24500	24500	95.5	95.8	95.2
Hg	0.85 ± 0.09	0.855	0.876	0.875	100.6	103.1	102.9
Mn	910. ±50	881	877	871	96.8	96.4	95.7
Ni	27.1 ±2.2	25.2	26.0	25.1	93.0	95.9	92.6
Pb	85 ± 5	86.7	87.0	85.8	102.0	102.4	100.9
Se*	0.96 ± 0.18	0.834	0.857	0.875	86.9	89.3	91.1
Sn*	9.4 ± 1.7	8.50	8.33	8.31	90.4	88.6	88.4
V	46.5 ± 2.8	44.4	44.6	43.9	95.5	95.9	94.4
Zn	319 ± 20	311	312	308	97.5	97.8	96.6

* non-certified concentration, indicative value only

Conclusions

The SPECTROGREEN with dual-side-on interface plasma observation offers a simple, fast, accurate, precise and cost-efficient method for the analysis of soil. It is perfectly suited for those challenging analyses due to its high matrix tolerance and perfect sensitivity, which is especially required for the heavy metals. Excellent precision and recovery values for the QC sample and the reference material BCR 320R confirmed the fulfillment of the requirements. In conjunction with an autosampler, the SPECTROGREEN can be fully automated. Independent from the number of lines and elements, an analysis (including three replicates and pre-flush) can be performed in less than four minutes.

References

- [1] Council Directive 86/278/EEC of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. Amended by Directive 91/692/EEC and Regulation (EC) No 219/2009
- [2] Council directive 1999/31/EEC of 26 April 1999 on the landfill of waste. Amended by Directive 2011/97/EU
- [3] Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control)
- [4] Decision No 1386/2013/EU of the European Parliament and of the Council of 20 November 2013 on a General Union Environment Action Program to 2020 'Living well, within the limits of our planet'
- [5] ISO 22036:2008; Soil quality – Determination of trace elements in extracts of soil by inductively coupled plasma – atomic emission spectrometry (ICP-AES)
- [6] US-EPA Method 6010C; Inductively coupled plasma – atomic emission spectroscopy; Revision 3; November 2000
- [7] US-EPA Method 3050B; Acid digestion of sediments, sludges and soil; Revision 2; December 1996
- [8] EN 16174:2012; Sludge, treated biowaste and soil – Digestion of aqua regia soluble fractions of elements
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- [10] HNO₃ Suprapur®, 65%, Merck, Darmstadt, Germany
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