

## ICP-Optical Emission Spectroscopy

## AUTHOR

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## High-Throughput Analysis of Geochemical Samples with the Avio 560 Max ICP-OES

### Introduction

Since the elemental composition of geochemical materials plays an important role in geological

investigations, the development of mineral resources, and environmental protection, elemental analysis of natural samples, such as rocks, soils, sediments, and plants, is essential routine testing in geochemical laboratories. The most commonly used technique for major and trace element analysis of geochemical samples is inductively coupled plasma optical emission spectroscopy (ICP-OES) because of its ability to simultaneously measure most elements over a wide concentration range with low detection limits. Compared to atomic absorption (AA) spectroscopy, laboratory productivity can be significantly improved with ICP-OES, given its multi-elemental analysis capabilities. However, sample turnaround time is still challenging in high-throughput geochemical laboratories due to the large number of samples. In addition, some analytes can be present over a wide concentration range, resulting in long washout times between samples. Therefore, a fast, reliable, and more productive method is in high demand by many laboratories to enhance testing efficiency.

In this work, a PerkinElmer Avio® 560 Max ICP-OES with an integrated High Throughput System (HTS) was used for analysis. The built-in HTS consists of a metal-free 7-port valve, sample loop and a high-speed vacuum pump.

The operating principle of the HTS is described in the PerkinElmer product note.<sup>1</sup> With the HTS configuration, sample throughput is up to 5 times faster by reducing sample uptake and washout times, compared to conventional sample introduction systems.<sup>2</sup> Moreover, on-line addition of internal standards through the HTS further enhances productivity by simplifying sample preparation. In addition, the whole system is fully controlled by Syngistix™ for ICP smart software for easy-to-use automation.

## Experimental

### Samples and Sample Preparation

Method development and validation were performed with five Stream Sediments certified reference materials (CRMs) from the China National Geophysical Research Institute: GBW 07303a (GSD-3a), GBW 07305a (GSD-5a), GBW 07307a (GSD-7a), GBW 07318 (GSD-14), GBW 07366 (GSD-23). These CRMs, named as “GSD series standard materials”, are specified for geological and geochemical investigation and mineral resource survey. The methodology was then applied to soil and sediment samples provided by national environmental monitoring stations.

Since the geological samples normally contain high amounts of silica and aluminum oxide, the most efficient digestion method is the four-acid total digestion with HNO<sub>3</sub>, HCl, HF and HClO<sub>4</sub> on a hot plate. In this work, all sediment samples were fully digested following the four-acid digestion procedure using PerkinElmer’s SPB 50-48 sample digestion block. Compared to the traditional hot plate, the SPB digestion block has the advantages of simplicity, less contamination and higher sample throughput.

A 0.5 g quantity of each sample was weighed into a PFA digestion vessel, followed by the addition of 3 mL HCl, 2 mL HNO<sub>3</sub>, 3 mL HF, and 2 mL HClO<sub>4</sub>. All of the acids were added in their concentrated forms. The sample vessels were placed in the SPB digestion block and heated at 180 °C for at least 2 hours. The temperature was then increased to 240 °C until white fumes formed when the samples were near complete dryness. The sample solutions were then cooled to room temperature and diluted to 50 mL with deionized water for analysis. A blank solution was prepared using the same procedure without the sample.

### Calibration Standards

PerkinElmer multi-element standards and single-element solutions were used to prepare the calibration standards. All standard solutions were prepared in 2% HNO<sub>3</sub> (v/v) at the concentrations listed in Table 1. The concentration ranges of the calibration standards were matched to their expected

concentrations in the samples to attain better accuracy.<sup>3</sup> A solution of 5 ppm scandium (Sc) was prepared and used as an internal standard.

Table 1: Concentration Range of Calibration Standards for Major and Minor Elements.

Analytes	Concentration Range (mg/L)
As, Be, Co, Ce, Cr, Cu, La, Li, Mo, Ni, Pb, Sr, V, Zn	0-1
P, Ba, Mn	0-20
Ti	0-40
Ca, Fe, K, Na, Mg	0-400
Al	0-600

### Correction Techniques

Inter-element correction (IEC) is a method for dealing with spectral interferences<sup>4</sup>. In this application, due to the presence of large amounts of Fe, Al and Ti in the samples, IECs were applied to Be, Co, Pb, Ni, and Mo to improve accuracy and detection limits<sup>5</sup>. Auto-background correction is the default setting and was used for all analytes.

