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Composition characterization of lithium-rich minerals as an exploitable source of lithium using ICP-OES

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Keywords

Green energy, high matrix, ICP-OES, lithium-ion battery, lithium mining, quality control

Goal

To demonstrate the suitability of the Thermo Scientific™ iCAP™ PRO X ICP-OES Duo for the elemental analysis of lithium mineral samples

Introduction

The transition to electric vehicles (EVs) is one of the key developments of the green energy revolution, and global demand for these vehicles is soaring. Lithium-ion batteries are one of the most important power storage materials for EVs due to their power density and life cycle performance. The lithium used in the production of electric vehicle batteries and other electronic devices is obtained from sources such as underground brines[1] and lithium-rich minerals and rocks. While brine solutions can be potentially rich, relatively easy-to-access sources of lithium, consideration must be given to the potential impact of the exploitation activities themselves on climate change, related environmental risks, and raw material supply.[2] Mining lithium containing minerals is an alternative source for regions where underground brines are not existing or not possible to exploit, but developing lithium mining sites also requires environmental impact consideration.

Lithium containing minerals differ significantly in their chemical composition, characteristics, and lithium content.[3] To determine whether a given mineral or brine is worth extracting, it is important to obtain quantitative information about certain major and trace components in the mineral/brine (Table 1). Portable X-ray fluorescence (pXRF) is a technique widely used in the mining industry as it is a non-destructive analytical technique that is effective for determining the elemental composition of a sample directly in the field.

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However, there are some limitations with XRF concerning the detection limits achievable. Inductively coupled plasma – optical emission spectroscopy (ICP-OES) is also widely used to screen minerals and ores for their major and trace elemental content. It is often the analytical technique of choice for the analysis of a large number of trace elements in a sample, as it allows simultaneous determination of major and minor elements in a single analysis due to its inherent multi-element capability and high dynamic range.

Table 1. Reasons for tracking specified elements in lithium mining samples[4]

Element	Information
Ca, Na, K	Indicates the amount of feldspar (one of the main rock-forming minerals) presents in the sample
K/Al ratio	Indicator of the degree of weathering (kaolinisation)
Ti	Associated with paramagnetic minerals that could dilute the final concentrate
Mn	Indicator enabling close tracking of lithium
Fe	Indication of the total amount of magnetic material not accounted for by zinnwaldite
Cr	Deleterious element for the hydrometallurgy process

This application note describes an optimized analytical method for the analysis of a lithium containing mineral (zinnwaldite, a silicate based mineral of the approximate composition $(KLiFeAl(AlSi_3)O_{10}(OH,F)_2)$ using the iCAP PRO X ICP-OES Duo. Thorough testing of the method was performed, including demonstration of accuracy and precision by certified reference material measurements, analysis of quality control standards, and the analysis of real samples as required in a mineralogical research laboratory.

Experimental

An iCAP PRO X ICP-OES Duo instrument was used for the analysis of previously digested minerals. Different digestion methods were tested and compared against each other to obtain optimal results for the elements under study. The iCAP PRO X ICP-OES Duo instrument was selected due to its robustness and ability to perform both Axial and Radial plasma measurements, enabling the different concentration ranges of the target elements to be measured in a single analytical run and ensuring fast sample turnaround.

As one of the digestion methods tested in this study included the use of hydrofluoric acid, the instrument was set up using the acid resistant kit, including an inert spray chamber (made from PTFE instead of quartz), a Burgener Mira Mist™ nebulizer, an alumina injector, and a ceramic D-torch.

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Details of the sample introduction setup and plasma settings can be found in Table 2.

Table 2. iCAP PRO X ICP-OES Duo instrument parameters

Parameter	Setting
Pump tubing	Sample: orange/white 0.64 mm i.d.
	Internal standard: orange/blue 0.25 mm i.d.
	Drain: white/white 1.016 mm i.d.
Peristaltic pump speed set	45 rpm
Torch	Ceramic D-torch for Duo instruments
Center tube size and material	2.0 mm i.d., alumina
Chamber	HF acid resistant spray chamber
Nebulizer	Burgener MiraMist nebulizer
RF power	1,150 W
Cool gas flow	12.5 L·min⁻¹
Auxiliary gas flow	0.5 L·min⁻¹
Nebulizer gas flow	0.55 L·min⁻¹
Radial viewing height	10.0 mm
Exposure time for all modes	15 s
Analysis repeats	3
Uptake time	35 s
Wash out time	30 s
Total analysis time (including uptake and wash out)	3 m 8 s

Data acquisition and data processing

The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software was used for data acquisition, processing, and reporting.

