



Application Note 120329
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ESI-MS Elemental Trace Analysis of Alkali metals in water

A) Introduction

Elemental analysis is usually a domain of analytical methods like AAS, ICP-OES and ICP-MS. A standard method for multi element trace analysis using mass spectrometry is the production of Kations by ICP techniques and the application of a corresponding interface to the MS analyzer. For mass spectrometric analysis of polar and non volatile molecules the method of choice are API-MS techniques. Ion production takes place by ESI or APCI methodologies and dedicated interfaces to the MS analyzer are applied. Usually, the common API-MS interfaces are not suitable or at least very much restricted regarding the analysis of low mass ions. We were interested to evaluate the capabilities of a specific ESI-MS system, especially for direct analysis of low atomic number elements.

B) Summary

ESI-MS analyses have been performed with the experimental version of a new bench-top double focusing mass spectrometer. The dedicated and miniaturized system is based on the original AMD QuAS³AR Technology. Emphasis has been placed to the analysis of low mass ions and logically, the analysis of Lithium as the lowest element of the alkali metals in the first main group of the periodic system got some priority. Within the scope of the reported quantification methods no official certified procedures or U.S. EPA methods were applied, since the aim was to achieve orientating results for possible future applications.

The ESI-MS interface and the mass analyzer are integrated with a multi-stage turbo pumping system. It has been demonstrated that the special features of a small double focusing mass spectrometer regarding peak shape, mass resolution and abundance sensitivity are of significant advantage for the qualitative and quantitative analysis of ions in the low mass range.

Quantitative Trace Analyses of Lithium in aqueous solutions and in mineral water as an exemplary real life example were performed. Detection limits in the low ppt range were achieved for Lithium. The influence of scan methodologies including raw data accumulation and selected ion monitoring techniques on the quality of the results and analysis time are described.

The response factors of other alkali metals have been determined, approximately and have been found to be similar for these elements. The response factors for the alkaline earth metals and other elements are expected to be lower and require more investigation in order to conclude a possible usefulness of ESI-MS for quantitative analyses.

The results of our evaluations of ESI-MS applications so far dedicated to the alkali metals indicate that at least the quantitative analysis of Lithium in aqueous samples can be performed, successfully and limits of detection in the low ppt range can be reached. This method does not require any specific sample preparation and no chromatographic separation.



C) Methodology

C.1 Mass spectrometer

The mass analyzer was a miniaturized dedicated version of the AMD QuAS³AR (Quasar070206.pdf) double focusing system, equipped with an API Interface in ESI mode (ESI-MS system). System details are not reported here since an evaluation model was used for the experiments.

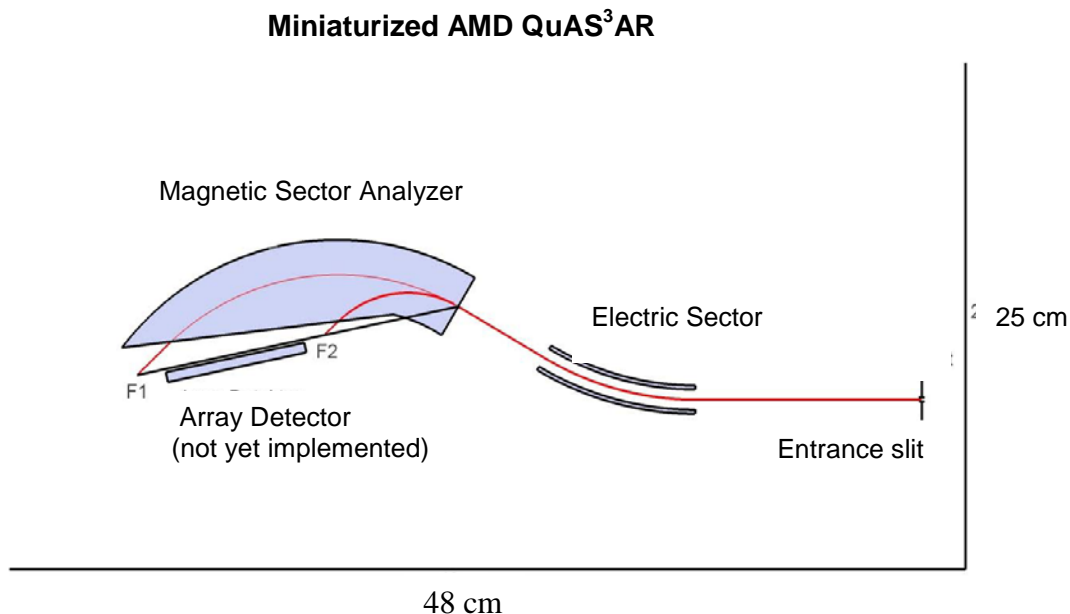
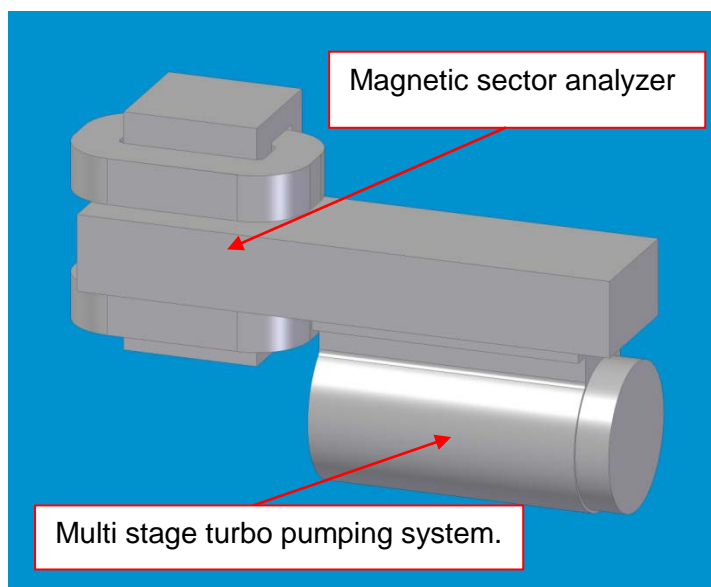


