APPLICATION NOTE

# Fast, simple analysis of soil and sediment according to German soil protection regulations

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#### Goal

To demonstrate the analytical performance of the Thermo Scientific<sup>™</sup> iCAP<sup>™</sup> PRO X ICP-OES Duo system for heavy metals analysis in soil samples based on the regulatory norms and methods in the EU and Germany.

#### Introduction

Soil protection laws in Germany were introduced in 1998–1999 in the form of the Federal Soil Protection Act and Federal Soil Protection and Contaminated Sites Ordinance.<sup>1,2</sup> These laws were created with the goal of enhancing environmental protection as well as effective waste management and recycling. The guidelines prescribe the monitoring of trace elements in soils that may cause human and animal health hazards as well as leading to deteriorating environmental conditions in the long run. Therefore, it is of vital importance to conduct investigations of trace element concentrations in soils from agricultural



land, construction sites, playgrounds, forests, and gardens, as well as wastelands. This may be ongoing or for a specific purpose, such as land development.

Soil measurements demand analysis that can provide the sensitivity required, but speed and robustness are of equal importance. ICP-OES is ideal for such analyses. In this application note, the iCAP PRO X ICP-OES Duo system was used to measure three samples with known trace elemental compositions and two standard reference materials (SRM) with certified reference trace elemental contents. These two independent soil sample analyses were submitted in a more extensive interlaboratory comparison with data of the same exact samples analyzed in different analytical testing laboratories using both ICP-OES as well as ICP-MS techniques. The SRMs were additionally digested and analyzed using a



Thermo Scientific<sup>™</sup> iCAP<sup>™</sup> RQ ICP-MS system at Laboratorien Dr. Döring GmbH, Bremen, Germany, for the purpose of the current study to compare with and demonstrate the reliability of analyses using the iCAP PRO X ICP-OES Duo system and the validity of the developed analytical method.

#### **Experimental**

Instrument parameters and experimental conditions An iCAP PRO X ICP-OES Duo instrument, operated in Axial iFR mode, was used to carry out measurements of 17 leachable trace elements, based on DIN ISO 22036, DIN EN ISO 11885 (E 22), and DIN EN ISO 17294-2 (E 29) methods.<sup>3,4,5</sup> Details of the sample introduction setup and instrument parameters are listed in Table 1. A standard sample introduction kit suitable for aqueous samples, consisting of a glass cyclonic spray chamber, standard glass concentric nebulizer, and quartz glass Duo torch, was used. Automatic sample introduction was carried out using a Teledyne CETAC<sup>™</sup> Technologies ASX-560 autosampler. The run time per sample was ~2 min including uptake and wash times.

#### Table 1. Instrument configuration and operating parameters

Instrument parameter	Setting
Pump tubing	Sample: Tygon™ orange/white Drain: Tygon white/white
Spray chamber	Glass cyclonic
Nebulizer	Standard glass concentric nebulizer
Center tube	2.0 mm (quartz)
Torch	Quartz Duo Torch
Pump speed	45 rpm
Uptake time	25 s
Pump stabilization time	10 s
Wash time	30 s
Nebulizer gas flow	0.70 L·min <sup>-1</sup>
Auxiliary gas flow	0.5 L·min <sup>-1</sup>
Coolant gas flow	12.5 L·min <sup>-1</sup>
RF power	1150 W
Repeats	3
Exposure time	15 s Axial iFR

#### Sample preparation

All soil samples and reference materials were digested according to the protocols in the DIN EN ISO 13657 method for the study of the leachable fractions.<sup>6</sup> An aliquot of 0.5 g of homogenized sample powder and 7 mL of freshly prepared aqua regia (35–37% HCI: 67% HNO<sub>3</sub> = 1:3, Fisher Chemical<sup>™</sup> TraceMetal<sup>™</sup> Grade acids, Fisher Scientific, UK) was placed in a closed vessel and digested in an ETHOS<sup>™</sup> EASY SK10, Milestone Microwave. The cooled digested extracts were recovered from the vessels, filtered, and made up to a final volume of 100 mL. Final acid concentration in analyzed samples was 7% (v/v) aqua regia.

#### Standards and reference materials

A calibration blank and a set of calibration standards up to 10,000 µg·L<sup>-1</sup> concentration (10, 100, 1000, and 10,000 µg·L<sup>-1</sup>) were prepared in 7% (v/v) aqua regia, using single element standards (1,000 mg·L<sup>-1</sup> and 10,000 mg·L<sup>-1</sup>, SPEX CertiPrep<sup>™</sup> Group, Metuchen, US).

Yttrium (1 mg· $L^1$ ) was added as an internal standard to all samples, calibration standards, and calibration blanks to track matrix effects.