Sample preparation

Precleaned polypropylene bottles were used for the preparation of all blanks, standards, and samples.

A certified reference material (SRM 2709a, San Joaquin Soil, NIST™ (National Institute of Standards and Technology) was used as a control material to ensure the ability of the digestion procedure to fully solubilize all the elements of interest. This material was chosen because of its similar matrix composition compared to the samples in this study, a potentially lithium-rich silicate mineral.

The certified reference material (CRM) and a total of four individual unknown samples (Figure 1) were prepared to evaluate the iCAP PRO X ICP-OES Duo system for this analysis. All samples were digested before analysis.
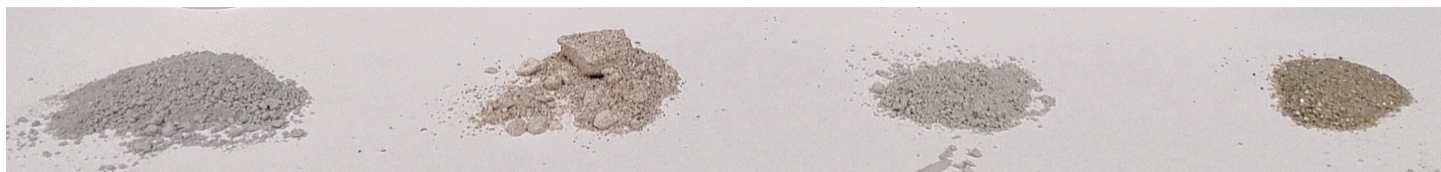
Figure 1. The four unknown samples supplied by British Lithium

An aliquot of approximately 0.1 g of each sample was accurately weighed and acid digested using three different acid mixtures. The acids employed for digestion were generally of the highest purity available and included HNO_3 (68% (m/v) Optima™ grade, Fisher Chemical™), HCl (35% (m/v) Optima™ grade, Fisher Chemical™), HF (48% (m/v) Optima™ grade, Fisher Chemical™), and H_3PO_4 (85% (m/v) trace metal grade, Sigma-Aldrich). The digestion procedure was executed as a closed vessel digestion using a microwave system (Milestone ETHOS One). Detailed information on the digestion procedures used is summarized in Table 3. After digestion, the samples were made up to a final volume of 50 mL (method 3 was made up to a final volume of 100 mL) using 1% (m/v) HNO_3, so that the amount of total dissolved solids was around 0.2% (m/v) in the measured sample solution.

Table 3. Summary of the tested digestion procedures and the microwave program applied

Method	Reagents	Element	Microwave heating program
Method 1	2 mL HF/ 4 mL HNO_3/ 2 mL HCl	Na, Ti, Mn, Li, Cr, Rb,	Ramp up temperature to 210 ˚C within 10 minutes and then hold at 210 ˚C for 20 minutes.
Method 2	6 mL aqua regia	Mg, Fe, Sn	
Method 3	5 mL H_3PO_4	Al, Ca, K, Cr	

The purpose of testing three different methods is that, due to the complexity of the matrix, a single method would not suffice to completely solubilize all the analytes, so further sample preparation steps would be required (e.g., removal of hydrofluoric acid using boric acid). To test the efficiency of each digestion procedure, a CRM of similar composition was used and the quantitative recovery of a range of analytes was assessed.

Results and discussion

Evaluation of sample preparation procedures

Figure 2 shows representative results for selected elements obtained using the three digestion protocols studied. The results show that none of the digestion procedures would allow the quantitative solubilization of all analytes and highlight the need to combine different methods to fully characterize the chemical composition of a sample. Titanium (Ti) is a representative example (A in Figure 2) of the need to use HF as part of the acid mixture. Only with HF added can the chemically stable titanium oxide bonds be broken, enabling quantitative recovery of Ti. However, other elements, such as the alkaline earth elements, form insoluble precipitates, such as CaF_2, in the presence of HF unless fluoride is removed in a subsequent step.

