AN APPLICATION REPORT FROM
SPECTRO ANALYTICAL INSTRUMENTS

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SPECTRO ARCOS/SPECTROBLUE

Multi-element Analysis of Sediments for Ecohydrological Research by ICP-OES with Radial Observation

Introduction

The analysis of sediment is of high interest in many academic fields. In ecohydrology the analysis of sediments helps to understand their hydrological and biological impact, the interactions between vegetation, land and water. E.g. the accumulation of heavy metals in sediments causes a potential risk to human health due to the transfer of those elements to aquatic media, uptake by plants and their subsequent introduction into the food chain [1].

Inductively coupled plasma optical emission spectrometry (ICP-OES) is a method of choice for the analysis of rock, sediments and soil, due to its multi-element determination capability, high dynamic linear range, sensitivity and robustness.

The report describes the analysis of river sediments using the SPECTROBLUE ICP-OES and the SPECTRO ARCOS ICP-OES with radial plasma observation. A comparison of



three digestion procedures is presented. The accuracy and precision of the method was investigated analyzing the certified reference material NIST 8704 (Buffalo River Sediment) and a synthetical QC sample with element concentrations in the expected range for the samples to be analyzed.

Experimental

Instrumentation

The measurements were performed with the SPECTROBLUE optical emission spectrometer and the SPECTRO ARCOS optical emission spectrometer with radial plasma observation (SPECTRO Analytical Instruments, Kleve, Germany). The SPECTROBLUE and ARCOS feature a Paschen-Runge spectrometer mount, employing the proprietary Optimized Rowland Circle Alignment (ORCA polychromator) technique. The SPECTRO BLUE consisting of two hollow section cast shells, optimized small volume and 15 linear CCD detectors. The wavelength range between 165 and 770nm can be analyzed, allowing complete spectrum capture within 4s. The SPECTRO ARCOS utilizes the same principle optic design, however 32 linear CCD detectors are installed and a wavelength range between 130 and 770 nm can be simultaneously analyzed, allowing complete spectrum capture within 2s.



Due to the unique reprocessing capabilities of the systems, a new measurement is not required even if additional elements or lines are to be determined at a later date. The optic of both instruments 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 for the determination

of non-metals as well as the use of prominent and interference free lines in this region. Utilizing SPECTRO's "Intelligent Calibration Logic" (iCAL), which normalizes the wavelength scale, the state of the optical system is automatically monitored.

Plasma power enters a whole new era with the systems' innovative generators. Air-cooled, 27.12 MHz, free running type LDMOS (laterally diffused metal oxide semiconductor) ICP-generators are installed, which ensure excellent stability of the forward power even in the case of rapidly changing sample loads. All relevant ICP operating parameters are software controlled, allowing for an easy selection of the optimum operating conditions. For sample introduction, a Cross-flow nebulizer with a Scott-type spray chamber was used. The operating conditions are given in Table 1.

Digestion methods

Table 1: Typical ICP Operating Conditions

Sample	SPECTROBLUE radial view	SPECTRO ARCOS radial view
Power	1350 W	1350 W
Coolant flow	13 L/min	13 L/min
Auxiliary flow	0.8 L/min	0.9 L/min
Nebulizer flow	0.86 L/min	0.86 L/min
Plasma torch	Quartz, demountable, 1.8 mm Injector tube	Quartz, demountable, 1.8 mm Injector tube
Spray chamber	Scott type	Scott type
Nebulizer	Cross-flow	Cross-flow
Sample aspiration rate	2 mL/min	2 mL/min
Replicate read time	50 s	50 s





Three digestion techniques were investigated:
1) Aqua regia digestion (9 mL HCl and 3 mL HNO_3);
2) Three acid digestion (9 mL HNO_3, 3 mL HF and 1 mL HCl).
3) Four acid digestion (3 mL HCl, 3 mL HNO_3, 2 mL $HClO_4$ and 2 mL HF)

The NIST reference material 8704 (Buffalo River Sediment) was used as sample. The sample weight used for the digestion was 0.5 g. All acids were suprapure grade and supplied from Merck (Darmstadt, Germany). Sample digestion was performed in duplicate. For digestion techniques No. 1 and 2 the Discover SP-D microwave digestion system (CEM Corp. NC, USA) was employed, whereas digestion technique No. 3 used a hotplate. Table 2 shows the microwave programs used for digestion techniques No. 1 and 2.

