Application note | 003719

Geosciences

Employing a novel AI/ML based semiquantitative approach for the calibration-free screening and estimation of multielement concentrations of geological samples

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Keywords

ICP-OES, SemiQuant, geosciences, sample preparation

Goal

Highlight the utility of the Thermo Scientific™ iCAP™ PRO Series ICP-OES powered by the Thermo Scientific™ Qtegra™ ISDS software for performing semiquantitative analysis of unknown geological samples

Introduction

Modern inductively coupled plasma optical emission spectroscopy (ICP-OES) systems are significantly advanced compared to prior generations. Current state systems can cover the complete wavelength range across the UV and the visible range of the spectrum in a single analysis. This allows for almost the entire periodic table of elements to be analyzed with high accuracy, low detection limits, and short analysis times. However, some understanding of the sample composition is highly beneficial for obtaining optimum results, finding the right instrument setup (i.e., sample inlet configuration) or defining calibration ranges that ensure all analytes are covered at the concentration levels in which they are present in a sample. To facilitate effective analysis, an estimate of the presence of elements and their concentration ranges, within reasonable uncertainty, might be sufficient for the laboratory to proceed with next steps in their workflow.

Such scenarios are common in the world of geosciences, for example in geochemical studies, where scientists or analysts often benefit from a rapid scan of unknown samples before further analysis, method development, targeted standards preparation, etc. A pre-screening step to ensure the absence of even trace-level contamination in solutions before proceeding to techniques such as multi-collector ICP-MS utilizing, for example, the Thermo Scientific™ Neoma™ MC-ICP-MS, is also a common requirement. Such sample screening is typically carried out using ICP-OES; however, with traditional methods, a calibration of the system is needed for a full quantification. The iCAP PRO Series ICP-OES with its unique capability to capture the full wavelength range between 167 and 852 nm allows confirmation of the presence of elements accessible for ICP-OES analysis. The Thermo Scientific™ Qtegra™ ISDS Software offers a novel approach of AI/ML-based semiquantitative assessment of the elemental composition of a sample.[1] This software tool estimates concentrations of a wide range of elements in unknown sample types without the need to prepare any calibration solutions, thus immensely reducing workload, time, and expenses. This application note describes how semiquantitative analysis can be used to screen typical geological and environmental samples to generate concentration estimates covering a wide range of analytes.

Experimental

Instrument parameters

A Thermo Scientific™ iCAP™ PRO XP ICP-OES Duo instrument was used with a Thermo Scientific™ iSC-65 autosampler for the semiquantitative evaluation of a large suite of elements in four different terrestrial rock and soil samples. Samples were analyzed using semiquantitative analysis (SemiQuant) without a preceding acquisition of a calibration curve or a reference standard but also quantified using the classical full quantification (eQuant) approach. The default tune set for aqueous samples was used for both evaluations, as listed in Table 1. The intelligent Full Range (iFR) mode available for the iCAP PRO Series ICP-OES instruments was used for viewing the full spectrum range of 167–852 nm, enabling truly simultaneous data acquisition for the eQuant approach in both Axial and Radial views.

Table 1. Instrument configuration and typical operating parameters

Instrument parameter	Setting
Spray chamber	Glass cyclonic
Nebulizer	Glass concentric nebulizer
Center tube	2.0 mm, quartz
Torch	EMT glass torch
Pump tubing	Sample: Tygon™ orange/white Drain: Tygon™ white/white
Pump speed	45 rpm for data acquisition 125 rpm for Fast Uptake
Nebulizer gas flow	0.5 L·min^{-1}
Auxiliary gas flow	0.5 L·min^{-1}
Coolant gas flow	12.5 L·min^{-1}
RF power	1,150 W
Autosampler	iSC-65 autosampler

Samples

Three rock digests and one soil digest were analyzed in this study (Table 2). Expected concentrations of the rock and soil samples are known from X-ray fluorescence (XRF) and other analytical techniques from previous studies.[2,3,4] The rock and soil digests were digested in acidic media (50 mg sample powder to final recovered volume of 25 mL) and at the final step diluted with 2% HNO_3 (full sample preparation details elsewhere[2]). To further test the utility of semiquantitative analysis for water samples (e.g., brackish waters, pore waters, seawater, etc.), the seawater reference material for trace metals NASS-6 from the National Research Council of Canada was diluted 10x and spiked with 0.1 mg·L^{-1} of a multielement standard to perform spike recovery tests using both semiquantitative and fully quantitative analysis.