The use of aqua regia is known as a powerful way of digesting complex sample matrices, and it provides excellent recovery in this study for a variety of elements, with iron being shown as a representative example in Figure 2 (B). This procedure also provides satisfactory results for a variety of other common transition metals but shows limitations for alkaline metals like sodium or potassium.

The last method, using H_3PO_4, provides excellent results for elements that were found to be problematic using the other two approaches. This is highlighted using aluminum as an example in image C in Figure 2. While method 2 (aqua regia) was not powerful enough to remove aluminum from the silicate crystal structure, method 1 (HF, HNO_3, and HCl) led to the formation of insoluble AlF_3. Therefore, three different microwave digestion methods were required to obtain accurate results for all the target analytes.
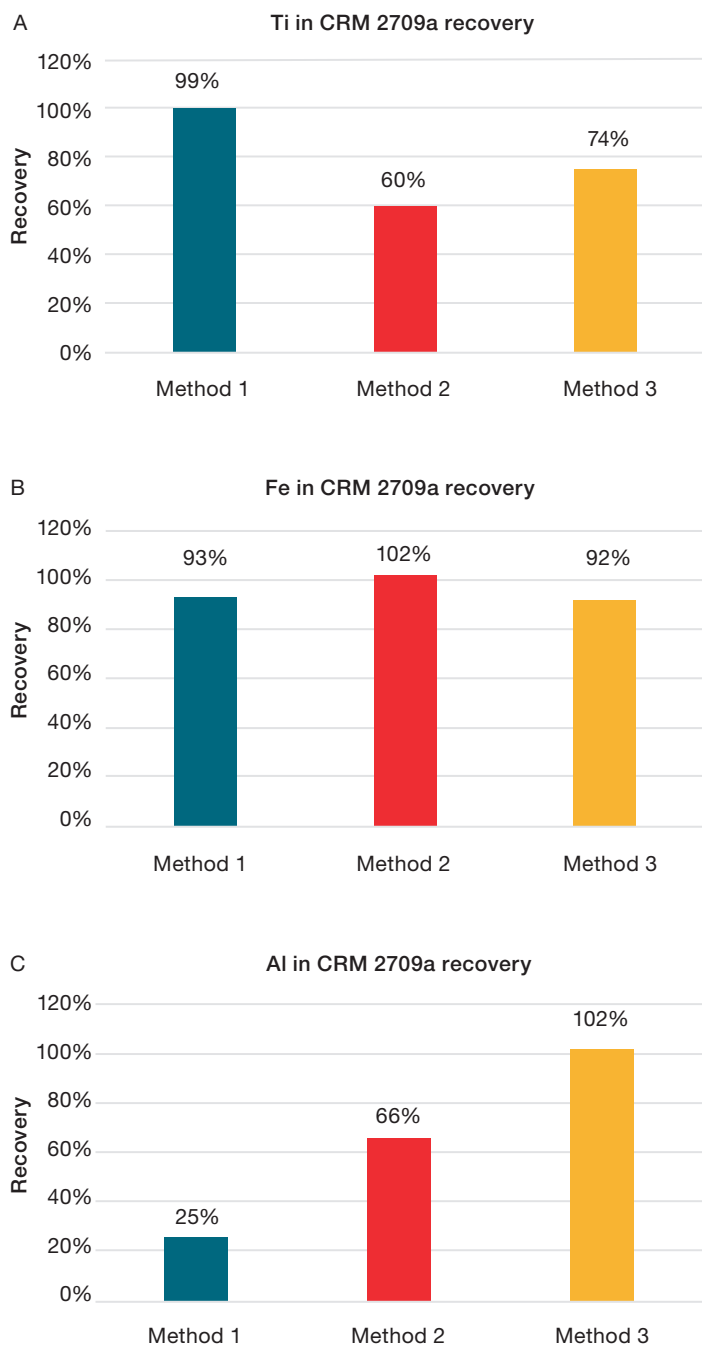
Figure 2. Recovery results for titanium, aluminum, and iron in CRM 2907a using the three different digestion protocols tested

All blanks, calibration standards, and quality control samples (QC, CCV (Continuing Calibration Verification)) were made from multi-element stock solutions prepared from single element standards (SPEX CertiPrep™, Metuchen, NJ, USA), in a matrix of 2% (m/v) HNO_3, to result in the concentrations listed in Table 4.