Fig. 1 Scheme of the ion optics and physical size of the bench-top double focusing MS analyzer



The **miniaturized AMD QuAS³AR** is based on the original AMD QuAS³AR Technology as a multifunctional high performance system and previously described in a system description: SD040617_ AMD Quasar.pdf.

The new current miniaturized version is downsized significantly, dedicated to low mass resolution and API-Interfacing only.

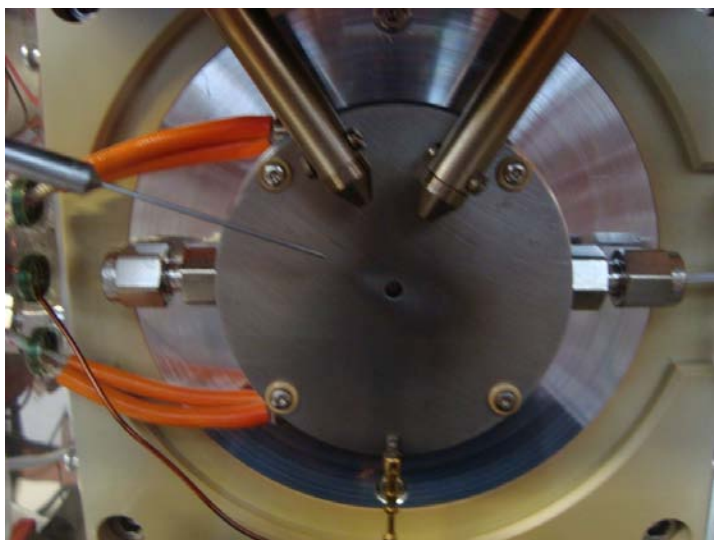
However, it incorporates the significant advantages of magnetic sector mass spectrometers for low mass ions regarding resolution and abundance sensitivity

Fig. 2 CAD Design of the **Miniaturized AMD QuAS³AR** API-MS system



C.2 ESI-MS Interface

As a dedicated API-MS bench-top system the interface and the mass analyzer are mounted on a multistage turbo pumping system. The system is fully optimized for highest transmission of low mass ions through the interface to the MS detector and in so far specifically **dedicated to trace analysis of Lithium, the lowest atomic number element of the alkali metals.**



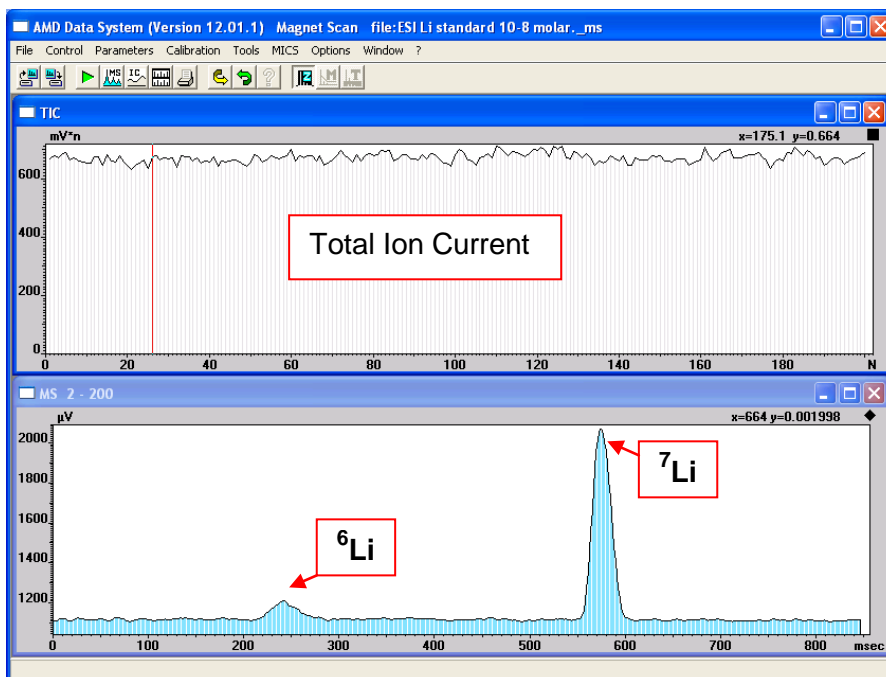
The **API ion source** of the miniaturized AMD QuAS³AR dedicated for ESI-MS applications consists of an API room including nebulizer assisted sprayer and hot air pipes for desolvatisation assistance.