Two different SRMs issued by the National Institute of Standards and Technology (NIST) were used in this study (Table 2):

- NIST SRM 2709a Joaquin Soil (Baseline Trace Element Concentrations)
- NIST SRM 2781 Domestic Sludge.

#### Quality control

A solution containing all the elements of interest at 200 µg·L<sup>1</sup> concentration and in the same acid matrix as the samples and calibration standards was used as a quality control (QC) standard to ensure analytical precision over time, as generally suggested by regulatory methods, (e.g., the DIN ESO ISO 11885:2009).

Table 2. True certified trace element concentrations of the two NIST soil SRMs used in this study. Concentration values in both undiluted and diluted SRMs are listed to demonstrate the range in which final measurements on the iCAP PRO X ICP-OES Duo system were performed. Units:  $1 \text{ mg} \cdot \text{kg}^{-1} \approx 1000 \text{ µg} \cdot \text{L}^{-1}$ 

	0			<b>3</b>	0 0 10
Element	Concentrations in NIST SRM 2709a Joaquin Soil (mg⋅kg⁻¹)	200x diluted (mg⋅kg⁻¹)	Element	Concentrations in NIST SRM 2781 Domestic Sludge (mg·kg <sup>-1</sup> )	200x diluted (mg·kg <sup>-1</sup> )
Ba	979	4.895	As	7.81	0.039
Cd	0.377	0.002	Cd	12.8	0.064
Со	12.8	0.064	Cr	202	1.01
Cr	130	0.65	Cu	627.8	3.139
Mn	529	2.645	Hg	3.68	0.018
Pb	17.3	0.087	Мо	46.6	0.233
Sb	1.55	0.008	Ni	80.2	0.401
V	110	0.55	Pb	200.8	1.004
			Se	16	0.08
			Zn	1273	0.039

#### Method validation via spike recoveries

A common way of ensuring method validity is by spiking a sample matrix with known concentrations of analytes to assess the concentration recoveries of the respective elements, and therefore judge the accuracy of the results. One sample in this study was spiked with 50  $\mu$ g·L<sup>-1</sup> (As, Cd, Co, Cu, Hg, Mo, Sb, Se, Sn, V, Zn) and 500  $\mu$ g·L<sup>-1</sup> (Ba, Mn, Ni, Pb, Zn) and analyzed using the same method as used for all other analyses in this study.

#### Data acquisition and data processing

The Thermo Scientific<sup>™</sup> Qtegra<sup>™</sup> Intelligent Scientific Data Solution<sup>™</sup> (ISDS) Software was used to create LabBooks for sample analysis, data acquisition, processing, and reporting.

#### **Results and discussion**

#### Wavelength selection

Wavelengths with interference-free spectra and high sensitivities were chosen for the analytes to ensure calculation of true concentrations of the respective elements in the solution being analyzed (Table 3).

#### Sensitivity

The limit of detection or instrument detection limit (LOD or IDL) is the smallest amount or concentration of an analyte in the test sample that can be reliably distinguished from zero.<sup>3</sup> The limit of quantification (LOQ) is the smallest amount or concentration of an analyte in the test sample that can be determined with acceptable precision. These two values

were determined for all elements as follows<sup>3</sup> to assess the sensitivity of the instrument and analytical method:

Equation 1  $LOD = 3 s_0$ 

Equation 2  $LOQ = 3 X_{LD} = 9 s_0$ 

where  $s_0$  is the standard deviation of the concentration of three measurements of the calibration blank with each blank described as "Average Blank" in the Sample List section of the Qtegra ISDS Software LabBook. The LODs and LOQs for the elements are listed in Table 3.

Table 3. List of suitable wavelengths, limits of detections (LOD), and
limits of quantification (LOQ) for individual elements

Element	Wavelength (nm)	LOD (µg∙L⁻¹)	LOQ (µg∙L⁻¹)	
As	189.042	1.73	5.19	
Ba	455.403	0.05	0.15	
Cd	214.438	0.05	0.15	
Со	228.616	0.34	1.02	
Cr	357.869	0.16	0.48	
Cu	324.754	0.29	0.88	
Hg	194.227	0.48	1.44	
Mn	257.610	0.02	0.05	
Мо	202.030	0.14	0.43	
Ni	231.604	0.56	1.67	
Pb	220.353	1.76	5.27	
Sb	217.581	1.87	5.62	
Se	Se 196.090		6.36	
Sn	189.989	0.51	1.52	
TI	190.856	1.20	3.61	
V	292.464	0.33	0.99	
Zn	213.856	0.61	1.84	

#### Linearity

A linear dynamic range of 0–10,000  $\mu$ g·L<sup>-1</sup> was obtained for all elements covered in the present study, and all final measured solutions had analyte concentrations inside this range. The calibration curves for the different wavelengths all gave R<sup>2</sup> values between 0.9999 and 1.0000 over the entire calibration range.