Table 2: Microwave digestion programs

Digestion	Temp [°C]	Ramp Time [min]	Hold Time [min]	Pressure max. [bar]	Power [W]	Stirring
Aqua regia	150	5:00	5:00	28	300	high
Aqua regia	200	2:00	15:00	28	300	high
Three acid digestion	190	10:00	20:00	28	300	medium

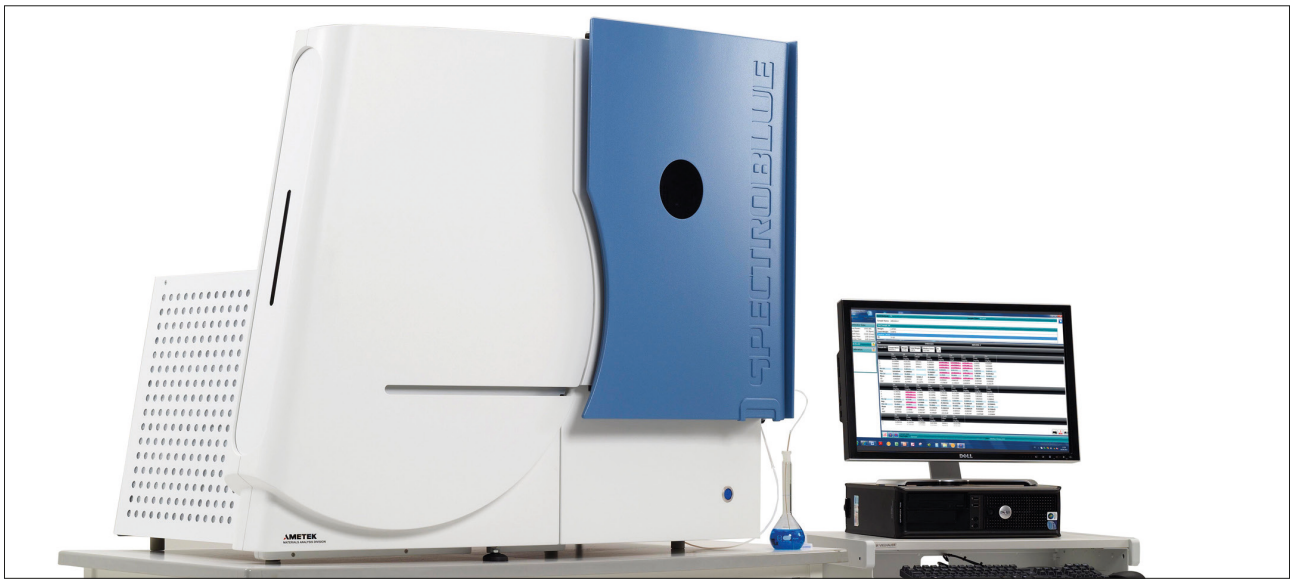
The digested samples were diluted with deionized water to a final volume of 25 mL. Lutetium at a concentration of 2mg/L was added to the samples as internal standard.
The following procedure was used for digestion technique No. 3: the sample was weighed into a PTFE vessel and rinsed from the side walls of vessel with a minimum of deionized water. Slowly, 3 mL conc. HCl and 2 mL conc. HNO_3 were added and the reaction was allowed to subside. Then, 1 mL of conc. $HClO_4$* and 2 mL conc. HF were added. The vessel was placed on a hot



plate with a preset temperature of 110°C and heated to incipient dryness. Then, the temperature was raised to 160°C to bring sample to complete dryness. After removal from the hotplate, 1 mL conc. $HClO_4$ was added and again the sample was taken to complete dryness at 160°C. After removal from the hotplate and cooling, 1 mL conc. HNO_3 and a few drops of H_2O_2 were added. After the reaction subsided, 19 mL 1% HNO_3 were added and the capped vessels was kept in a in a drying oven at a temperature of 100°C for 30 minutes. For analysis, the solution was diluted to 25 mL using a 1% HNO_3 solution.