Table 2. List of samples measured in the study

Sample name	Description
SDO-1	Black shale rich in organic matter[3] Certified reference material
CAST	Deep sea carbonate[e.g., 4] In-house reference material
BE-N	Basalt rich in Fe, Ca, Mg[3] Certified reference material
LOESS	Soil sample resembling the upper crust[e.g., 2] In-house reference material

Standards

No calibration solutions are required for semiquantitative analysis using the iCAP PRO Series ICP-OES. The SemiQuant data acquisition feature within the Qtegra ISDS Software employs artificial intelligence and machine learning to automatically evaluate a series of available wavelengths per analyte to detect the potential presence of interferences and estimate an approximate concentration of a large suite of elements within the sample. The number of elements for which data is generated can be selected individually, and groups of elements can be selected and saved as a template for subsequent analysis. By default, a total of 57 elements can be selected for semiquantitative analysis. The wide range of elements that can be assessed using semiquantitative analysis also benefits analysts with useful information about the presence (or absence) of analytes not included in the calibration standards. This complete assessment of a sample also allows the monitoring of elements indicative for important steps in the sample preparation (i.e., addition of correct amounts of internal standards, or acid composition to ensure adequate stability of solutions).

For fully quantitative analysis, performed in this study only to compare with data obtained from semiquantitative analysis and to demonstrate accuracy of the latter, calibration standards were prepared in 2% (v/v) HNO_3 and 0.5% HCl using multielement standard mixes (10 mg·L^{-1}, SPEX CertiPrep Group, Metuchen, NJ, US) at concentration levels of 0.5, 1, and 10 mg·L^{-1} for a range of analytes.

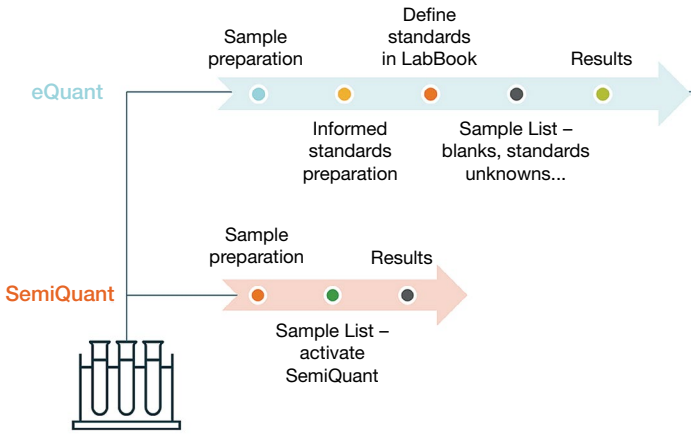

Figure 1. Workflows for eQuant and SemiQuant analysis using the iCAP PRO Series ICP-OES

Results and discussion

Analysis of water samples

The accuracy of the results obtained using semiquantitative analysis was first tested using a spiked NASS-6 seawater reference material. The CRM was diluted 10x prior to spiking to mimic the matrix load often found in pore waters or brackish waters. The sample was divided into two aliquots—one was spiked with 0.1 mg·L^{-1} concentration of a mixture of several trace elements, while the other aliquot was spiked with a similar volume of 2% (v/v) HNO_3. The samples were analyzed using both semiquantitative and fully quantitative analysis. Comparing the results obtained using semiquantitative analysis to the expected concentrations (and those in fully quantitative analysis), as illustrated in Figure 2, a total of 23 elements showed highly acceptable recovery, in the ±20% range. Typically, semiquantitative analysis is expected to yield accuracies within ±30%,[1] which was exhibited by nine elements. This demonstrates the possibility of obtaining nearly accurate data even in the absence of any calibration solution or an internal standard, including several elements where the AI model suspects an interference. Accurate concentration estimation of possibly interfered elements is a unique benefit of the SemiQuant feature, which profits from the use of multiple wavelengths captured in the Full Frame by the iCAP PRO Series ICP-OES instruments (Figure 3) vs. typically one or two pre-selected wavelengths per element.