### Instrumentation

All analyses were performed on the Avio 560 Max fully simultaneous ICP-OES using an S23 autosampler.

The Avio 560 Max ICP-OES features patented Flat Plate™ plasma technology, which delivers a robust plasma with lower argon consumption. The combination of the vertical torch with dual view capability allows for flexible analysis of complex samples while measuring major and trace elements in the same analytical method. In addition, Universal Data Acquisition (UDA) can be applied. UDA collects data for every available wavelength in every sample, regardless of the elements specified in the analytical method<sup>6</sup>, an important tool for geochemical samples which can be highly variable.

All data obtained from the Avio 560 Max ICP-OES was collected and processed using Syngistix for ICP software (version 5.1 or higher). The software’s icon-based design and smart features help simplify method development and data evaluation.

The standard sample introduction system, consisting of a MEINHARD® nebulizer and cyclonic spray chamber, was used in this work. The Avio 560 Max instrumental conditions are listed in Table 2. All analytes were measured using auto-integration, which ensures a fast analysis for high-concentration analytes and accurate analysis for low-level analytes. Because of the complexity of geological sample matrices, Sc was used as an internal standard and added on-line through the HTS valve to all calibration standards and samples.

The analytical wavelengths and plasma view modes used for each analyte are listed in Table 3. Taking advantage of the dual view capability, radial view was used for major elements and axial view was used for trace elements. The wavelengths were selected based on the sensitivity, linear dynamic range, and freedom from spectral interference.

Table 2: Avio 560 Max ICP-OES with HTS Instrumental Parameters.

Avio 560 Max Parameter	Setting/Description
Nebulizer	MEINHARD® Type K
Spray Chamber	Baffled glass cyclonic
Sample Uptake Rate	1.0 mL/min
RF Power	1400 W
Nebulizer Gas Flow	0.65 L/min
Auxiliary Gas Flow	0.4 L/min
Plasma Gas Flow	12 L/min
Carrier Flow Rate	0.8 mL/min
Integration Time	Auto
Read Time Range	0.5 – 5 sec
Read Delay	8 sec
Replicates	2
Sample Uptake Tubing	Black/black (0.76 mm id)
Internal Standard Tubing	Green/orange (0.38mm id)
Drain Tubing	Gray/gray (1.30 mm id)
Internal Standard	Sc
HTS Parameter	Setting/Description
Sample Loop Volume	1 mL
Loop Fill Time	4 sec
Loop Rinse Time	3 sec
Carrier Solution	2% HNO <sub>3</sub> (v/v)

## Results and Discussion

### Smart Software

Syngistix for ICP software provides smart features and smart monitoring to ensure accurate results. In Data Viewer, the concentration of analytes in calibration units and in sample units can be quickly viewed during and after an analysis, as shown in Figure 1. The calibration linearity is also easy to check: with just one click, the details of the calibration curve will be displayed, including the calibration correlation coefficients, entered and calculated concentration, as well as the relative error of the calibration standards.

Table 3: Elements, Wavelengths, and Plasma View Modes

Analyte	Wavelength (nm)	Plasma View
Al	308.215	Radial
As	188.979	Axial
Ba	455.403	Radial
Be	313.107	Axial
Ca	317.933	Radial
Ce	413.704	Axial
Co	228.616	Axial
Cr	267.716	Axial
Cu	327.393	Axial
Fe	234.349	Radial
K	766.490	Radial
La	408.672	Axial
Li	670.784	Radial
Mg	285.213	Radial
Mn	257.610	Axial
Mo	202.030	Axial
Na	589.592	Radial
Ni	231.604	Axial
P	213.617	Axial
Pb	220.353	Axial
S	181.975	Axial
Sr	407.771	Radial
Ti	334.940	Axial
V	290.880	Axial
Zn	213.857	Axial
Internal Standard	Wavelength (nm)	Plasma View
Sc	361.383	Radial/Axial

For laboratories with high sample volumes, system robustness is most important. Syngistix for ICP software has the ability to continuously monitor internal standards throughout long analytical runs in Data Viewer, as shown in Figure 2 for the analysis of 500 geochemical samples where the internal standard intensities from each sample were normalized to the intensity of the calibration blank and plotted in real-time. The results show that intensities differed by less than 10% during the long analytical run, demonstrating the exceptional stability of the system.

