

Soil analysis

Reliable analysis of soil samples for environmental monitoring using triple quadrupole ICP-MS

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Keywords

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Goal

This application note focuses on the analysis of soil samples using the Thermo Scientific™ iCAP™ TQe ICP-MS. The use of oxygen as the only reactive gas provides a simple and straightforward method for analysis, combining superior interference removal and improved sensitivity with sample throughput typically achieved on single quadrupole ICP-MS systems.

Introduction

Land resources are important components of an ecosystem that provide the basis for the normal survival of organisms. Soil quality and quantity are essential for ensuring ecological security and flourishing of plants in the environment, which will ultimately affect the health of animals and human beings and the development of human society. With rapid economic development, people are paying more and more attention to environmental pollution. Therefore, dealing with pollutants in soil is a key point in the current policy for environmental protection, driven both by governmental institutions as well as public interest. Applicable standards governing the determination of toxic metals in soils, but also sewage sludges often used as fertilizers, are put in place globally to achieve consistent monitoring of common pollutants. Researchers and applied testing laboratories work to fully understand the root cause and potential impact of soil pollution, as well as its distribution through mobilization or diffusion. Thus, accurate and rapid analysis of the content of metal substances in soil has become an increasingly important scientific research direction.

Inductively coupled plasma mass spectrometry (ICP-MS) is a rapid multi-element analysis technique, widely used for the analysis of highly complex samples such as soil and sludge digests. Commercial laboratories engaged in the commissioned testing of environmental samples strive to establish a set of simple and consistent analysis procedures, typically analyzing more than 30 elements. To meet the required performance criteria, allowing to analyze a high number of samples with highest accuracy, precision, and robustness over extended periods, the iCAP TQe ICP-MS can use Argon Gas Dilution (AGD) to enhance the overall matrix tolerance of the system. AGD enables laboratories to analyze complex and variable high-matrix samples, eliminating the need for sample dilutions beforehand or preparation of matrix-matched calibration standards. Manual dilution is laborious and incurs the risk of contamination and human error, both of which can impact the ability of the method to meet regulatory limits. Routine analysis of high-matrix samples after long runs can also cause signal stability issues and increase the frequency of instrument maintenance. At the same time, spectral interferences may cause positive bias on key analytes if not accounted for. Whereas single quadrupole ICP-MS systems are often applied in high-throughput laboratories, triple quadrupole instruments are known to provide advanced interference removal, and hence assure consistent data quality regardless of the matrix. However, the use of multiple reactive gases is causing methods to take longer and may limit throughput, especially for high-throughput analysis and fast data reporting for large batches of samples.

This application note describes the analysis of different soil samples using the iCAP TQe ICP-MS to deliver a full multi-elemental analysis with unmatched accuracy and throughput. All measurements were performed in a single mode using oxygen as the only reaction gas. This single O₂ measurement mode can significantly save the analysis time without mode switching, which is the most time-consuming step besides acquisition time, sample uptake, and rinse. Different soil samples were analyzed, and reliable performance is demonstrated over 12 hours, allowing the analysis of more than 300 samples per day.

Experimental Instrumentation

An iCAP TQe ICP-MS system was used to analyze different soil samples. To extend the matrix tolerance of the system beyond the often perceived limit of 0.2% (m/v) total dissolved solids (TDS) (due to constraints imposed by the interface cones on all ICP-MS systems) and to assure consistent results independent of the sample type, the iCAP TQe ICP-MS was operated using

argon gas dilution (AGD). To overcome interferences, the instrument was operated using the O₂ reaction mode for all analytes. This facilitates complete removal of related interferences while maintaining high sensitivity for critical elements.

The instrument parameters used for this application work are shown in Table 1.