***Please note:**

When working with perchloric acid, appropriate safety precautions must be taken. In addition to being a corrosive liquid, while not combustible, under some circumstances perchloric acid may act as an oxidizer and/or present an explosion hazard. Perchloric



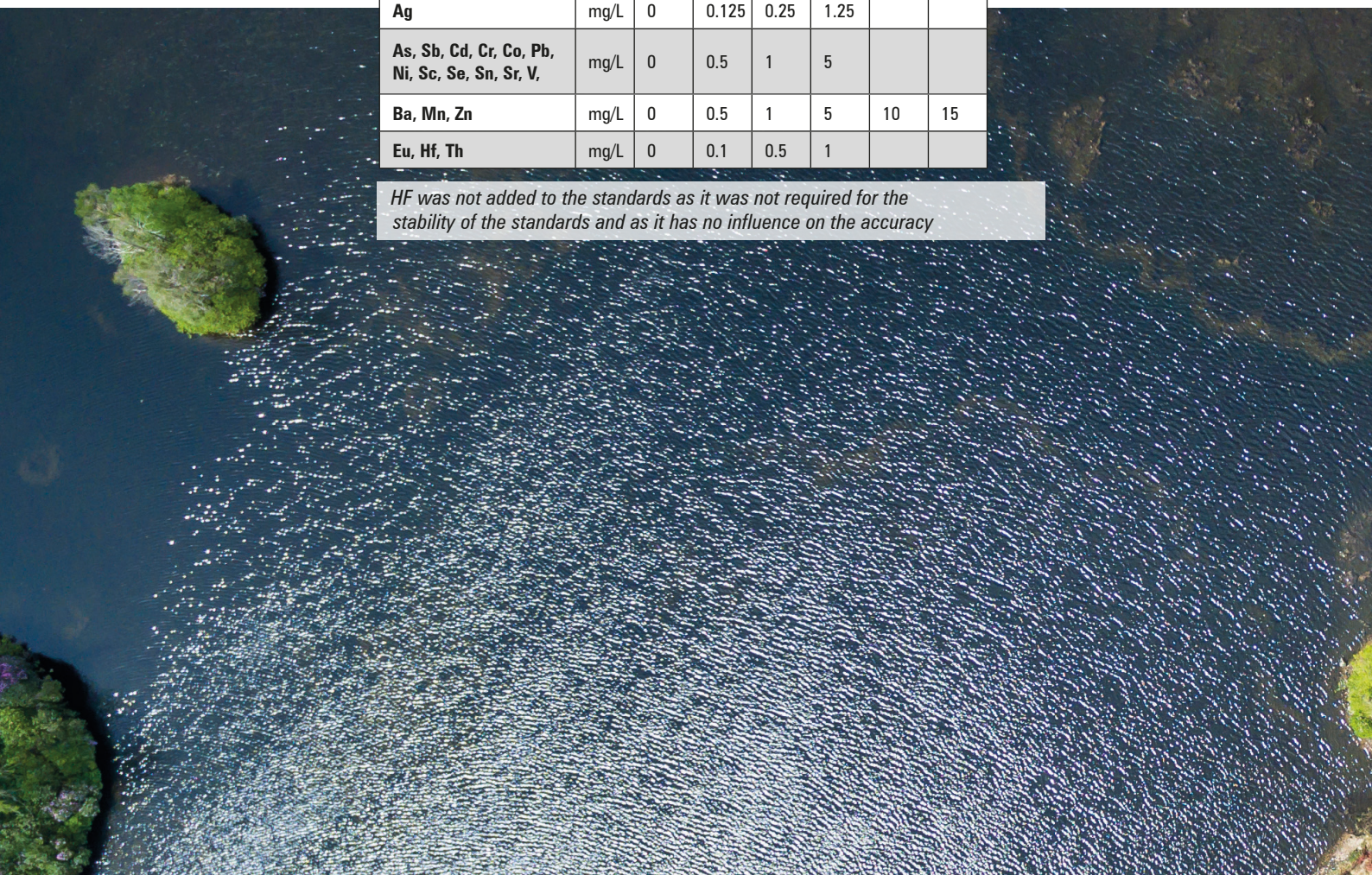
crystals, or perchloric acid in crystalline form, is an extremely dangerous inorganic compound. Accordingly, for any perchloric acid work, a suitable fume hood, certified for perchloric acid work (e.g. equipped with washing systems) and according equipment and infrastructure is required, to avoid any dangers from the specific properties of perchloric acid. If in doubt, consult with a qualified expert before commencing any work.

For calibration, a commercially available multi-element standard (EPA 200.7, Bernd Kraft GmbH, Germany) and single element standards (Inorganic Ventures, Christiansburg, USA) were used. All standard solutions were matrix and acid matched to the respective digestion method and diluted to the concentrations given in Table 3.