Table 4. Calibration standard concentration details (all values are in mg·L^{-1})

Label	STD-1	STD-2	STD-3	STD-4
Li, Na, Al, Ca, Fe, Ca, Mg, Rb	5	10	50	100
Ti, Mn, Sn	0.5	1	5	10
Cr	0.005	0.01	0.05	0.1
QC (CCV)	STD-1 of each calibration set			

To improve accuracy and compensate for potentially occurring instrument drift during longer sequences, internal standardization was used. A solution containing 10 mg·L^{-1} yttrium was added on-line to all samples via a T-piece (mixing ratio between internal standard and samples was 1:2) before entering the nebulizer.

Sensitivity, linearity, and limit of detection

The wavelengths selected for analysis of all the elements studied and the corresponding plasma viewing mode used for data acquisition are shown in Table 5. The intelligent Full Range (iFR) analysis mode, available on all models of the Thermo Scientific™ iCAP™ PRO Series ICP-OES system, can measure the complete wavelength range between 167.021 and 852.145 nm in a single measurement, allowing simplified method development and reduced sample turnround times without compromising sensitivity or accuracy. The plasma was observed both axially (to increase sensitivity for elements occurring in lower concentration ranges) and radially (to reduce matrix effects and self-absorption for major components of the sample).

Table 5. Linearity (coefficient of determination, R^2) and LOD (in mg·L^{-1}) data for the twelve elements measured

Analyte	Wavelength [nm]	Mode	Coefficient of determination, R^2	LOD (mg·L^{-1})
Al	167.079	Radial	0.9996	0.0014
Fe	238.204	Axial	0.9999	0.0005
Sn	242.949	Axial	0.9997	0.0155
Mn	257.610	Axial	0.9995	0.0001
Mg	279.553	Radial	0.9994	0.0002
Cr	283.563	Axial	>0.9999	0.0001
Ti	323.452	Axial	0.9999	0.0005
Ca	393.366	Radial	0.9996	0.0006
Na	588.995	Radial	0.9998	0.0910
Li	610.362	Axial	>0.9999	0.0024
K	766.490	Radial	0.9999	0.0550
Rb	780.023	Radial	0.9997	0.0210

Table 5 shows the linearity and limits of detection (LODs) obtained. The LODs were calculated as three times the standard deviation of ten replicate measurements of the calibration blank. For all elements, excellent coefficients of determination ($R^2 > 0.9994$) and detection limits were achieved.

Method validation with CRM and lithium mining samples analysis

As part of this study, a soil reference material and a total of four samples, consisting of zinnwaldite from different sources (and hence different compositions), were analyzed as technical replicates to assess the repeatability of the results. The results obtained for the CRM show that the calculated concentrations of the target elements closely matched the certified values, demonstrating the accuracy of the method. The method delivered

excellent precision through the analysis of at least three individual sample preparations for each of the microwave digestion methods, as demonstrated by data in Table 6. The different concentrations found in the four unknown samples are shown in Table 6 and Figure 3. Excellent method detection limits (MDLs) were achieved (based on the instrumental detection limits shown previously) and are summarized in Table 6, with the dilution factor of 500 incurred during the digestion process taken into consideration here.

Figure 3 shows the results obtained for the four unknown samples. It shows that the samples vary considerably in the content of lithium but also for the other components. For example, sample D showed the highest concentration of lithium and iron, compared to samples A–C, while sample B was found to contain much higher levels of calcium than the other samples.

Table 6. Analysis results summary (all results are given in mg·kg^{-1})