Table 1. Instrument parameters

Parameter	Value
Nebulizer	Borosilicate glass Micromist™, 400 µL·min ⁻¹
Peristaltic pump tubing	PVC orange green tubing, 0.38 mm i.d. for both internal standard and sample
Peristaltic pump speed	25 rpm
Sample depth	8 mm
Spray chamber	Quartz cyclonic, cooled at 2.7 °C
Torch	Quartz torch
Injector	2.5 mm i.d., Quartz
Interface	Nickel sampler and nickel skimmer cone with high matrix insert
Plasma power	1,550 W
Nebulizer gas	0.35 L·min ⁻¹
Additional gas flow (AGD)	55% (1,000 mL·min ⁻¹ MFC)
QCell setting	TQ-O ₂
QCell gas flow	O ₂ at 0.2 mL·min ⁻¹
Scan setting	0.1 s dwell time, 5 sweeps, 3 main runs
Analysis time per sample	Total 2 min 41 s, including uptake and wash out

To automate the analysis, a Thermo Scientific™ iSC-65 Autosampler was used. The iSC-65 Autosampler was specifically designed to meet the needs of analytical testing laboratories and features a series of innovative solutions to facilitate highest reliability and efficient use in the laboratory. This includes not only a visualization of the instrument status by means of an LED panel, but also a Step Ahead function, allowing analysis of two adjacent samples to be overlapped, as the rinsing of the autosampler probe is already started while the data acquisition is still ongoing. In this work, a Step Ahead time of 10 s was applied and shortened the time required for data acquisition by approximately 50 min.

Samples and sample preparation

One of the main challenges associated with the analysis of soil samples is the highly variable matrix load. Whereas soil samples may vary mostly in the concentrations of major analytes, such as the alkali and alkaline earth elements, sediment samples may also contain higher amounts of transition metals. In addition, rare earth elements (REEs) in soil samples can cause doubly charged ion interferences, potentially causing interferences on key analytes, such as $^{75}\text{As}^+$ (interfered by $^{150}\text{Sm}^{++}$, for example) and Se (interfered by various isotopes of gadolinium). In order to cover a wide variety of potential sample matrices, a total of eight samples (including three certified reference materials), covering different types of soils and sludge, were analyzed in this study. An overview of all the samples is shown in Table 2.

Table 2. List of the eight different soil samples including CRM samples analyzed during this work

	Item	Place
1	Sample 1	Rock
2	Sample 2	Estuary sediment
3	Sample 3	Rock
4	Sample 4	Sludge
5	Sample 5	Domestic soil
6	CRM	NIST CRM 2709a, San Joaquin Soil
7	CRM	NIST CRM 2702, Inorganics in marine sediment
8	CRM	NRCC CRM PACS-2, marine sediment

An aliquot of 0.1 g of the sample to be tested (weighed accurately to 0.0001 g) was placed into a vessel of microwave digestion system (ETHOS™ EZ SK10, Milestone, Italy). After the addition

of 1 mL HCl, 4 mL HNO_3 , and 1 mL H_2O_2 in a fume hood, the vessel was sealed and placed in the microwave system. The temperature was ramped up to 180 °C in approximately 15 min and remained at 180 °C for 20 min. At the end of the microwave digestion program, the vessels were allowed to cool to room temperature before removing them from the microwave system. After cooling, the digested solutions were quantitatively recovered and made up to a final volume of 50 mL using ultra-pure water. The sample preparation accomplished with microwave digestion using aqua regia is suitable for analysis of extractable analytes but would not provide information regarding total content of the soil matrix. For determination of total content, samples need to be digested using hydrofluoric acid (HF) to ensure complete digestion of all components, especially silicates. However, due to health and safety concerns associated with HF, many laboratories avoid its use during sample preparation and use aqua regia as an alternate sample preparation approach.

Method development

In a routine operation procedure, the instrument was switched on and after an automatic warm-up time of 15 minutes, the instrument's settings and performance were verified. This basic system suitability test comprised a performance report in STD mode to verify that the required signal intensity and stability were obtained, as well as to verify other important plasma parameters, such as oxide ratio ($^{140}\text{Ce}^{16}\text{O}^+ / ^{140}\text{Ce}^+$) and the formation of doubly charged ions ($^{137}\text{Ba}^{++} / ^{137}\text{Ba}^+$). After completion of the initial performance check, the TQ- O_2 mode performance was also checked for consistent performance using the software supplied performance report. The process of interference removal using O_2 as a reactive gas is highlighted using ^{75}As and ^{111}Cd as examples in Figure 1.