Table 3: Calibration standards

Element	Unit	S1	S2	S3	S4	S5	S6
Al	mg/L	1600	1500	1400	1300	1200	1100
Ca	mg/L	650	450.5	501	555	600	400
Fe	mg/L	500	900	701	805	600	1000
Mg	mg/L	0	100.5	201	305	400	500
K	mg/L	500	452.5	405	355	300	250
Na	mg/L	200	150.5	101	5	50	0
Ti	mg/L	0	40	60	80	100	120
Ag	mg/L	0	0.125	0.25	1.25		
As, Sb, Cd, Cr, Co, Pb, Ni, Sc, Se, Sn, Sr, V,	mg/L	0	0.5	1	5		
Ba, Mn, Zn	mg/L	0	0.5	1	5	10	15
Eu, Hf, Th	mg/L	0	0.1	0.5	1		

HF was not added to the standards as it was not required for the stability of the standards and as it has no influence on the accuracy



Results and Discussion

Different replicate read times, from 19 s up to 33 s were tested on the SPECTROBLUE to investigate the influence of the read time on the Limits of Detection (LOD). Table 4 shows the selected wavelengths and the achieved LODs. The LODs were calculated according to the equation:

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

Where:

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



Table 4: Typical limits of detection (LOD) for the selected lines in aqua regia matrix

	Unit	19 s	24 s	33 s
Element	λ [nm]	LOD (3σ) [mg/L]	LOD (3σ) [mg/L]	LOD (3σ) [mg/L]
Ag	328.068	0.006	0.004	0.004
As	189.042	0.019	0.019	0.012
Ba	455.404	0.0005	0.0006	0.0004
Be	313.042	0.0002	0.0001	0.0001
Cd	228.802	0.0006	0.0005	0.0006
Co	228.616	0.002	0.002	0.002
Cr	267.716	0.003	0.002	0.002
Cu	324.754	0.003	0.004	0.002
Eu	420.505	0.006	0.004	0.002
Hf	264.141	0.003	0.004	0.002
Hg	184.95	0.006	0.003	0.003
Li	670.78	0.006	0.006	0.005
Mg	279.079	0.02	0.01	0.01
Mn	257.611	0.001	0.001	0.001
Mo	202.095	0.006	0.005	0.005
Na	589.592	0.05	0.02	0.02
Ni	231.604	0.003	0.002	0.002
Pb	220.353	0.02	0.02	0.02
Sb	206.833	0.02	0.02	0.02
Sc	361.384	0.004	0.002	0.001
Se	196.09	0.03	0.02	0.02
Sn	189.991	0.009	0.009	0.008
Sr	421.552	0.001	0.001	0.001
Th	401.913	0.02	0.015	0.015
Ti	336.121	0.003	0.002	0.001
Tl	190.864	0.03	0.02	0.02
V	292.464	0.009	0.008	0.004
Zn	206.200	0.004	0.003	0.002

As shown in Table 4, best LODs were achieved using a longer replicate read time. But also with a shorter read time, good LODs can be achieved, which enables higher sample throughput. Since this was not relevant for this test, but it was also the aim to compare best practices, an integration time of 50 seconds was chosen for all measurements.

The practical limit of detection depends on the dilution factor of the solid sample material. For the LODs given in Table 5, a dilution factor of 50, as used in the method, was applied. The typical relative short-term precision for the measurement of a blank sample was found in the range between 0.3% and 0.9%, depending on the element.

The emission lines were chosen in accordance with their achievable sensitivity for the respective analytes and the (expected) concentrations of the elements in the samples to be analyzed. In general, axial plasma observation offers on average a factor 4 higher sensitivity compared to the radial view technique, making it the preferred method for ultimate sensitivity. However, the advantages of radial plasma observation are that higher precision for major constituents can be achieved and its overall larger tolerance for higher matrix concentrations, being suitable for TDS concentrations of up to 20%.

Table 5: Comparison of typical limits of detection (LOD) with both instruments for the selected lines in the solid (1:50 dilution)

		SPECTROBLUE	SPECTRO ARCOS
Element	λ [nm]	LOD (3σ) [mg/kg]	LOD (3σ) [mg/kg]
Ag	328.068	0.14	0.11
As	189.042	0.7	0.64
Ba	455.404	0.02	0.02
Be	313.042	0.005	0.004
Cd	228.802	0.04	0.04
Co	228.616	0.17	0.17
Cr	267.716	0.10	0.10
Cu	324.754	0.14	0.13
Eu	420.505	0.06	0.06
Hf	264.141	0.10	0.10
Hg	184.95	0.17	0.15
Li	670.78	0.12	0.12
Mg	279.079	0.01	0.01
Mn	257.611	0.02	0.02
Mo	202.095	0.24	0.24
Na	589.592	1.1	1.1
Ni	231.604	0.12	0.12
Pb	220.353	1.5	1.5
Sb	206.833	1.3	1.3
Sc	361.384	0.01	0.01
Se	196.09	1.5	1.5
Sn	189.991	0.40	0.40
Sr	421.552	0.01	0.01
Th	401.913	0.70	0.70
Ti	336.121	0.07	0.07
Tl	190.864	1.2	1.2
V	292.464	0.15	0.15
Zn	206.200	0.15	0.15