The multistage vacuum interface is integrated with the analyzer multistage turbo pumping system.

A continuous eluent ESI spray of 85 $\mu\text{L}/\text{min}$ was maintained by a syringe pump and assisted by a nebulizer gas flow of 1.2 l/min.

Fig. 3 ESI-MS interface front view of the miniaturized API-MS Evaluation Model

C.3 Measurement procedure for Lithium analysis



Analysis Details C.3

Sample: 10^{-8} molar Lithium standard in aqueous solution, diluted 1:2 with ultra pure Methanol

Scan method: magnet scan,

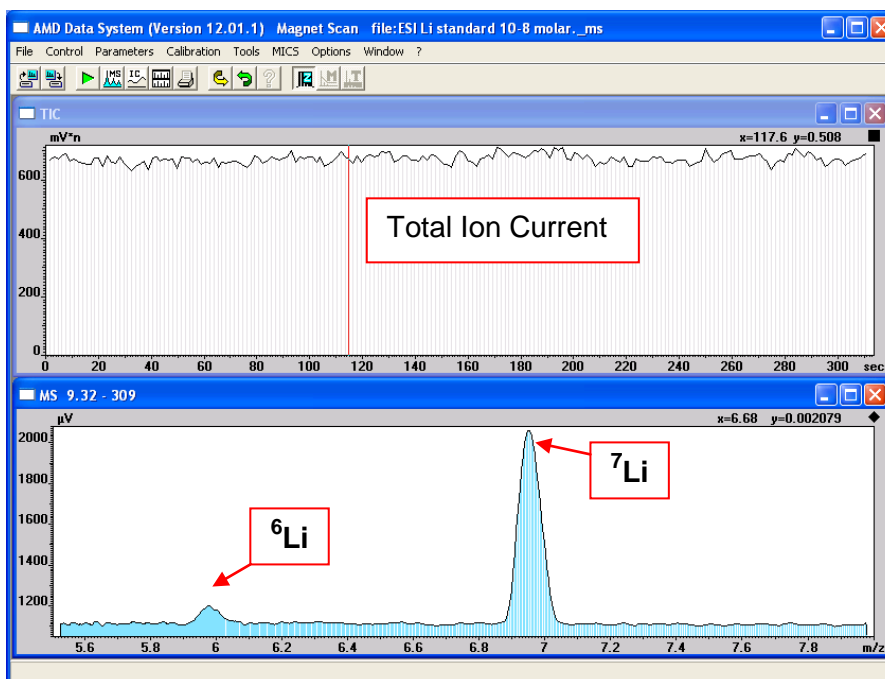
Scan duration: 850 msec

Measuring time per peak: 40 msec

Data acquisition: raw data accumulation (200 spectra)

Detector: post acceleration and Channeltron type SEM

Fig. 4 ESI-MS spectrum of the Lithium Isotopes at a concentration of 10^{-8} Mol/L



Analysis Details C.3 cont'd

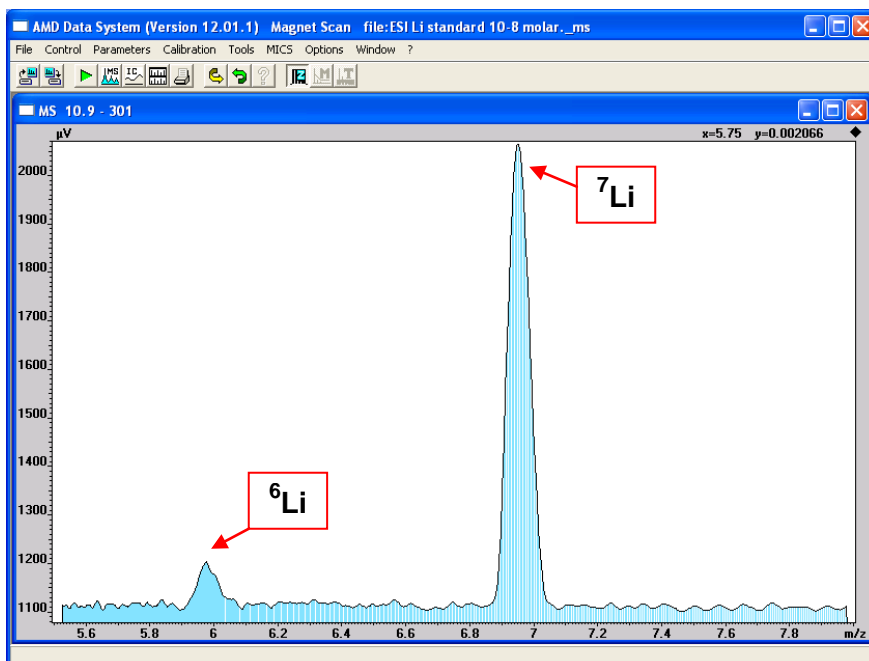
Mass resolution: 50 at 10% valley with fixed slits