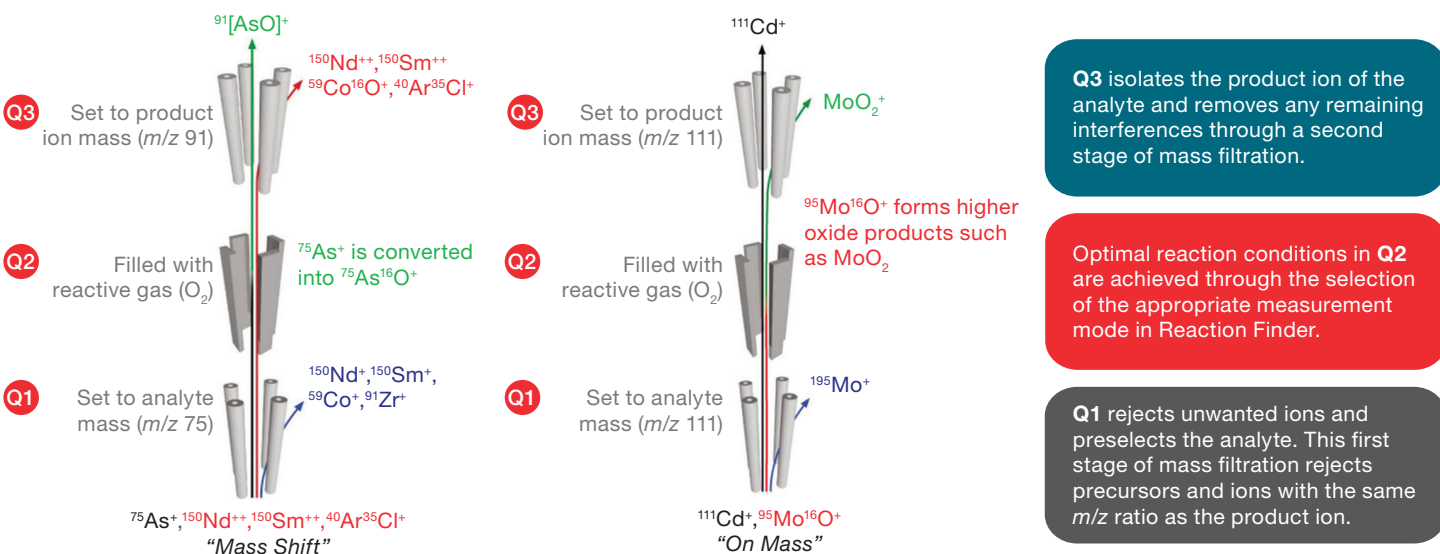


Figure 1. The process of interference removal using O_2 as a reactive gas for analysis of ^{75}As and ^{111}Cd

The selected target analytes $^{75}\text{As}^+$ and $^{111}\text{Cd}^+$ Q1 enter together with all interferences, here mostly polyatomic interferences formed from other components of the sample matrix and the ambient air surrounding the plasma. In the first quadrupole (Q1) all ions apart from the target analyte are rejected, so that possible side reactions and contributions of other interferences at the intended product ion mass are eliminated.

In Q2, the target analyte or the interfered compound are reacting to form $^{91}[\text{As}^{16}\text{O}]^+$, which is called “Mass Shift”, and $^{127}[\text{Mo}^{16}\text{O}]^+$, which is called “On Mass”, by using the reactive gas, whereas the interference is not reacting in the same way.

The third quadrupole (Q3) performs a final mass filtration step and isolates the product ion once again from other ions with different m/z ratios. The target analyte can therefore be detected free from interference and hence any unwanted bias.