Analysis of rock/soil digests

The accuracy of the data obtained from semiquantitative analysis was further evaluated by measuring geological rock and soil digests. Recoveries were calculated for the CRMs against nominal values, and for the in-house reference materials against values obtained by X-ray fluorescence (XRF) (backed by ICP-OES data), as acquired in the Institute for Chemistry and Biology of the Marine Environment, Carl von Ossietzky University, Oldenburg, and published in previous studies.[e.g., 2] The data are summarized in Table 3 and illustrated in Figure 4. The data from the two different techniques—fully quantified XRF and the semiquantitative approach of this study—show very good comparability with each other. Several elements showed exceptional accuracy in the ±10–15% range, for example, Ca in all four samples, Sr and V in SDO-1 and Loess. Overall, the elements were again found to fall well within the typically expected ±30% range, with elements possibly overlaid with interferences or exceedingly high concentrations in the samples showing poorer recoveries. The data from semiquantitative analysis was again compared to the results obtained in a fully quantitative analysis, and also in this comparison, showed good agreement with similar accuracy levels. The results indicate that even for complex matrices like rock/soil digests the SemiQuant software tool provides a useful overview of the presence and the concentration of different elements without the need to prepare any calibration solutions.

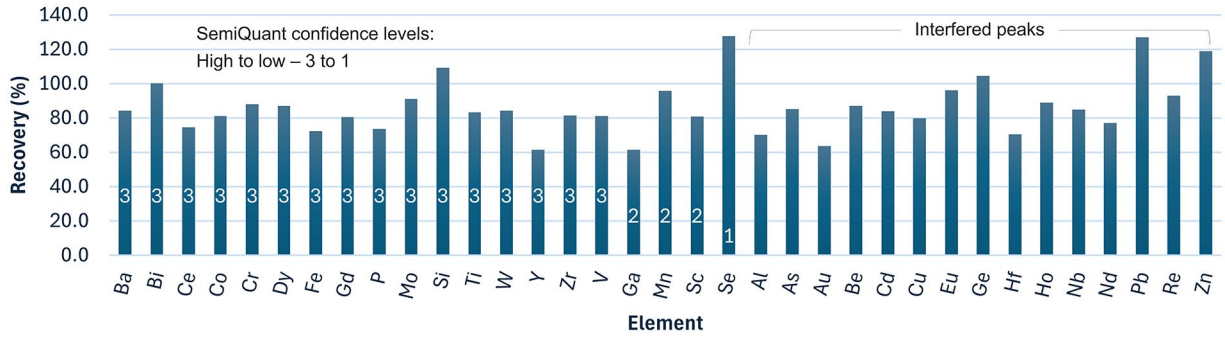

Figure 2. Spike recovery estimates, and respective confidence levels based on the number of reliable wavelengths used by the AI model, from semiquantitative analysis compared to expected spiked concentration of 0.1 mg·L^{-1} in 10x diluted NASS-6