Accuracy and Precision

The accuracy and precision of the instrumental method using SPECTROBLUE was investigated by analyzing a synthetic QC sample containing matrix element concentrations in the expected range for the samples to be analyzed and a certified reference material, NIST 8704 (Buffalo River Sediment). As shown in Table 6, excellent recoveries were found for all the elements in the synthetic QC sample.

Quantitative results for digested samples of NIST 8704 Buffalo River Sediment according to the three digestion procedures using SPECTROBLUE and SPECTRO ARCOS are summarized and compared with certified values in Table 7. The samples were analyzed in a single run. All measurements just required a single 1:50 dilution.

Table 6: Results for the synthetic QC sample

Element	λ [nm]	QC Standard conc. [mg/L]	Measured conc. [mg/L]	Recovery [%]
Ag	328.068	0.5	0.51	101
Al	396.152	802	810	101
As	189.042	2	2.03	102
Ba	455.404	2	2.05	102
Be	313.042	2	2.01	101
Ca	315.887	652	644	99
Cd	228.802	2	2.03	101
Co	228.616	2	2.07	103
Cr	267.716	2	2.05	102
Cu	324.754	2	2.03	102
Fe	239.562	1002	979	98
Hg	184.95	2	2.12	106
K	766.491	260	257	99
Li	670.78	2	2.04	102
Mg	279.079	500	508	102
Mn	257.611	2	1.98	99
Mo	202.095	2	2.07	104
Na	589.592	2	2.09	105
Ni	231.604	2	2.08	104
Pb	220.353	2	2.02	101
Sb	206.833	2	2.08	104
Se	196.09	2	2.05	102
Sn	189.991	2	1.99	99
Sr	421.552	2	2.03	101
Ti	336.121	120	118	98
Tl	190.864	2	2.03	101
V	292.464	2	2.06	103
Zn	213.856	2	1.97	99

In this study, three sample digestion procedures for sediment samples were applied and compared. Of those, aqua regia extraction is one of the most widely used acid leaching methods, whereas the so-called “three acid” digestion with HF and the “four acid” digestion with HF and $HClO_4$ are considered to be total decomposition methods. It is reported that recoveries between 80% and 120%, obtained by microwave digestion with aqua regia, are being deemed acceptable [2]. Using the aqua regia extraction for NIST 8704, 9 elements (Ca, Fe, Mg, Cd, Co, Mn, Ni, Pb and Zn) could be recovered in a range between 76% and 87%. A lower leaching efficiency was found for Al (53%), K (54%), Ba (49%), Cr (71%), Sc (60%), Th (68%) and V (67%). Unsatisfactory results were obtained for Na (9%) and Ti (12%). The low accuracy obtained for Al, K and Na by aqua regia digestion can be explained by the binding of these metals to the silicate core of the stream sediment, which cannot be dissolved using this method. Reported low recoveries of Ti could be explained by the fact that Ti forms insoluble oxo-complexes [3]. Using the three acid digestion, successful digestion was achieved for 10 elements: Fe, Ti, Cd, Co, Cr, Mn, Ni, Pb, V, Zn (87-110%). A lower digestion efficiency was found for K (60%), Na (71%), Ba (45%) and Hf (55%). Unsatisfactory results were obtained for Al (9%), Ca (25%), Mg (6%) and Sc (9%). The low

recoveries of these elements can be explained by the fact that there are a number of insoluble fluorides, e.g. for alkaline earths elements, such as MgF_2, CaF_2, BaF_2, ScF_3, as well as complex metal fluorides, such as $MgAlF_5$. The reported digestion losses of alkali elements may be traceable to the formation of compounds as e.g. $KSiF_6$, K_2AlF_6 and K_2FeF_6 [4]. A comparison of the first two digestion methods showed significant differences in the element concentrations determined for Al, Ca, Mg, Ba, Na, Ti and Sc. Excellent recoveries for almost all investigated elements (85% - 112%) were obtained using the four acid digestion procedure. Only for Hf (70%), a slightly lower digestion efficiency was found.