To create a method for analysis using O_2 as the only reactive gas, the proposed settings of the Reaction Finder Method Development Assistant, provided in the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software, were manually overwritten.

Results and discussion

Linearity assessment

The linearity of the instrument was demonstrated using a seven-point calibration curve. All calibration curves from trace elements to major elements were established in the same run and showed excellent correlation coefficients (>0.999 or higher). The calibration solutions used for establishing multielement calibration curves and the QC standards for all elements are summarized in Tables 3 and 4.

Calibration standards were prepared in 2% (v/v) nitric acid, with analyte concentrations covering the range expected in the samples. An internal standard solution, containing $100\ \mu\text{g}\cdot\text{L}^{-1}$ Ge as well as $20\ \mu\text{g}\cdot\text{L}^{-1}$ Rh and Re in 2% (v/v) nitric acid was added to all samples on-line via a T-piece (with a mixing rate between internal standard and samples of 1:1) before entering the spray chamber.

Table 3. Concentration levels for calibration standards. All concentrations are given in $\text{mg}\cdot\text{L}^{-1}$.

Elements	STD 1	STD 2	STD 3	STD 4	STD 5	STD 6
Na, Mg, K, Ca	100	20	10	5	2	1
Fe	40	8	4	2	0.8	0.4
Al	4	0.8	0.4	0.2	0.08	0.04
Ba	2	0.4	0.2	0.1	0.04	0.02
V, Se, Mo	1	0.2	0.1	0.05	0.02	0.01
Cr, Cu, Zn	0.4	0.08	0.04	0.02	0.008	0.004
Be, Mn, Co, Ni, As, Ag, Cd, Tl, Pb	0.2	0.04	0.02	0.01	0.004	0.002

Table 4. Concentration levels for QC standard. All concentrations are given in $\text{mg}\cdot\text{L}^{-1}$.

QC elements	Concentration	QC elements	Concentration
Mn	3.0	As	0.080
Ba	1.3	Co	0.050
Zn	1.0	Mo, Tl	0.015
V, Cr	0.6	Se	0.008
Cu, Pb	0.2	Be	0.005
Ni	0.15	Ag, Cd	0.0015

Detection limits

Detection limits (DLs) in solution were established by measuring a reagent blank solution, which was prepared in parallel to the samples. This solution was analyzed 10 times, with the resulting instrumental detection limits being calculated by Qtegra ISDS Software automatically using the 3σ criterion.

A full comparison of all DLs achieved by using TQ- O_2 mode versus KED mode are listed in Table 5. TQ- O_2 mode DLs are lower than the single KED mode, especially for the elements which use “Mass Shift” or “On Mass” reactions, for example arsenic, cadmium, and selenium. In particular for selenium, a dramatic improvement can be realized due to the fact that the prevailing argon based polyatomic interferences on the most abundant isotope ^{80}Se can be fully eliminated, whereas in KED, normally a less abundant, but less interfered isotope has to be selected. For elements that do not immediately benefit from advanced interference removal, like manganese, copper, or lead, the observed detection limits are at least equivalent, if not improved as well using TQ- O_2 mode. Beryllium is a very important example, as this light element would normally be analyzed even without the use of a CRC for interference removal, as the use of a gas would lead to severe ion losses and decreased sensitivity. Nonetheless, the detection limit is improved by a factor of 6 when using a heavier gas (O_2) compared to helium. This can be explained by effects such as collisional focusing that lead to an improved ion transmission in the cell. Using TQ- O_2 mode, two benefits can be achieved at once—more effective and complete removal of interferences and reduced limits of detection. The DLs obtained by the measurement are much lower than the requested DLs, and this proves that the performance of the instrument greatly exceeded the requirements of the regulation methods, even including the dilution factor incurred during sample digestion.