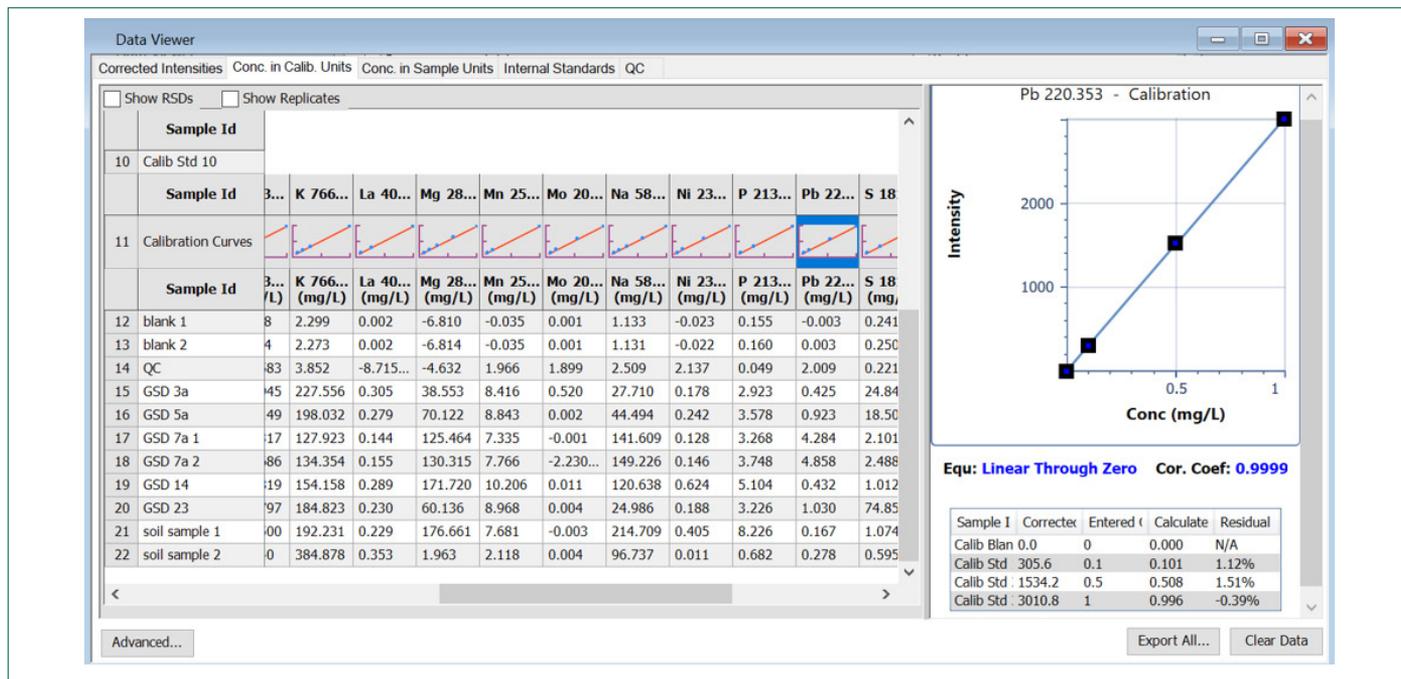


Figure 1: Calibration information displayed in Syngistix software's Data Viewer.