Data System: AMD Version 12.01.1

Analysis time:

Since no chromatography was used, data were recorded over a time of about 300 sec and accumulated, accordingly

Fig. 5 ESI-MS spectrum of the Lithium Isotopes at a concentration of 10^{-8} Mol/L



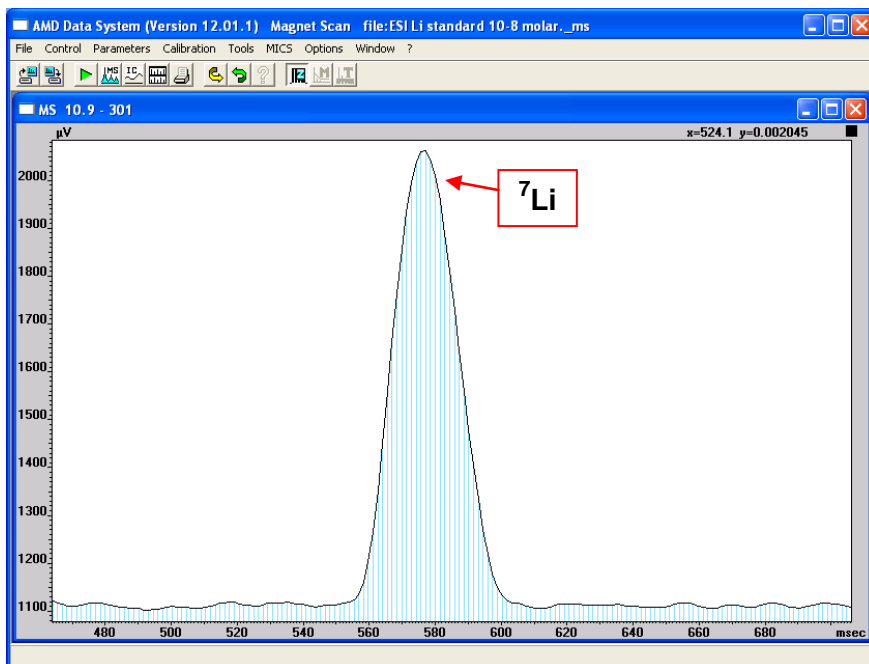
Analysis Details C.3 cont'd

Detection Limits:

Both Lithium Isotopes are well detected at a concentration of $c = 7 \times 10^{-8}$ g/L or $c = 7 \times 10^{-11} = 70$ ppt

The ^6Li Isotope with a low abundance of 7.5 % yields still a S/N ratio of about 4:1

Fig. 6 Details of the Lithium Isotopes at a concentration of 10^{-8} Mol/L

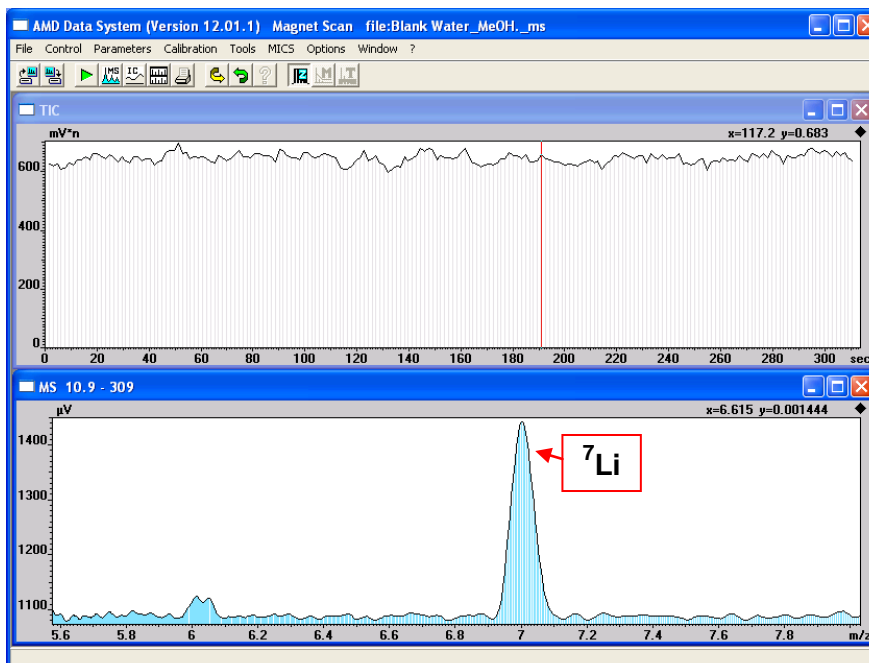


Analysis Details C.3 cont'd

The major isotope ${}^7\text{Li}$ yields a Signal to Noise ratio of about $S/N = 1000 \mu\text{V}/25 \mu\text{V}$ or $S/N = 40:1$

If the limit of detection is reached at a $S/N = 4:1$ a value $\text{LOD}_{\text{Lithium}} = 7 \text{ ppt}$ can be derived, if a linear calibration function is assumed and the background (blank) signal may be neglected or small enough for deduction

Fig. 7 S/N for the ${}^7\text{Li}$ Isotope at a concentration of 10^{-8} Mol/L (70 ppt)



Analysis Details C.3 cont'd

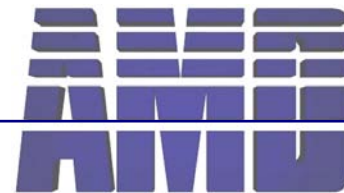
Background signal

The limit of detection (LOD) may be influenced by a background signal.