Table 5. Comparison of DLs between TQ-O₂ mode and single KED mode

Element	DL (TQ-O ₂) (ng·L ⁻¹)	DL (KED) (ng·L ⁻¹)	Element	DL (TQ-O ₂) (ng·L ⁻¹)	DL (KED) (ng·L ⁻¹)
¹⁰⁷ Ag	0.2	0.8	⁹⁸ Mo	0.6	3.0
⁷⁵ As	1.0	7.0	⁶⁰ Ni	2.0	2.0
¹³⁸ Ba	0.9	0.7	²⁰⁸ Pb	0.7	2.0
⁹ Be	11.0	6.7	¹²¹ Sb	0.2	6.8
¹¹¹ Cd	0.003	0.6	⁸⁰ Se	5.7	22,940
⁵² Cr	19.0	15.0	²⁰⁵ Tl	0.3	0.3
⁵⁹ Co	12.0	4.0	⁵¹ V	0.9	4.7
⁶³ Cu	0.2	3.3	⁶⁶ Zn	1.2	1.7
⁵⁵ Mn	2.6	1.2			

Quality control procedure and results

For reliable analysis in an essential testing laboratory, it is important that the results obtained are also accurate and precise in longer batches comprising different sample types. Commonly, quality control (QC) standards containing a known concentration of all analytes are analyzed periodically during a batch to monitor the analysis performance.

To simulate a high-volume sample analysis, a larger sample batch was scheduled for analysis containing all the samples collected as well as certified reference materials. The batch was designed to allow for an approximate runtime of 12 hours continuously, including a total of 300 samples, which included about 270 unknown samples, split into the calibration block and a series of fixed sample sequences. Each sequence in the batch consisted of 15 individual samples and was concluded with a quality control standard (continuing calibration verification, QC sample) before continuing with the next sequence. A full overview of all QC samples that were successfully acquired is shown in Figure 2. As can be seen from the data, the average recovery was excellent, being within 86% and 113%.

As part of this study, three certified reference material (CRM) samples, NIST™ SRM™ 2702 - Inorganics in marine sediment; NIST™ SRM™ 2709a - San Joaquin soil and PACS 2 - Marine Sediment Reference Materials (National Research Council of Canada) were also periodically analyzed through the whole batch. The results obtained for minor and major elements concentrations of three CRM samples are shown in Table 7.