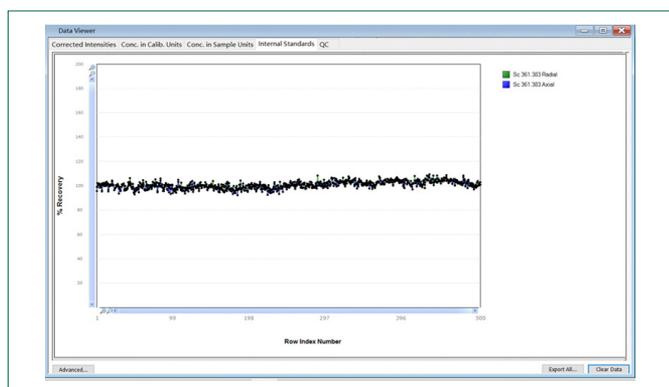


Figure 2: Internal standard stability over 8-hour run of geochemical samples.

### Method Detection Limits (MDLs)

The analysis was carried out using an external standard calibration method. The obtained linear correlation coefficients for all elements were greater than 0.999. The method detection limits (MDLs) of trace elements in the solid sample are shown in Figure 3, which were determined by analyzing 10 replicates of the blank solution 10 times and multiplying by 100 to account for the dilution of sample preparation (0.5 g of the sample dissolved in 50 mL). The obtained MDLs of all analytes were below or around 1 mg/kg, indicating that the HTS system can fully meet the analytical requirements of geochemical applications.

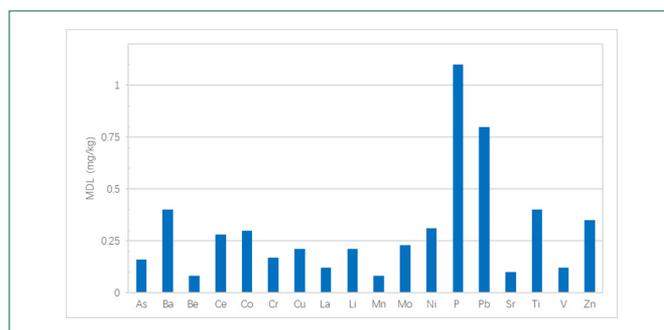


Figure 3: MDLs of trace elements achieved on the Avio 560 Max ICP-OES.

### Memory Effects

To check the memory effect, the washout times of high concentration elements in geochemical samples were evaluated. A standard solution containing 500 ppm Al and Fe and 200 ppm Ca, Mg, K and Na was run, followed by a blank solution using the timings in Table 1. As shown in Figure 4, the recoveries of analytes in the blank solution are all less than 0.1%, demonstrating that high analyte concentrations can be washed out in as little as a few seconds with the HTS introduction system, significantly reducing sample-to-sample carryover and improving sample throughput.

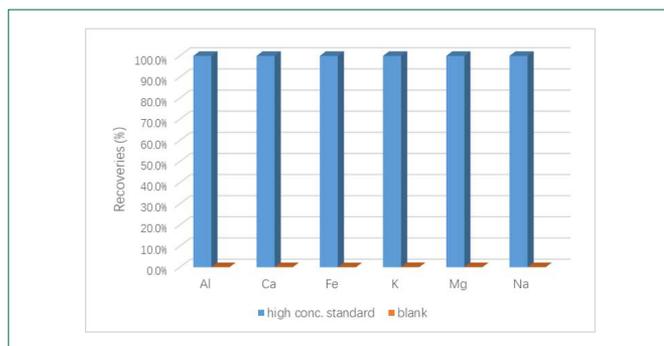


Figure 4: Memory effect test with the HTS system on Avio 560 Max ICP-OES.

## Accuracy

To verify the method accuracy, five sediment CRMs were analyzed. The certified concentrations in the CRMs are listed in the Table 4, and, as shown in Figure 5, all the recoveries were within 10% of their certified values, demonstrating the capabilities of the Avio 560 Max ICP-OES to accurately analyze samples with difficult matrices.

Table 4: Certified Values of Analyte in Five Stream Sediment Reference Materials.