#### Accuracy and robustness

The accuracy and robustness of the method was assessed by analyzing two NIST soil SRMs prepared and analyzed in exactly the same way as real soil samples. The calculated concentrations of the elements in the SRMs were compared to the certified values with recoveries ranging from 85 to 104% for all elements analyzed using the iCAP PRO X ICP-OES Duo system (Table 4) except barium. In order to obtain higher recovery of barium, a different digestion method with different reagents (higher HNO<sub>3</sub> content or addition of HF) is required. The same is true for the data from Laboratorien Dr. Döring with good recoveries for most elements in the SRMs (Table 4), with a few exceptions like Cr and Mo due to differences in digestion procedures.

Additionally, concentration recoveries of a real soil sample spiked with 50  $\mu$ g·L<sup>-1</sup> or 500  $\mu$ g·L<sup>-1</sup> of the target elements were determined and found to be within the accepted range of 80–120% (Figure 1).

Table 4. Measured trace elemental concentrations of two NIST soil SRMs from two different laboratories and techniques. The data from the Thermo Fisher Scientific laboratory was acquired on an iCAP PRO X ICP-OES Duo system using the methods described in this study. Further details regarding the data are discussed in the text. Units:  $1 \text{ mg-kg}^{-1} \approx 1000 \mu\text{g-L}^{-1}$ 

0 0		5 <b>3 3 4 4</b>	5				
Element	Certified value (mg⋅kg⁻¹)	Determined value in laboratory 1 * (mg⋅kg⁻¹)	Recovery in laboratory 1 (%)	Determined value in laboratory 2 ** (mg·kg <sup>-1</sup> )	Recovery in laboratory 2 (%)		
NIST SRM 2709a Joaquin Soil							
Ba	979	454.93	46	448.29	46		
Cd	0.377	0.392	104	0.380	101		
Со	12.8	12.0	94	12.4	97		
Cr	130	111	85	76	58		
Mn	529	490	93	93 545			
Pb	17.3	17.3	100	12.1	70		
Sb	1.55	1.35	87	1.23	79		
V	110	94	85	80	73		
NIST SRM 2781 Domestic Sludge							
As	7.81	7.7	98	8.0	103		
Cd	12.8	11.8	92	12.6	99		
Cr	202	176	87	172	85		
Cu	627.8	610.2	97	651.6	104		
Hg	3.68	3.5	94	4.22	115		
Мо	46.6	39.8	85	24.9	53		
Ni	80.2	73.0	91	72.9	91		
Pb	200.8	174.8	87	199.9	100		
Se	16	14	90	17	105		
Zn	1273	1155	91	1218	96		

\*Values obtained in the Thermo Fisher Scientific laboratory, Bremen, Germany.

\*\*Values obtained using ICP-MS in the Laboratorien Dr.Döring, Bremen, Germany.



Figure 1. Spike recoveries in soil samples. The dashed lines represent the allowed recovery interval (±20%) as specified in the DIN ESO ISO 11885:2009 method.<sup>3</sup>

#### Matrix effects-enhancements/suppressions

Recovery of 1 mg·L<sup>1</sup> yttrium internal standard was between 90 and 110% over the entire duration of the experiments and in all different types of sample matrices. This demonstrates that the analyses were free of matrix suppression or enhancement effects and yielded accurate data.

### Robustness validation and real sample analysis in analytical testing laboratories

The developed method for soil analysis in this study must be applicable to real soil sample analysis in analytical testing laboratories with high sample throughput, sensitivity, and robustness demands. To validate that the developed method is suited perfectly for such applications, a robustness experiment was conducted over the duration of a typical working day. Instrument and method parameters as described in Table 1 were used.

All samples and standards measured in the robustness test were spiked with 1 mg·L<sup>-1</sup> yttrium as an internal standard. The robustness experiment design started with at least three calibration blank measurements and a calibration standard block. This was followed by analyzing

the two SRMs and a 200  $\mu$ g·L<sup>1</sup> QC standard. Real samples were measured after this and the QC standard was repeated after every 10 unknown samples.

The internal standard remained stable throughout the experiment with excellent recoveries between 90 and 110% (Figure 2). The QC recoveries were found to be between 95 and 120% over 8 hours of continuous analysis (Figure 3). The recoveries of concentrations of pooled soil samples during the stability experiment is within 90–110%, demonstrating the high robustness of the method and analyses over the duration of a typical working day (Figure 4).

Trace elemental compositions of three soil samples analyzed using the same method are presented in Table 5. Values presented as "Measured value, this study" in bold are the data acquired in the current study using an iCAP PRO X ICP-OES Duo system. These samples were also analyzed in several other laboratories using both ICP-OES and ICP-MS techniques in the past as a part of a round robin test; the averages of all the results obtained by participating laboratories for each element are listed as certified values in Table 5.