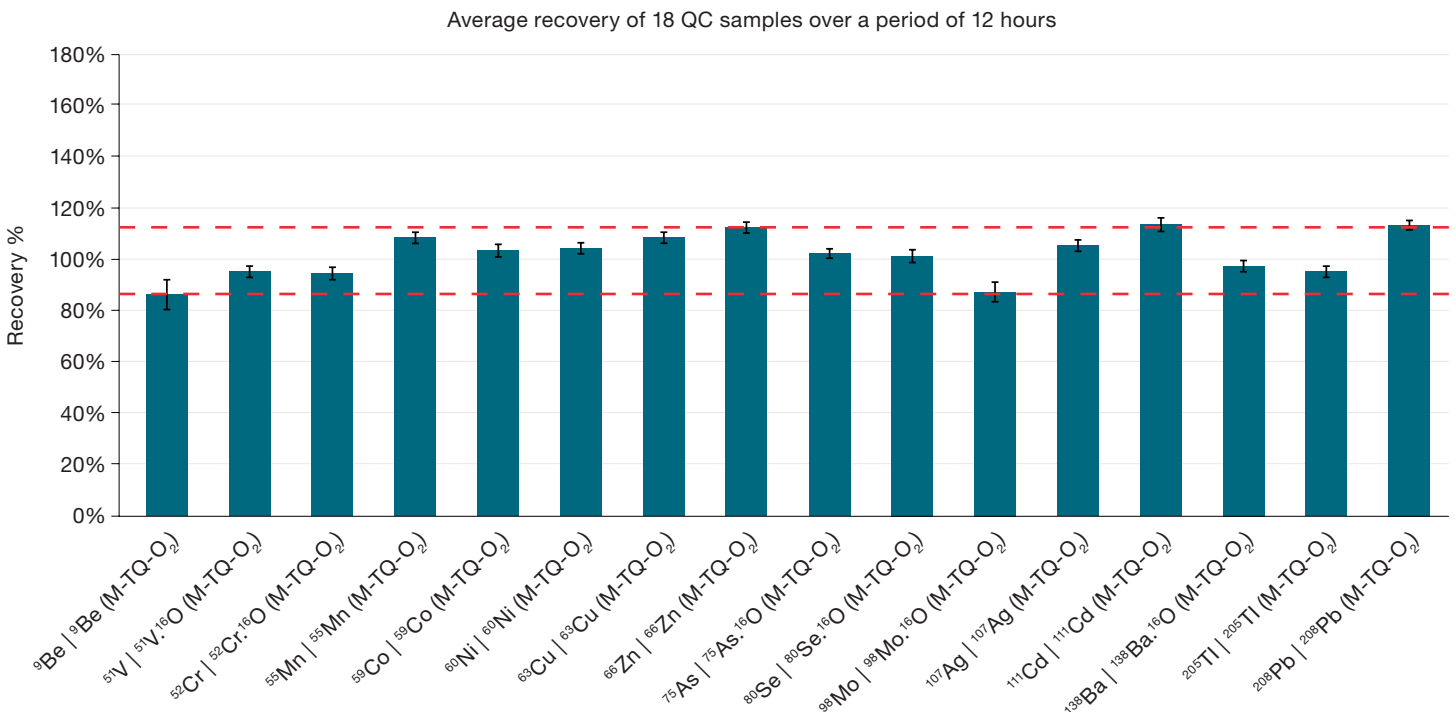


Figure 2. QC samples recovery (86–113%) observed during the full duration of this study

Table 7. Certified quantity values and measured values for CRM samples

Elements	2702			2709a			PACS-2		
	Certificated (mg·kg ⁻¹)	Measured (mg·kg ⁻¹)	%	Certificated (mg·kg ⁻¹)	Measured (mg·kg ⁻¹)	%	Certificated (mg·kg ⁻¹)	Measured (mg·kg ⁻¹)	%
Ag	0.622	0.653	105%	–	–	–	1.22	1.34	110%
As	45.3	46.1	102%	10.5	9.65	92%	26.2	26.3	100%
Ba	397.4	384.7	97%	979	995	102%	–	–	–
Be	3	2.58	86%	–	–	–	1	1.08	108%
Cd	0.817	0.923	113%	0.371	0.377	102%	2.11	2.16	102%
Cr	352	332	94%	130	108	83%	90.7	79.7	88%
Co	27.76	28.71	103%	12.8	13.0	102%	11.5	10.4	90%
Cu	117.7	126.6	108%	33.9	34.4	101%	310	353	114%
Mn	1757	1895	108%	529	539	102%	440	389	88%
Mo	10.8	9.37	87%	–	–	–	5.43	4.46	82%
Ni	75.4	78.6	104%	85	83.2	98%	39.5	40.4	102%
Pb	132.8	150.6	113%	17.3	15.2	88%	183	199	109%
Se	4.95	5.02	101%	–	–	–	0.92	0.91	99%
Tl	0.826	0.783	95%	0.58	0.585	101%	–	–	–
V	357.6	338.6	95%	110	97.5	89%	133	116	87%
Zn	485.3	541.4	112%	103	99.8	97%	364	370	102%

All results for the CRM samples were also found to be in excellent agreement with the reference values. It is noteworthy to mention that the CRMs used in this study covered a concentration range between sub mg·kg⁻¹ up to several thousand mg·kg⁻¹.

Long term stability

The recovery of the internal standards (a plot with percent recovery is generated by the Qtegra ISDS Software automatically)

observed during the analysis of more than 300 samples in a 12-hour measurement is shown in Figure 3. All isotopes used as internal standards showed excellent recoveries within 82% and 108% over the entire duration of the experiment and in different types of sample matrices. This recovery demonstrates stability and accuracy through the run, with no adverse effects caused by the sample matrix (e.g., signal suppression or enhancement).