Certified Values					
	GSD-3a	GSD-5a	GSD-7a	GSD-14	GSD-23
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
As	16.7 ± 1.3	75 ± 8	11.3 ± 1.0	18 ± 2	304 ± 20
Ba	550 ± 41	681 ± 16	437 ± 12	760 ± 47	590 ± 10
Be	2.7 ± 0.1	2.5 ± 0.1	1.6 ± 0.1	6.0 ± 0.6	2.4 ± 0.1
Ce	86 ± 4	82 ± 2	54 ± 2	106 ± 5	79 ± 2
Co	13.6 ± 0.5	15.3 ± 0.5	15.2 ± 0.7	28 ± 2	14.4 ± 0.5
Cr	48 ± 2	68 ± 2	43 ± 1	243 ± 16	72 ± 3
Cu	202 ± 7	118 ± 4	22.5 ± 1	66 ± 6	483 ± 20
La	43 ± 1	41 ± 1	27 ± 2	54 ± 3	40 ± 1
Li	35 ± 3	42 ± 2	37 ± 3	24 ± 2	38 ± 2
Mn	792 ± 25	917 ± 25	886 ± 25	1230 ± 82	1030 ± 0.003
Mo	48 ± 2	1.64 ± 0.09	0.82 ± 0.05	2.7 ± 0.3	1.56 ± 0.2
Ni	20 ± 1	31 ± 1	22 ± 0.6	87 ± 9	29 ± 1
P	426 ± 33	575 ± 23	633 ± 14	1000 ± 30	589 ± 39
Pb	40 ± 3	102 ± 4	555 ± 19	66 ± 6	126 ± 5
Sr	85 ± 4	78 ± 2	236 ± 6	216 ± 6	111 ± 4
Ti	4300 ± 400	4600 ± 200	4100 ± 200	14400 ± 500	4500 ± 200
V	74 ± 2	99 ± 3	77 ± 4	190 ± 25	101 ± 3
Zn	102 ± 2	263 ± 5	780 ± 19	165 ± 15	874 ± 19
	%	%	%	%	%
Al <sub>2</sub> O <sub>3</sub>	12.45 ± 0.07	13.4 ± 0.09	11.02 ± 0.08	13.39 ± 0.16	13.61 ± 0.12
Fe <sub>2</sub> O <sub>3</sub>	4.72 ± 0.07	5.27 ± 0.07	4.18 ± 0.05	9.5 ± 0.1	7.05 ± 0.11
MgO	0.72 ± 0.02	1.29 ± 0.03	2.5 ± 0.05	3.4 ± 0.1	1.25 ± 0.05
K <sub>2</sub> O	2.87 ± 0.06	2.5 ± 0.05	1.83 ± 0.05	2.3 ± 0.1	2.76 ± 0.07
Na <sub>2</sub> O	0.39 ± 0.03	0.64 ± 0.03	2.27 ± 0.05	2.0 ± 0.1	0.41 ± 0.04
CaO	0.44 ± 0.02	0.77 ± 0.02	2.96 ± 0.05	3.5 ± 0.1	1.64 ± 0.05

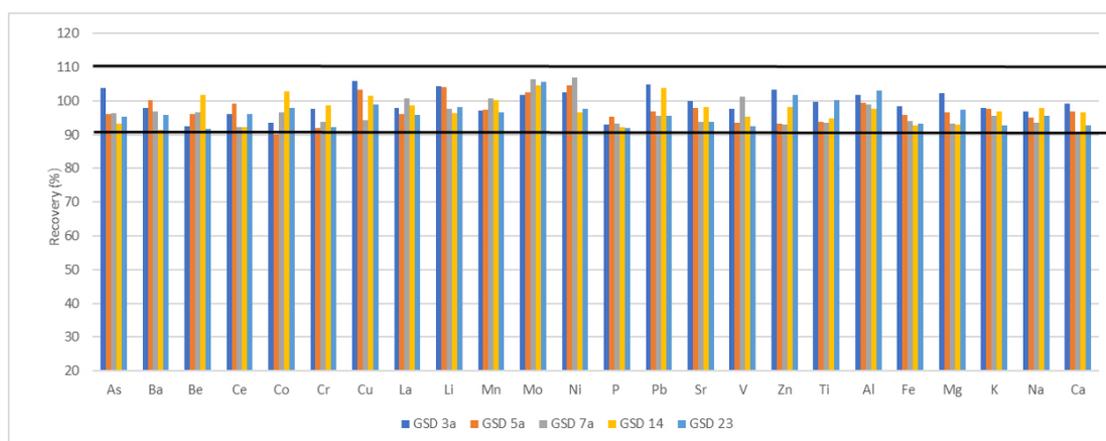


Figure 5: Recoveries of analytes in five different stream sediment reference materials.