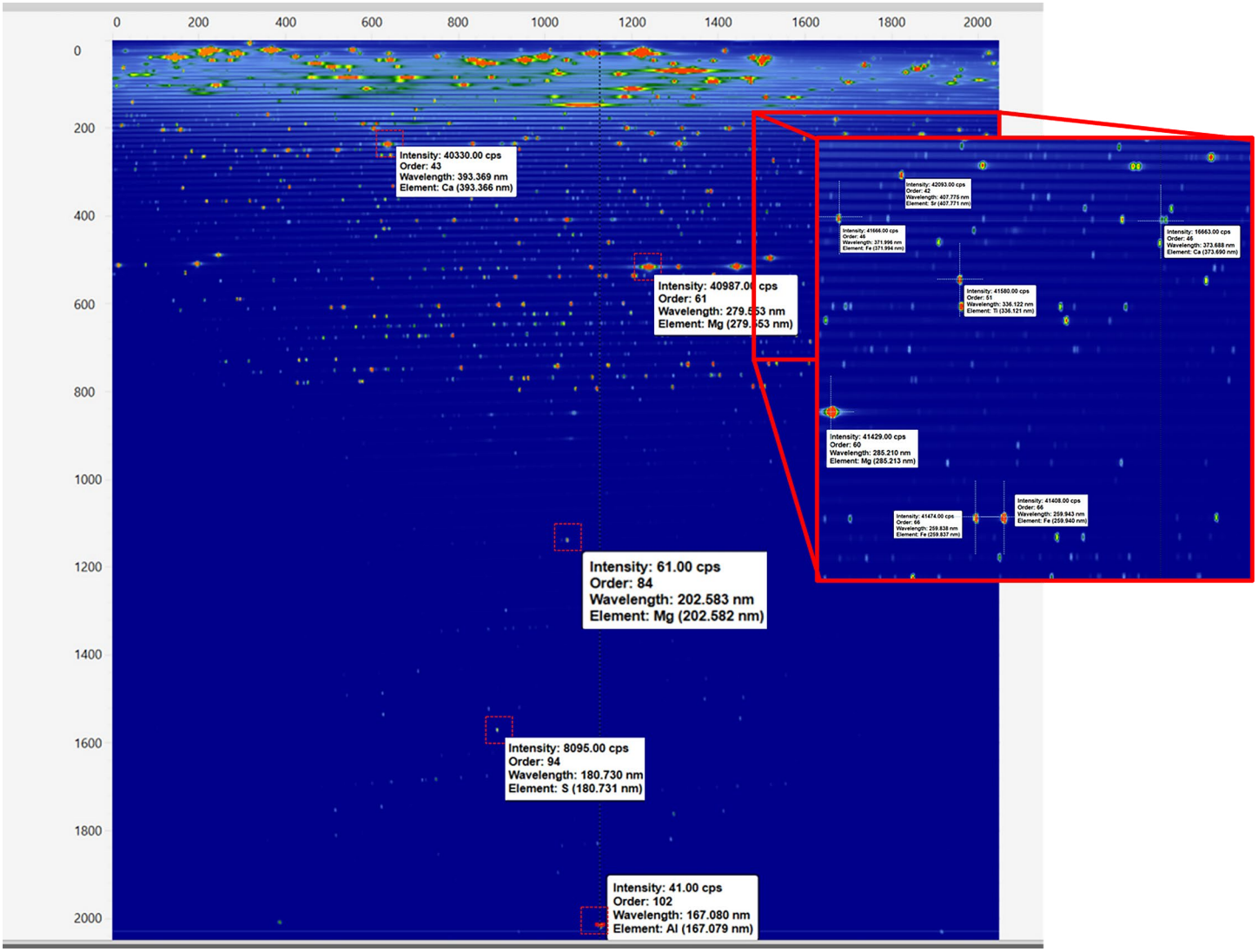

Figure 3. Full Frame image of an unknown sample from the iCAP PRO Series ICP-OES where the entire spectrum from 167 to 852 nm is captured simultaneously in a single exposure

Table 3. Elemental concentrations found in rock and soil sample digests—concentrations from XRF (from a different study[2,3,4]), from SemiQuant, and the accuracy of SemiQuant expressed as recovery against XRF concentrations. The elements for which SemiQuant data is missing are those that were highly interfered and can be resolved with means such as Inter Element Correction (IEC)[5], also a part of the Qtegra ISDS Software.

	Concentrations ($mg \cdot kg^{-1}$)		Recovery SemiQuant vs. Nominal (%)	Concentrations ($mg \cdot kg^{-1}$)		Recovery SemiQuant vs. XRF (%)
	Certified	SemiQuant		XRF	SemiQuant	
Elements	Sample 1 – SDO-1			Sample 2 – CAST		
Ti	4256	3400	80	1197	1147	96
Al	61921	55313	89	18393	12608	69
Fe	61342	37652	61*	12364	7888	64*
Mn	325	259	80	462	-	-
Ca	7504	6601	88	292956	256703	88
Na	2671	3356	126	11719	12510	107
K	27810	23075	83	5649	-	-
P	567	424	75	423	491	116
S	53500	53744	100	-	-	-
Cr	66.4	57.1	86	45.0	38.9	86
Cu	60.2	45.7	76	53.0	45.7	86
Mo	134	129.3	96	-	5.7	-
Ni	100	73.2	73	40.0	33.3	83
Sr	75.1	74.1	99	1291	984.0	76
V	160	146.4	92	37	32.0	86
Y	40.6	28.3	70	14.0	9.5	68
	Sample 3 – BE-N			Sample 4 – Loess		
Ti	15647	13397	86	3982	3458	87
Al	53295	37674	71	41810	31773	76
Fe	89529	49860	56*	18326	11673	64*
Mn	116	-	-	410	313	76
Ca	99342	91475	92	44506	43657	98
Na	23591	22073	94	8160	9267	114
K	11539	14754	128	16112	14495	90
P	4582	4281	93	516	422	82
S	300	311	104	-	-	-
Cr	360	305.3	85	73.8	67.2	91
Cu	72.0	68.4	95	4.0	-	-
Ni	267	175.3	66	21.3	16.0	75
Sr	1370	1065.5	78	164	153.5	94
V	235	206.4	88	50.2	47.7	95
Y	24.7	19.7	80	29.3	22.0	75