The ${}^7\text{Li}$ blank signal is here about $330 \mu\text{V}$ which would have to be deducted from the signal in Fig.7, resulting in a LOD of about 10 ppt.

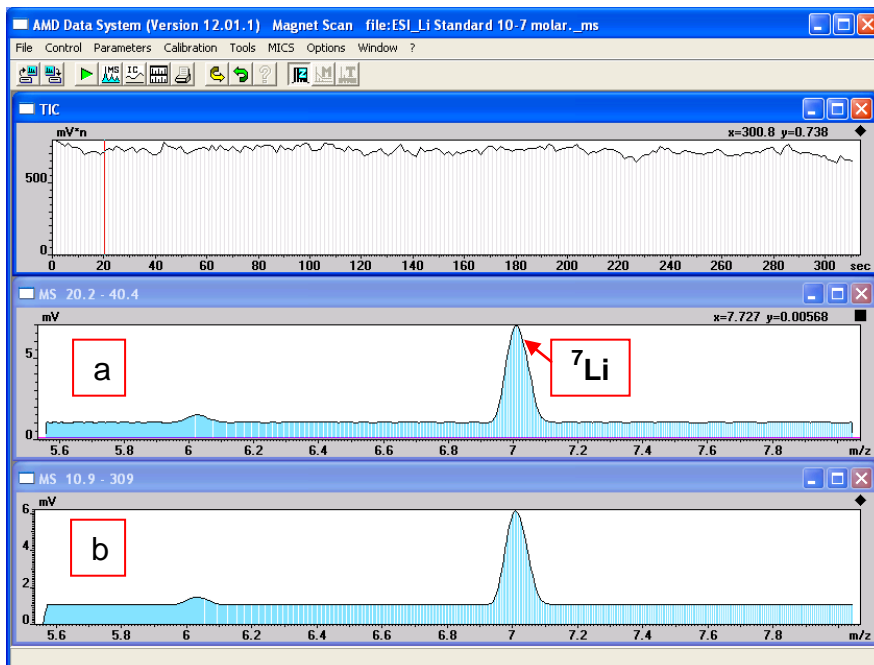
For precise quantification a calibration curve has to be established

Fig. 8 Background (Blank) signal for Lithium determined after a number of measurements



D) Results

D.1 Lithium Analysis in Mineral Water



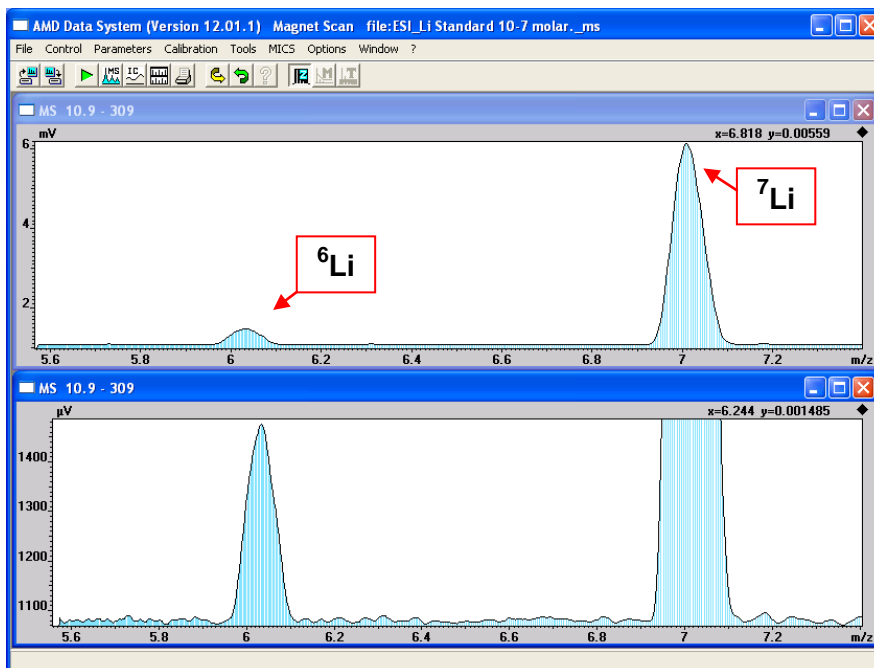
Analysis Details D.1

In preparation of a quantitative analysis of Lithium in a Mineral Water sample a 10^{-7} molar (0.7 ppb) Lithium standard has been measured.

Spectrum **a** has been obtained with an accumulation time of 20 sec and spectrum **b** with a longer accumulation of about 300 sec.