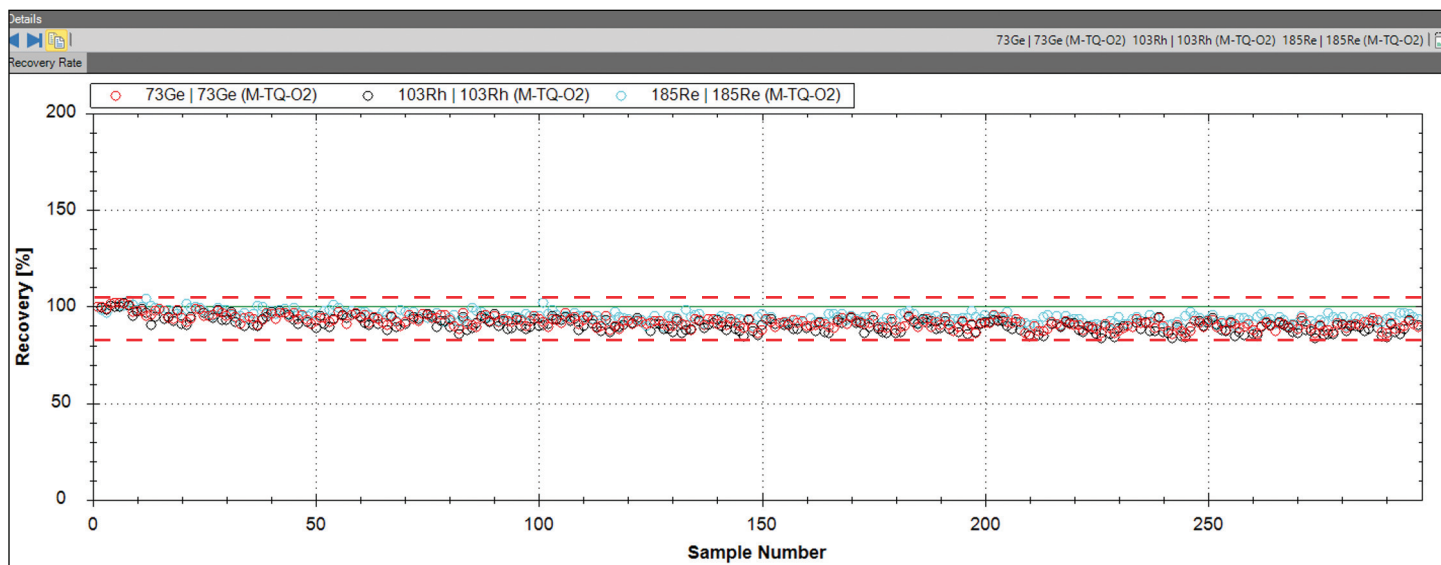


Figure 3. Recoveries of the internal standards from the analysis of 300 samples over 12 hours showing recoveries within 82% and 108%

Conclusion

This application note shows how rapid, accurate, and precise routine monitoring of soil samples, with respect to elemental composition can be effortlessly achieved using the iCAP TQe ICP-MS system combined with the iSC-65 Autosampler. The instrument meets all the requirements of the Chinese regulations tasked with the analysis of different type of soil samples. Key takeaways from this study were:

- All analytes were measured using a single measurement mode on the iCAP TQe ICP-MS using oxygen as the collision/reaction cell gas, a new approach developed and tested to prove the suitability of these instruments also in applied testing applications.
- The single mode analysis allowed for highly sensitive and accurate analysis of all analytes of interest, including the potentially challenging analytes arsenic, selenium, and cadmium, in highly challenging matrices.
- The TQ-O₂ mode allowed the analysis from light element ⁷Li to heavy element ²³⁸U with excellent detection limits and accuracy.
- The robust and stable analytical performance of the system was demonstrated over 12 hours during an uninterrupted measurement of 300 different kind of soil samples

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