Table 7: Comparison of certified and measured concentrations (n=2) for NIST 8704 (mean values expressed on a dry-mass basis)

	SPECTROBLUE							SPECTRO ARCOS		
		Aqua Regia			Three Acid Digestion			Four Acid Digestion		
Element	**Certified conc. [%]**	**Measured conc. [%]**	**Recovery [%]**	**SD [%]**	**Measured conc. [%]**	**Recovery [%]**	**SD [%]**	**Measured conc. [%]**	**Recovery [%]**	**SD [%]**
Al	6.1 ± 0.18	3.227	53	1.7	0.577	9	1.5	6.2	101	0.4
Ca	2.641 ± 0.083	2.077	79	1.5	0.648	25	4.0	2.6	89	0.1
Fe	3.97 ± 0.10	3.223	81	3.2	3.440	87	0.8	4.0	102	1.5
K	2.001 ± 0.041	1.081	54	4.1	1.197	60	1.0	2.0	102	0.8
Mg	1.2 ± 0.018	0.916	76	2.5	0.069	6	0.6	1.2	101	1.2
Na	0.553 ± 0.015	0.049	9	1.1	0.392	71	1.7	0.6	109	0.5
Ti	0.457 ± 0.020	0.055	12	1.3	0.399	87	2.1	0.5	100	0.5
Element	**Certified conc. [mg/kg]**	**Measured conc. [mg/kg]**	**Recovery [%]**	**SD [%]**	**Measured conc. [mg/kg]**	**Recovery [%]**	**SD [%]**	**Measured conc. [mg/kg]**	**Recovery [%]**	**SD [%]**
Ba	413 ± 13	202	49	4.4	186	45	1.1	415.3	101	0.3
Cd	2.94 ± 0.29	2.6	87	1.3	2.91	99	0.4	3.2	107	0.6
Co	13.57 ± 0.43	11.2	83	1.9	14.31	105	0.5	13.3	98	1.8
Cr	121.9 ± 3.8	86.1	71	3.9	114.5	94	1.4	119.5	98	0.2
Eu	1.31 ± 0.038	< LOD	-	-	< LOD	-	-	1.5	112	3.8
Hf	8.40 ± 1.5	< LOD	-	-	4.63	55	2.4	5.9	70	0.5
Mn	544 ± 21	435	80	2.5	498	92	0.2	564.6	104	0.6
Ni	42.9 ± 3.7	35.5	83	2.8	47.2	110	0.9	41.5	97	3.4
Pb	150 ± 17	118.9	79	5.1	150.1	100	3.4	152.5	102	3.3
Sb	3.07 ± 0.32	< LOD	-	-	< LOD	-	-	3.2	106	1.1
Sc	11.26 ± 0.19	6.7	60	4.1	0.984	9	1.8	11.4	101	1.5
Th	9.07 ± 0.16	6.1	68	0.6	< LOD	-	-	7.7	85	1.7
V	94.6 ± 4.0	63.7	67	2.6	96.0	102	1.9	92.3	98	1.2
Zn	408 ± 15	326	80	3.3	371	91	0.3	407.1	100	0.2

Conclusions

The report demonstrates that above all, the challenge with this application is the development of a suitable sample preparation method, which enables the quantitative recovery of the elements as per the requirements. In cases where full recovery is needed, the $HClO_4$ "four acid" digestion method was found to be successful for most of the elements.

Both SPECTROBLUE and SPECTRO ARCOS are suitable instruments and both radial or axial plasma observation are principally suitable techniques for the analysis of complex geological samples and should be selected according to individual requirements. The SPECTROBLUE with radial plasma observation offers a robust and cost-efficient method. The radial view technique provides excellent matrix compatibility and high precision for the determination of main constituents. The SPECTRO ARCOS offers the highest flexibility. Both instruments are available with axial and radial interfaces, but both techniques can also be combined. The Twin Interface, available for the SPECTROBLUE, enables automatic dual axial and radial observation, offering an expansion of the axial view capabilities with regards to dynamic range and the elimination of matrix effects. The MultiView technique available with the SPECTRO ARCOS offers dedicated true axial and radial observation in a single instrument, delivering the highest sensitivity on one hand and the highest matrix compatibility and precision on the other.
Due to the sensitivity and large dynamic range of all SPECTRO ICP models, major, minor and trace analyte concentrations in sediments can be analyzed using a single analytical method.
In combination with an autosampler, SPECTRO ICPs can be fully automated. Independent from the number of lines and elements, an analysis (including two replicates, pre- flush and method rinse) can be performed in less than three minutes.





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