### Stability

System robustness ensures that there will be no need to rerun the calibration standards during long analytical runs. To further verify the stability of the method, a continuing calibration verification (CCV) standard was repeatedly analyzed every 30 minutes throughout the 8-hour analytical run. The CCV standard contained 0.4 ppm of most analytes and 100 ppm of Al, Ca, Fe, K, Mg, and Na. As shown in Figure 6, the recoveries of all elements were within a  $\pm 10\%$  range throughout the entire analysis.

To further test the consistency of the calibration, the certified reference material sample GSD-7a was analyzed six times during the 8-hour analysis. Figure 7 shows the recoveries of all 24 elements were within 10% of known values. The results demonstrate that the HTS system provides reliable, automated sample introduction, allowing for fast analysis while still meeting accuracy requirements.

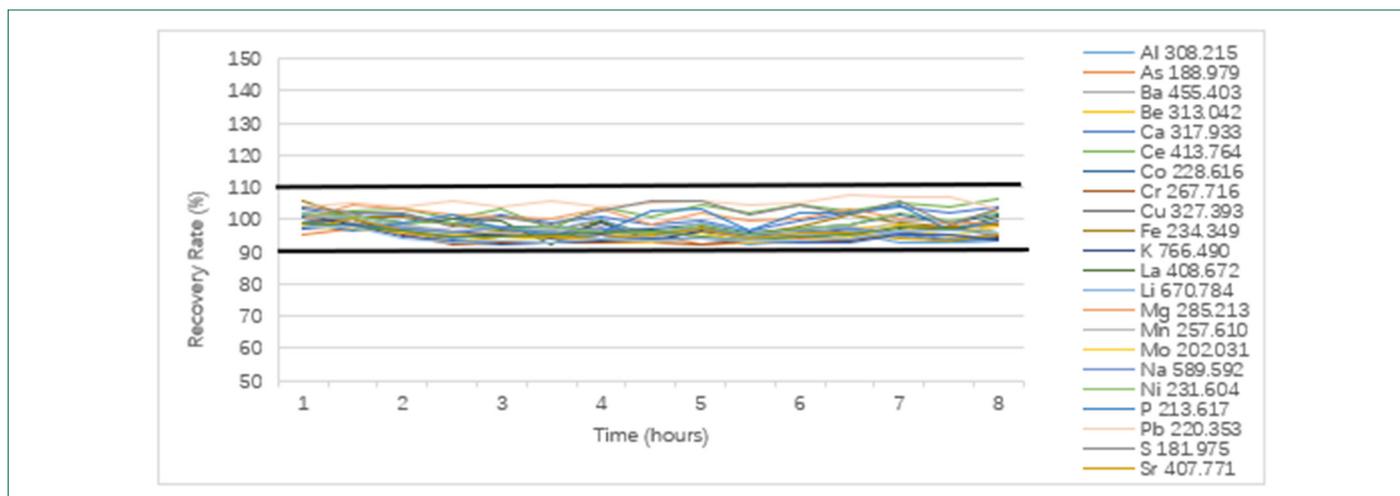


Figure 6: Recoveries of CCV standard during 8-hour analysis of geological samples.