|	MDL	CRM measured value (n=3)	CRM reference value	CRM recovery (%)	Concentration range in unknown samples
Al	0.7	75,256 ± 104	73,700 ± 1600	102	52,402–90,241
Fe	0.3	34,316 ± 79.4	33,600 ± 700	102	7,966–37,942
Sn	7.8	332.7 ± 2.4	-	-	206–937
Mn	0.04	528.2 ± 1.0	529 ± 18	100	775–2,532
Mg	0.1	15,400 ± 50	14,600 ± 200	105	32–1,231
Cr	0.03	118.7 ± 1.8	130 ± 9	91	13–41
Ti	0.3	3,329 ± 9	3,360 ± 70	99	74–1,155
Li	1.2	53.9 ± 0.2	-	-	936–9,657
Na	45.5	11,754 ± 48	12,200 ± 300	96	5,631–46,946
Ca	0.3	18,627 ± 9	19,100 ± 900	98	3,751–179,176
K	27.5	17,972 ± 58	21,100 ± 600	85	24,467–50,456
Rb	10.5	95.6 ± 1.4	99 ± 3	97	7,961–29,918
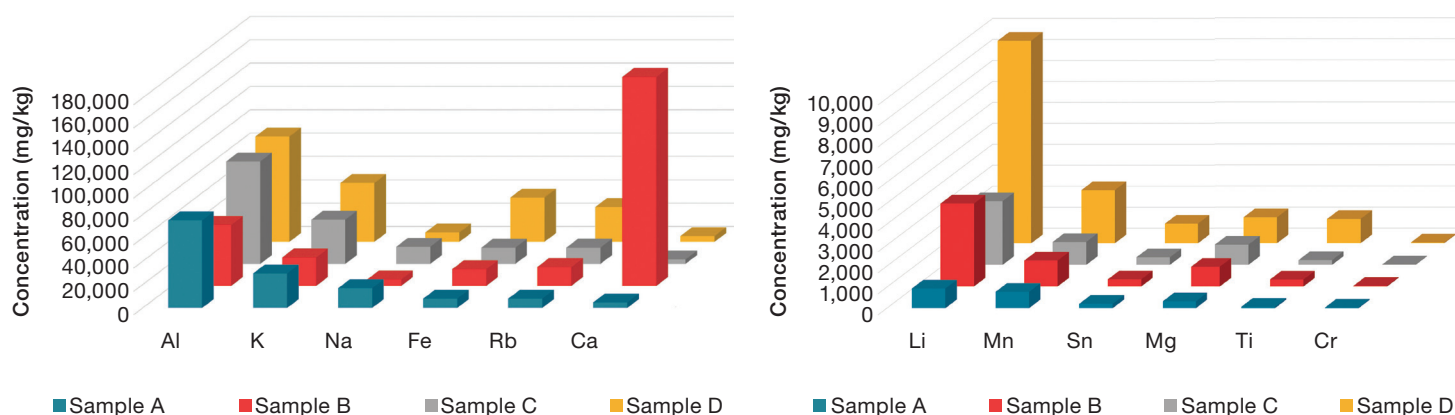
Figure 3. Analysis results mapped for the four different lithium mining samples

Robustness

To evaluate the robustness of the measurements, a batch containing 110 samples, amounting to a total runtime of approximately 6 hours, was scheduled for analysis. The batch contained sequences of 12 individual samples, that were each followed by a continuing calibration verification (CCV) quality control standard (with the concentrations shown in Table 3) to monitor the ongoing validity of the calibration curve. In addition, the internal standard signals were also monitored. In summary, seven CCVs were analyzed as part of the batch, together with a total of 90 unknown samples (zinnwaldite and CRM, covering all three digestion methods). Figure 4 shows the results obtained for the CCV samples. The relative standard deviation of all CCVs analyzed in the batch (n=7) did not exceed ± 1.9% for both Axial and Radial plasma viewing modes, which indicates that the iCAP PRO X ICP-OES Duo system allows for robust and reliable long-term analysis.
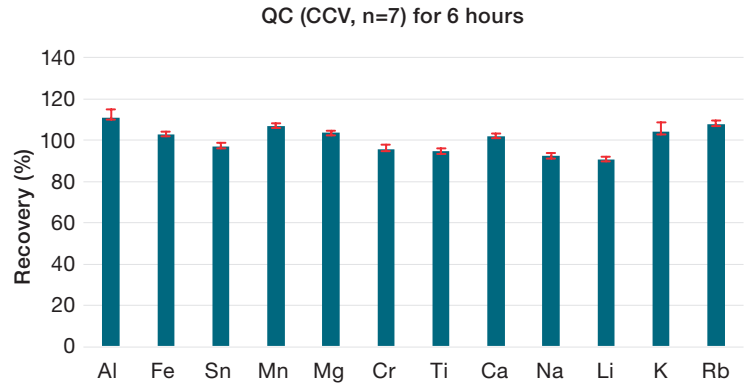
Figure 4. QC calibration verification results (n=7)