It is obvious that the S/N ratio and the LOD improve at longer accumulation times

Fig. 9 ESI-MS spectrum of the Lithium Isotopes at a concentration of 10^{-7} Mol/L



Analysis Details D.1 cont'd

Both Lithium Isotopes yield intensities which allow a precise **determination of the isotopic ratio** at a concentration of 0.7 ppb

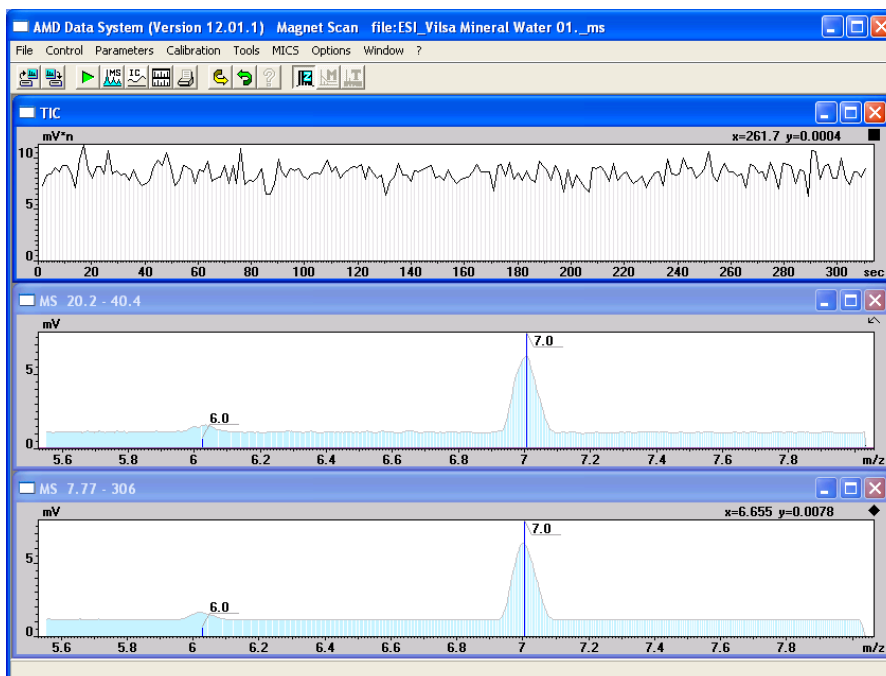
This will be of importance if isotope dilution techniques will be applied for accurate and precise quantification.

This technique was not available within the scope of this application note.

Fig. 10 Details of the Lithium Isotopes at a concentration of 10^{-7} Mol/L



D.2 Analytical Result of Lithium Analyses in **Vilsa Medium** Mineral Water

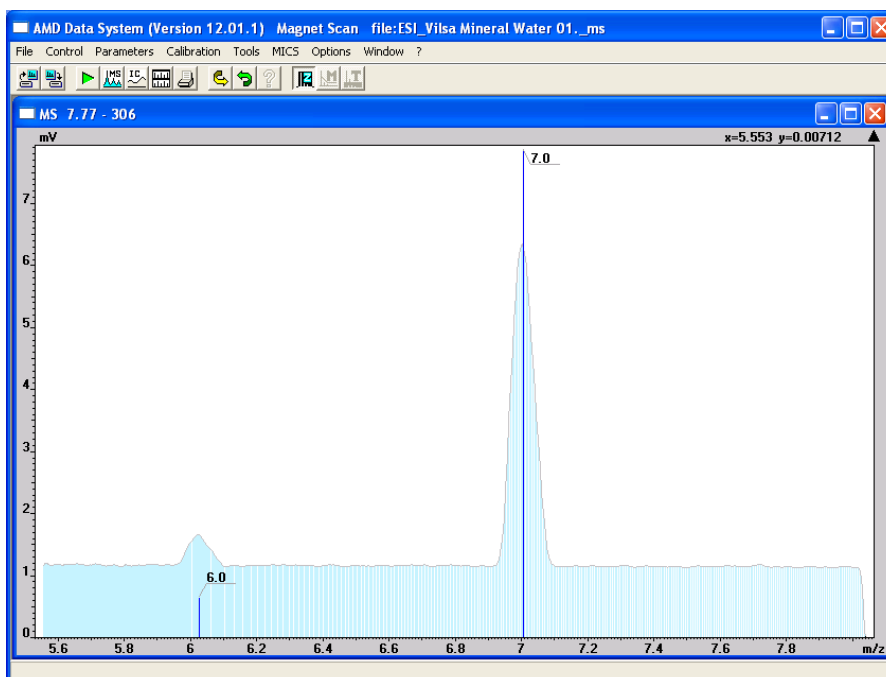


Analysis Details D.2

A sample of **Vilsa Medium** Mineral Water has been analyzed for the Lithium content.