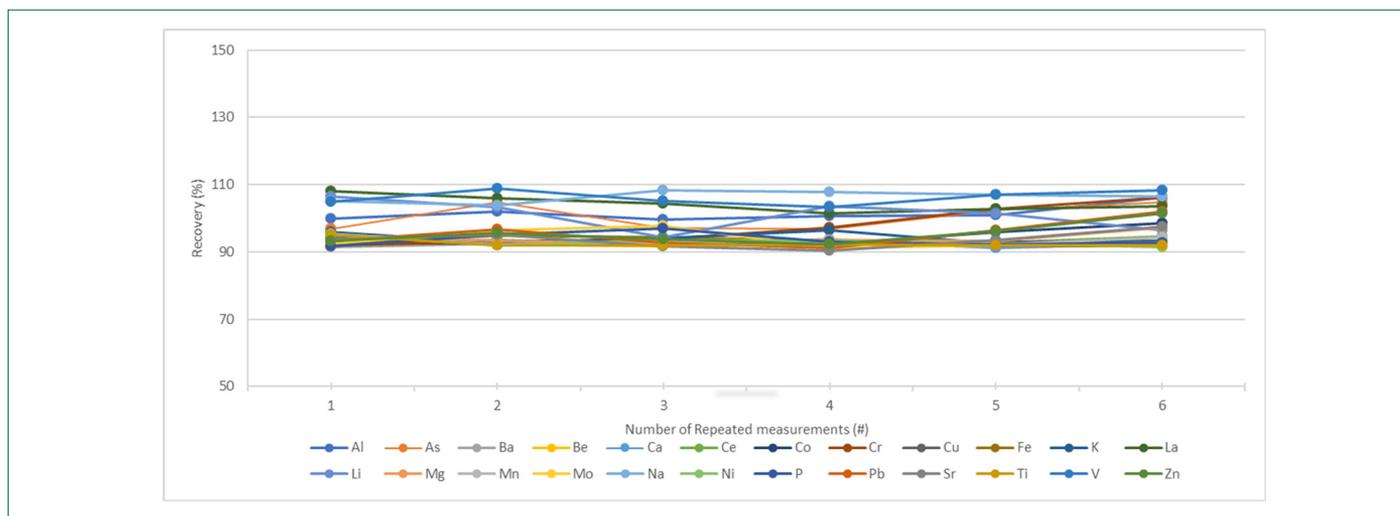


Figure 7: Analyte recovery in GSD-7a sample during 8-hour analysis.

## Conclusion

In this work, 24 elements in sediment samples were simultaneously determined using the Avio 560 Max ICP-OES. Excellent recoveries and stability for all elements were obtained with a sample-to-sample time of less than 60 seconds. These results have shown that the built-in HTS system on the Avio 560 Max can significantly reduce sample turnaround time and improve laboratory productivity by reducing sample uptake, stabilization, and washout times, demonstrating that the Avio 560 Max ICP-OES is well suited for geochemical laboratories, offering superior performance and high sample throughput.

## References

1. "High Throughput System for ICP-MS/OES", Product Note, PerkinElmer, 2020.
2. "Avio 550 and 560 Max Fully Simultaneous ICP-OES Systems", Product Note, PerkinElmer, 2020.
3. "Sensitivity, Background, Noise, and Calibration in Atomic Spectroscopy: Effects on Accuracy and Detection Limits", White Paper, PerkinElmer, 2018.
4. "Concepts, Instrumentation and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry", PerkinElmer, 1996.
5. "Increased Laboratory Productivity for ICP-OES Applied to U.S. EPA Method 6010C", Application Note, PerkinElmer, 2010.
6. "Universal Data Acquisition in Syngistix Software for the Avio 550/560 Max ICP-OES", Technical Note, PerkinElmer, 2020.

## Consumables Used

Component	Part Number
Sample Uptake Tubing, Black/Black (0.76 mm id), PVC	N0777043
Drain Tubing	09908585
Instrument Calibration Standard 1: 5000 mg/L Ca, K, Mg, Na	N9300218 (125 mL)
Instrument Calibration Standard 2: 100 mg/L Ag, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, V, Zn	N9301721 (125 mL)
Al Standard, 1000 mg/L	N9300184 (125 mL)
Fe Standard, 1000 mg/L	N9303771 (125 mL)
Li Standard, 1000 mg/L	N9303781 (125 mL)
Ce Standard, 1000 mg/L	N9303765 (125 mL)
La Standard, 1000 mg/L	N9303780 (125 mL)
P Standard, 1000mg/L	N9303788 (125 mL)
Ti Standard, 1000 mg/L	N9303806 (125 mL)
Ba Standard, 1000 mg/L	N9300181 (125 mL)
Mn Standard, 1000 mg/L	N9303783 (125 mL)
Autosampler Tubes, 50 mL	N0193234
PTFE DigiTUBEs, 50 mL	N9308024