Figure 2. Internal standard recovery in real samples during the robustness test



Figure 3. Robustness data demonstrating CCV (continuous calibration verification) recoveries of target elements in a QC standard (200  $\mu$ g·L<sup>-1</sup>). The dashed lines represent the accepted recovery interval ( $\pm$ 20%).



Figure 4. Calculated concentrations (as % recovery from expected values) of elements in a pooled soil sample during the robustness test run over the entire duration of a typical working day

Table 5. Certified and measured trace elemental concentrations of real soil samples using ICP-OES and ICP-MS techniques. Data acquired exclusively for this study (presented in bold) were measured using an iCAP PRO X ICP-OES Duo system. Not analyzed (NA); analyzed but not detected (ND).

Element	Concentration (mg·kg <sup>-1</sup> )								
	Sample 48679/17			Sample 48680/17		Sample 61203/17 (AB07)			
	Certified value*	Measured value, this study	Laboratorien Dr. Döring Lab**	Certified value*	Measured value, this study	Dr. Döring Lab**	Certified value*	Measured value, this study	Dr. Döring Lab**
As	22.2	21.5	21.95	17.8	17.7	17.2	147	132	147
Ba	NA	456	NA	ND	433	ND	732	573	684
Cd	5.7	6.0	5.7	4.6	6.0	4.6	10.9	9.6	11.96
Cr	129.7	149.0	123.5	119	127.2	111	324	362	324
Cu	105.5	110.4	109	84.9	82.9	86.1	619	624	546
Hg	7.1	ND	7.1	5.6	5.3	5.7	0.13	<dl< td=""><td>0.1</td></dl<>	0.1
Mn	NA	489	NA	NA	484	NA	NA	2733	ND
Мо	NA	7.9	NA	NA	6.0	NA	3.89	3.6	4.3
Ni	40.6	40.8	38.8	38.7	36.2	35.8	300	289	271
Pb	146.7	143.8	143.5	120.5	110.2	117.5	93.8	83.2	103
Sb	NA	2.0	NA	NA	3.3	NA	3.7	3.1	3.0
Se	NA	<dl< td=""><td>NA</td><td>NA</td><td><dl< td=""><td>NA</td><td>2.4</td><td><dl< td=""><td>1.8</td></dl<></td></dl<></td></dl<>	NA	NA	<dl< td=""><td>NA</td><td>2.4</td><td><dl< td=""><td>1.8</td></dl<></td></dl<>	NA	2.4	<dl< td=""><td>1.8</td></dl<>	1.8
Sn	NA	29.0	NA	NA	11.2	NA	36.2	35.6	46.5
TI	NA	NA	NA	NA	<dl< td=""><td>NA</td><td>NA</td><td>NA</td><td>NA</td></dl<>	NA	NA	NA	NA
V	28.6	NA	22.2	32.4	37.6	25.4	NA	NA	NA
Zn	361.4	369	358	298.8	282.4	292	2370	2061	2085

\*Certified values are the average values from interlaboratory round robin test following DIN 38402-A 45<sup>7</sup>, data from iCAP RQ ICP-MS analysis. \*\*Data from Laboratorien Dr. Döring, from previous study using both ICP-MS and ICP-OES techniques.

#### Conclusions

The results obtained in these experiments demonstrate the suitability of the iCAP PRO X ICP-OES Duo system for soil and sediment analysis according to the DIN EN ISO methods 11885, 22036, and 17294. Interlaboratory results were comparable to the round robin test results from previous publications. The iCAP PRO X ICP-OES Duo system results were consistent with the data from other systems and techniques, demonstrating the suitability of this technology for multielement analysis of environmental samples.

Typical performance parameters expected in analytical testing laboratories were assessed and the results are summarized below:

- A linear dynamic range of 0–10,000 µg·L<sup>1</sup> was obtained for all analytes, critical for accurately detecting trace elements at high and low concentrations in soil samples.
- Excellent sensitivity (low µg·L<sup>-1</sup> or ppb range) was achieved for all target elements in the Axial iFR mode, meeting the sensitivity requirements for soil analysis according to existing DIN methods.

- The recovery values (85–104%) obtained from the SRM sample analysis with the iCAP PRO X ICP-OES Duo system were within the expected limits (±20%), demonstrating the method accuracy. Interlaboratory accuracy was tested and verified with iCAP PRO X ICP-OES Duo system data compared against ICP-MS data from Laboratorien Dr. Döring.
- Excellent system robustness and reproducibility was demonstrated over a typical 8-hour working day, with stable analyte recoveries in both QC standards as well as real life soil samples.
- Fast analysis of all target elements, with ~2 minutes per sample, allows for high sample throughput without any user interaction necessary for long time periods, making the iCAP PRO X ICP-OES Duo system an ideal option for analytical testing laboratories.

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