The internal standard showed excellent recovery (within 89% to 103%) over the entire batch, demonstrating robust analytical performance with digested minerals, even when different acid matrices are run in one and the same batch, as shown in Figure 5.
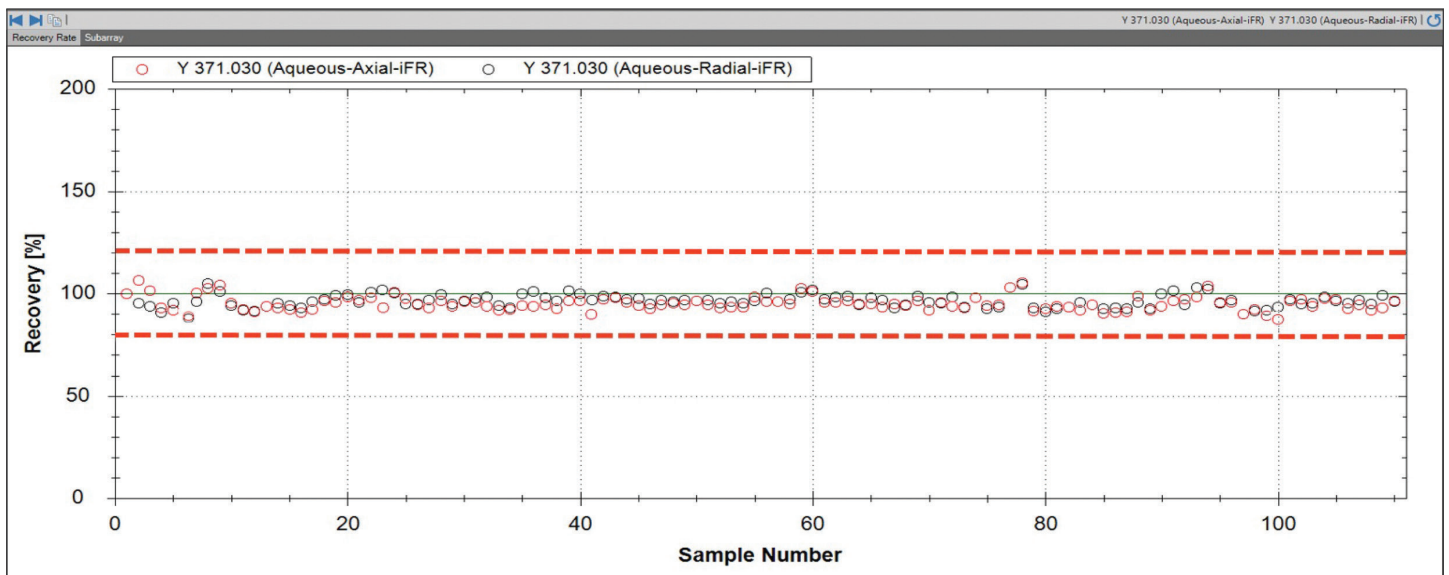

Figure 5. Response of the internal standard (yttrium) over a period of ~6 h of uninterrupted acquisition of 121 samples

Conclusions

The iCAP PRO X ICP-OES Duo instrument, equipped with a ceramic D-torch, was used to analyze 12 elements in digested rock samples containing commercially viable amounts of lithium. The results of this study showed that the analysis can be easily performed using a straightforward method to yield high accuracy and excellent analytical robustness. The method was rigorously tested, and the results obtained using a certified reference material clearly demonstrate the following analytical advantages:

- The large linear dynamic range for major and minor elements achievable with the instrument allows for precise determination of multiple elements at both low and high concentrations without further sample pre-concentration or dilution.

- Excellent accuracy was demonstrated using a certified reference material. Results of a QC (CCV) measurement performed during the analysis demonstrated the potential of the method for delivering high quality data, even for long sequences, without the need to perform maintenance.

- Robust and stable analytical performance was demonstrated over 6 hours of continuous acquisition of 120 samples, including 90 real samples, containing an average of 0.2% TDS and variable acid composition.

- The flexibility of the Qtegra ISDS Software allows customization of the analytical method by enabling selection of both plasma viewing modes (Axial and Radial) in a sample analysis, which provides a flexible range of development for analytical research.

Acknowledgements

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