SENSMET µDOES® Application Note Li-1

Analysis of main components and trace impurities of lithium salt solutions

Introduction

Lithium is an indispensable component for many of today's technologies and is essential for a greener, more environmentally friendly future. Due to its excellent electrical properties, lithium is widely used in a variety of applications including batteries for mobile devices (smartphones, tablets) or electric cars, but also grid storage applications. Depending on the raw material, various process steps are necessary to remove unwanted impurities (like Na, K or Ca) and obtain the pure end products Li_2CO_3 or LiOH, which are used as precursors for the battery industry.

Figure 1: Typical lithium raw material.

The fast and precise on-site and on-line analysis of industrial process solutions, such as lithium salt solutions, is becoming increasingly important. To guarantee optimal production, it is essential to conduct comprehensive analytics across the entire process chain. Traditional laboratory methods have decisive disadvantages such as a long waiting time for results, high consumption of chemicals or energy and are not suitable for such on-line measurements at an industrial plant. The SENSMET µDOES® technology solves all these problems and enables on-line analyses in real time.

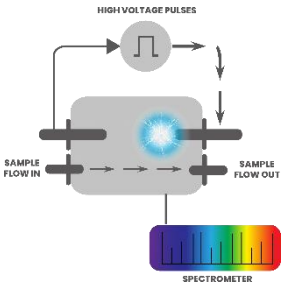

Figure 2: Principle of the µDOES® Online Multi-metal Process Liquid Analyser.

The method is based on the generation of micro-plasmas directly in the sample by high-voltage pulses, without need for carrier gases (e.g. Ar) like conventional analysis methods, and with only a fraction of the energy required. At the same time, the system is fully automated from sampling to data analysis, allowing continuous measurement 24/7 with high precision.

Experimental

Instrumentation

In this study the SENSMET µDOES® Online Multi-metal Process Liquid Analyser in standard configuration (mD-mDOES-E-4-3), equipped with tungsten electrodes (99.95% purity) and PTFE sample tubing was used. The operating parameters can be found in Table 1.

Table 1: Operating parameters of the µDOES® Analyser.

Parameter	Setting
Conductivity (µS/cm)	10 000
Number of pulses	15
Spectra averaging	200
Frequency (Hz)	750
Duty cycle (%)	40
Spectrometer mode	Continuous

Spectra evaluation

The analyser software SenSpec™ was used for evaluating the generated spectra. For each element investigated a suitable emission line (range) was selected. The analysis algorithm takes interferences (e.g. water vapour) that may occur into account, performs background corrections, and analyses the spectra based on a least square regression.

Standard solutions and reagents

Certified standard reference solutions containing the elements Al, Ca, K, Li, Mg, Na and Rb (Merck, 10 000 mg/L respectively) were used for sample preparation. Ultrapure water (Merck Milli-Q®, 18.2 MΩ/cm) was used to dilute the solutions and 5% nitric acid (Merck, analytical grade) to adjust the conductivity. All samples were prepared and stored in metal-free Falcon™ tubes (50 mL) or plastic container (10 L).

Measurement procedure

Based on the certified reference materials, calibration standards and quality control samples (QC) were prepared accordingly by diluting the standard solutions with ultrapure water. The element concentrations of the QC samples are listed in Table 2.

Table 2: Composition of the QC samples for long-term stability and recovery experiments.

Element	Concentration (mg/L)	
	QC 1	QC 2
Al	0.05	0.10
Ca	0.25	0.50
K	0.25	0.50
Li	2.00	1.00
Mg	0.25	0.50
Na	1.00	2.00
Rb (IS)	0.35	---

Measurements with the µDOES® are fully automated: After diluting the sample with ultrapure water, 5% nitric acid is stepwise added using a micro-pump until the conductivity target value (here: 10 000 µS/cm) is achieved. At the same time, the sample is homogenised and mixed. After this fast sample preparation step, the measurement is carried out, whereby a sequence of micro-plasmas is generated by applying high voltage pulses and the emission spectra are recorded by the spectrometer. After performing the calibration, the QC samples were analysed.

Results and discussion

Detection limits

The detection limits (LOD) in Table 3 were calculated based on the three-sigma method and are all in the single digit µg/L-range or lower.

Table 3: Detection limits and calibration ranges.

Element and Wavelength (nm)	LOD (µg/L)	Calibration range (mg/L)
Al 394.4 + 396.1	2.3	0 - 0.5
Ca 396.8	0.3	0 - 2.0
K 766.4 + 769.8	7.0	0 - 1.0
Li 670.7	0.6	0 - 4.0
Mg 279.5 + 280.2	1.1	0 - 0.5
Na 588.9 + 589.5	2.0	0 - 4.0

Long-term stability

Long-term stability was tested by analysing the prepared QC 1 sample for a total of approx. 4 h (50 times) in succession at a typical on-site interval of 5 minutes without any rinsing or cleaning of the system in between the measurements. The relative standard deviations of all elements were less than 10% and as low as 1% without and with the utilisation of Rb as internal standard, respectively, as can be seen in Table 4. The µDOES® Analyser is highly reliable during the entire analysis run, offering a very good repeatability and accuracy.

Table 4: Long-term stability of QC sample 1 measured 50x in succession without rinsing the analyser.

Element and Wavelength range (nm)	RSD% (n = 50)	
	Without IS	With IS (Rb)
Al 394.4 + 396.1	5.59	3.59
Ca 422.6	8.38	2.22
K 766.4 + 769.8	8.13	1.05
Li 610.3	8.82	1.35
Mg 279.5	8.45	3.22
Na 589.5	8.19	1.33

Recovery rates

To verify the trueness of the method, the samples QC 1 and QC 2 were analysed. The recovery rates (RR) are shown exemplary for Li and Na in Figure 3. For both elements, RR in the range of 100% were achieved, confirming the suitability of the method for the analysis of lithium process solutions on-line.

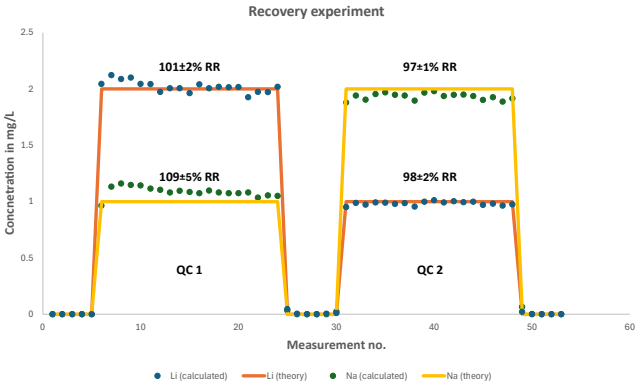

Figure 3: Comparison of the µDOES® results with the theoretical concentration values.

Conclusion

The SENSMET µDOES® Online Multi-metal Process Liquid Analyser was used to quantify 6 elements which are typically present in industrial lithium process solutions. In addition to low detection limits in the single-digit µg/L range, very good long-term stability with relative standard deviations as low as 1% and good recovery rates were achieved. The µDOES® technology proved to be well suited to the analysis of lithium process solutions and is an environmentally friendly (no gases, minimal use of chemicals), energy-saving on-site and on-line method for continuous measurements.