*Low recoveries associated with very high concentrations of respective matrix elements in the samples.

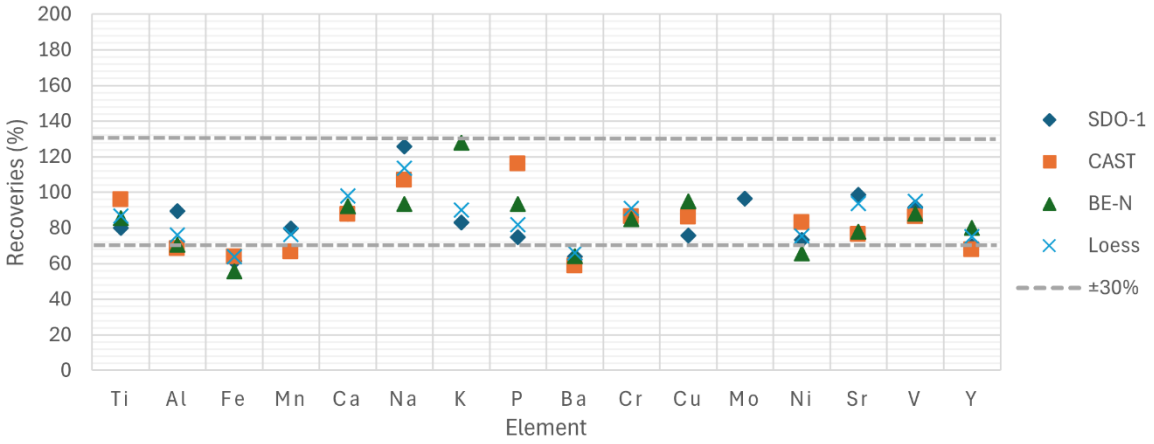

Figure 4. Accuracy of the semiquantitative measurements of geological samples in the present study compared to results obtained from XRF analysis. Low recoveries below 70% are linked to high concentrations of the respective matrix elements (e.g., up to 9% Fe in the rock samples).

Conclusions

The study demonstrates that the SemiQuant feature of the Qtegra ISDS Software is a powerful tool for screening geological samples for the presence of a wide range of elements despite the challenging matrices. Accurate concentration estimates of several elements within the unknown samples are achieved automatically by employing a novel calibration-free AI/ML approach. This can help laboratories to quickly scan fresh digests for complete and effective sample processing, without the need to spend valuable time on preparation of a series of calibration standards. It can facilitate finding the right calibration ranges for the analysis of previously unknown samples with better accuracy. The highlights of the study are listed below:

- The accuracy of the SemiQuant analyses was tested and proven by a spike recovery test on NASS-6, a seawater reference material, as well as by measuring rock and soil digests where concentrations were known from previous XRF measurements.
- Very good agreement was seen across all data sets—fully quantitative, semiquantitative analysis using ICP-OES, as well as XRF as a reference—confirming the potential of AI/ML-based semiquantitative analysis when compared to other classical techniques of quantification.
- SemiQuant results are obtained purely by using the iCAP PRO Series ICP-OES instrumentation along with the powerful features of the Qtegra ISDS Software, without the need for running any calibration solutions. This helps accelerate workflows by saving analysts and laboratories valuable time, effort, and costs.

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