The analysis was based on a direct comparison of the Lithium ion intensities with the 0.7 ppb standard. In so far the result (see below) may be considered to be semi-quantitative

Fig. 11 ESI-MS spectrum of the **Lithium Isotopes** of **Vilsa Medium** Mineral Water

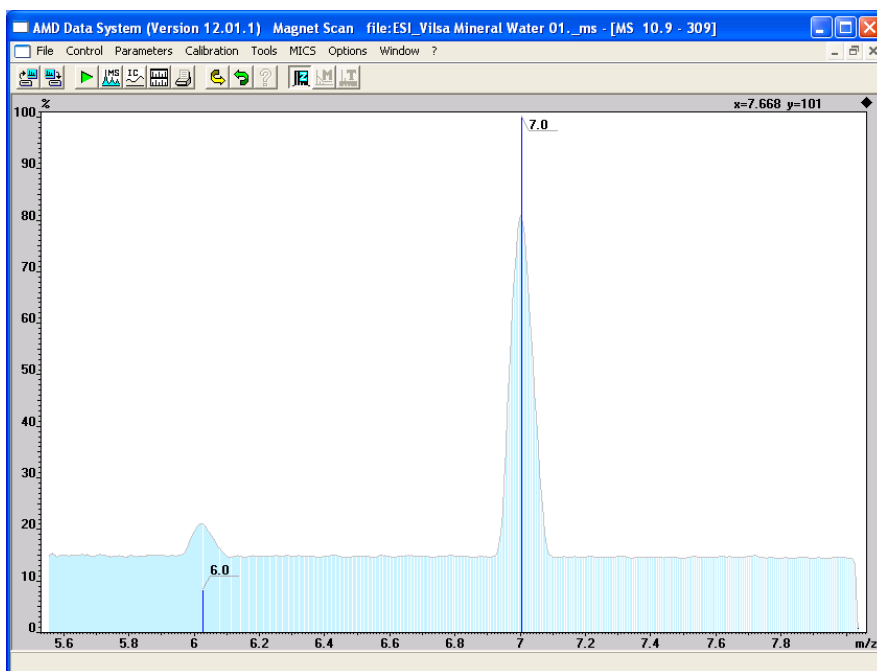
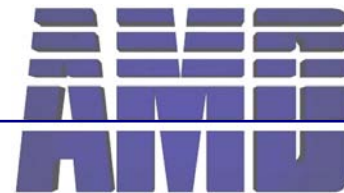


Analysis Details D.2 cont'd

The intensities and the ratio of the Lithium Isotopes in the **Vilsa Medium Mineral Water** sample have been determined, precisely

The details of the peak shapes and the very high S/N ratio indicate the quality potential for a quantitative data evaluation (see below), typical for a magnetic sector mass spectrometer

Fig. 12 Details of the **Lithium Isotopes** of the **Vilsa Medium** Mineral Water



Analysis Details D.2 cont'd

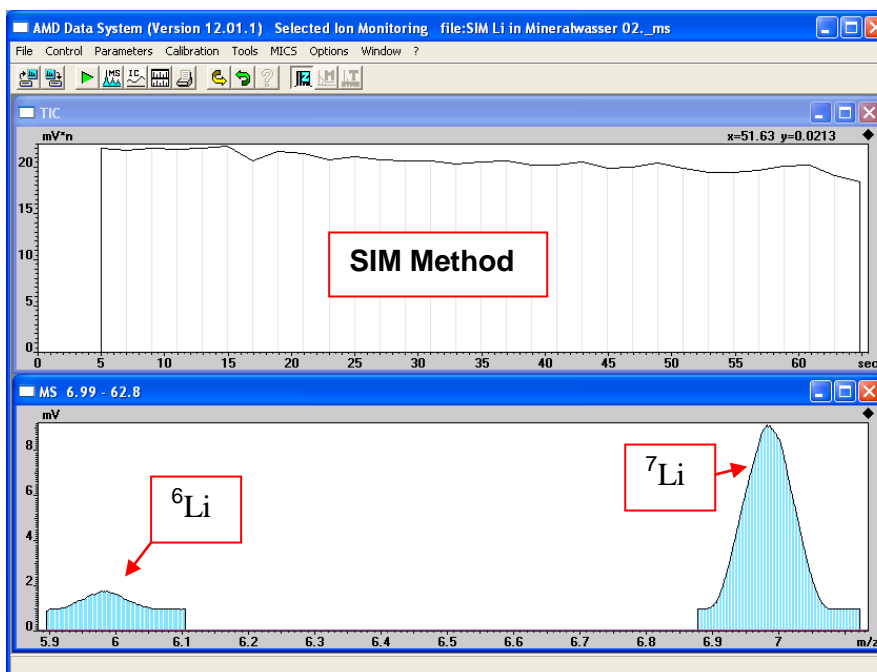
The Lithium isotope ratio has been determined by evaluation of the peak areas (blue lines in the figure)

The theoretical ratio is ${}^6\text{Li}/{}^7\text{Li} = 0.0813$

The measured value is ${}^6\text{Li}/{}^7\text{Li} = 0.0828$

The relative deviation is $\Delta = 1.84\%$

Fig. 13 Isotopic ratio determination of the Lithium Isotopes of the **Vilsa Medium** Mineral Water sample



Analysis Details D.2 cont'd

While all above measurements have been performed in scan mode, another measurement of the **Vilsa Medium** Mineral Water was performed in SIM mode.

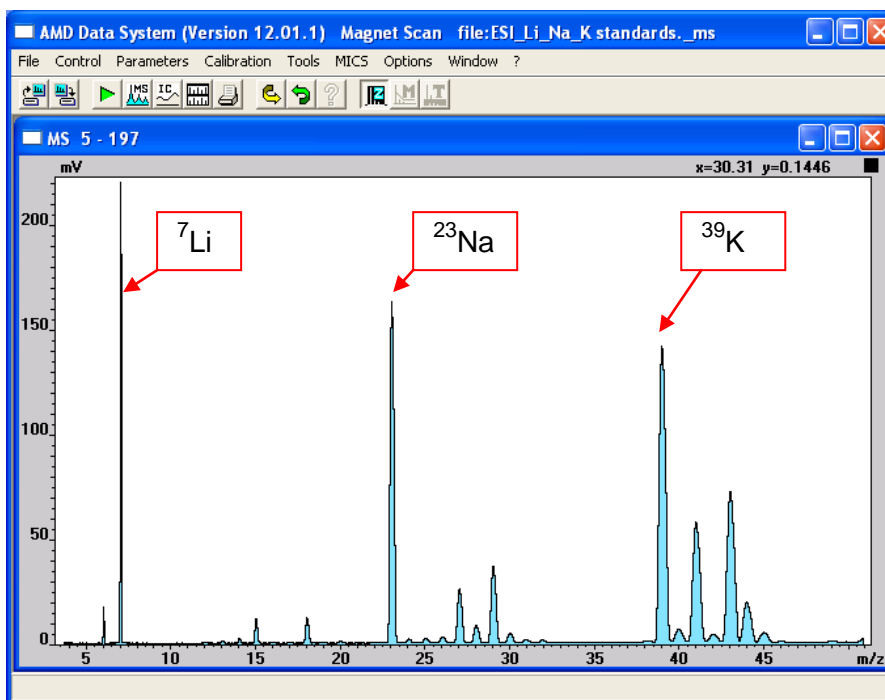
Due to longer measuring time per peak, this results in shorter analysis time of about 60 sec for the same S/N ratio and precision result.

This may be of importance for automated multi-sample analysis

Fig. 14 ESI-MS SIM measurement of the Lithium Isotopes of **Vilsa Medium** Mineral Water



D.3 Analysis of Alkali Metals in aqueous solution



Analysis Details D.3

The response of three **Alkali Metals** for ESI-MS has been tested in scan mode

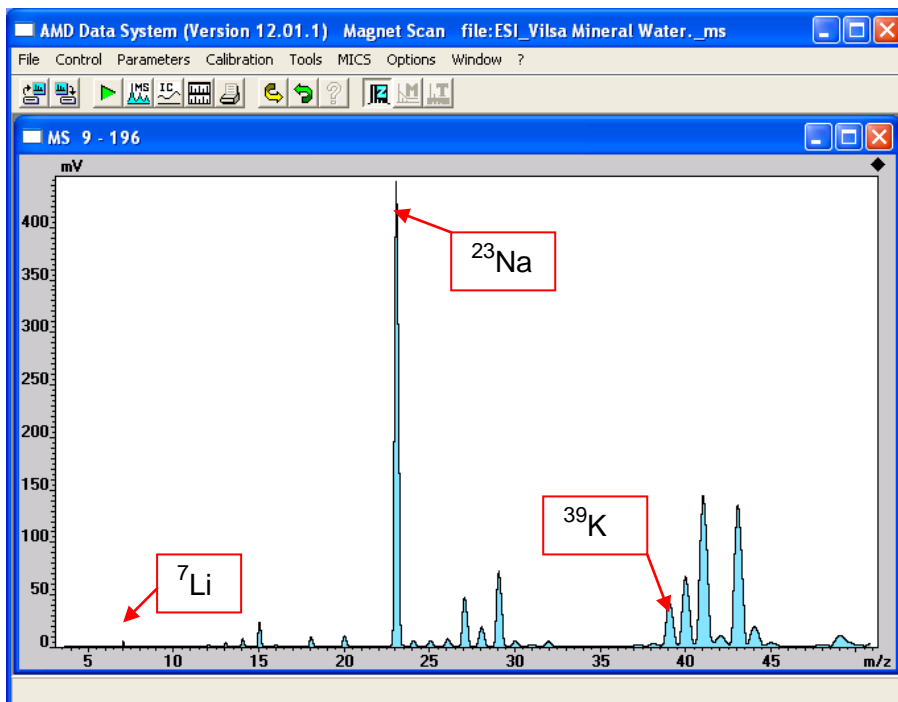
The result for a 10^{-5} molar standard mixture is shown in this figure.

The response factors are similar for all elements, which is also valid for ^{133}Cs which has been measured but is not shown in this spectrum.

Background ions of organic nature occur, too and will especially influence the detection limits for elements with low response factors.

Fig. 15 ESI-MS spectrum of Alkali Metals in a 10^{-5} molar standard mixture

D.4 Analysis of Alkali Metals **Vilsa Medium** Mineral Water



Analysis Details D.4

This survey spectrum of **Vilsa Medium** Mineral Water has not been evaluated, quantitatively.

There is some background contribution to the ^{39}K ion while the ^7Li intensity is in accord to the quantitative measurements above and the strong ^{23}Na intensity corresponds to an estimated concentration of about 1 ppm. This is lower than indicated on the bottle but corresponds with the label. “natriumarm”.

Fig. 16 ESI-MS spectrum of Alkali Metals in of **Vilsa Medium** Mineral Water