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# New Approach of a transient ICP-MS measurement method for samples with high salinity

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## Abstract

In the near future it is necessary to establish a disposal for high level nuclear waste (HLW) in deep and stable geological formations. In Germany typical host rocks are salt or claystone. Suitable clay formations exist in the south and in the north of Germany. The geochemical conditions of these clay formations show a strong difference. In the northern ionic strengths of the pore water up to 5 M are observed. The determination of parameters like  $K_d$  values during sorption experiments of metal ions like uranium or europium as homologues for trivalent actinides onto clay stones are very important for long term safety analysis. The measurement of the low concentrated, not sorbed analytes commonly takes place by inductively coupled plasma mass spectrometry (ICP-MS). A direct measurement of high saline samples like seawater with more than 1% total dissolved salt content is not possible. Alternatives like sample clean up, preconcentration or strong dilution have more disadvantages than advantages for example more preparation steps or additional and expensive components. With a small modification of the ICP-MS sample introduction system and a home-made reprogramming of the autosampler a transient analysing method was developed which is suitable for measuring metal ions like europium and uranium in high saline sample matrices up to 5 M (NaCl). Comparisons at low ionic strength between the default and the transient measurement show the latter performs similarly well to the default measurement. Additionally no time consuming sample clean-up or expensive online dilution or matrix removal systems are necessary and the analysis shows a high sensitivity due to the data processing based on the peak area.

**Abbreviations:**

CPS, Counts per second; HLW, High level radioactive waste; HMI, High matrix introduction system; ICP-MS, Inductively coupled plasma mass spectrometry; IS, Internal standard; LOD, Limit of detection; LOQ, Limit of quantification

**Keywords:** High salinity; ICP-MS; Ionic strength; Transient measurement; Europium; Uranium

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## 1 Introduction

The realisation of a HLW disposal in deep and stable geological formations is a very important task for the next years or rather generations. In Germany argillaceous rock as host rock for such a disposal is one of the possibilities. The safety assessment for more than a hundred thousand years needs an understanding of all processes of interaction between the radioactive waste and the surrounding formations. For the estimation of relevant geochemical parameters like  $K_d$  values that are used in geochemical modelling experiments [1-4], sorption experiments using (natural) clay minerals are necessary. The  $K_d$  value is the distribution coefficient which describes the distribution of the relevant cations between solid and liquid phase. Among various long-lived nuclides such as  $^{126}\text{Sn}$ ,  $^{129}\text{I}$ ,  $^{36}\text{Cl}$ , and others, the long-lived actinides uranium, neptunium, plutonium, americium and curium determine the radiotoxicity of the waste for a long time period and merit special interest for long-term safety considerations [5, 6]. As the principal component of nuclear fuel and partly of high level radioactive waste, both natural and depleted uranium can be measured as such. However, the work with the other actinides requires special safety precautions. Alternatively, homologues of such actinides like europium (homologue of americium) can be used.

Former studies [7-9] focused mainly on Opalinus clay and its pore water. But in Germany other types of clay rocks apart from Opalinus clay are considered as potential host rocks for a HLW disposal, too. In northern Germany, the clay pore water of the clay shows a very high salinity up to 5 M. The main component of this pore water is sodium chloride with magnesium or calcium as additional cations.

The measurement of small concentrations of europium or uranium after sorption onto the clay in the presence of high salinity is very difficult. Previous studies performed with relatively low concentrations ( $< 0.5$  M) of sodium perchlorate or synthetic pore water as matrix made use of mass spectrometry with inductively coupled plasma (ICP-MS) as analytical method with high sensitivity. However, the analysis of the undiluted samples with high salinity shows no reproducible results, and reduces the lifetime of the cones, the quadrupole and other components of the ICP-MS due to excessive salt deposits. Furthermore, an extreme decrease in sensitivity is observed. The highly saline matrix has to be diluted several tens or hundred times thus decreasing the analyte concentration below the respective limits of detection (LOD). With the high matrix introduction (HMI) system of Agilent for the 7500 and 7700 series measurements of samples with high salt content like sea water are generally possible. The maximum of the total dissolved solids (TDS) should be at 3% depending on the matrix, which increases the matrix tolerance about ten times. A 1 M NaCl solution shows a TDS of nearly 6% which is already too much for the HMI. For the new Agilent 7900 ICP-MS an ultra-high matrix introduction system (UHMI) is available which tolerates 25% of TDS, nearly 10 times higher than the previous generation HMI. Unfortunately, an upgrade of older Agilent ICP-MS

instruments with this new system is not possible. The same holds true for the integrated sample introduction system (ISIS) that can only be ordered together with a new Agilent 7900 ICP-MS. Alternatively to the dilution procedure described above, a matrix separation step during the sample preparation might lead to success. In literature the manual pre-concentration with ion exchangers (AmberliteCG-120, Dowex Marathon C, Rexyn 101) or chelating resins (Muromac, Chelex 100, NOBIAS-CHELATE PA1, Hitachi High-Tech Co., Japan) is discussed [10, 11]. Some research groups developed functional methods by separation and concentration of trace elements like thorium, uranium or neodymium in seawater samples [12-15]. Already in 1980 Pakalns and Mykytiuk *et al.* described independently of one another the functionality of Chelex 100 for separation of uranium from natural waters at pH 4.5 [16, 17]. In the near past, many authors used the Chelex 100 for separation of actinides from aqueous solutions, even with a high salinity or containing humic acids [18-21]. In most cases, the described resins are used in an offline column. The offline separation with Chelex or other resins consumes a lot of time for optimisation steps and has to be optimised separately for each element of interest due to different functionality of the resins. Partly the resins are very expensive like the transuranic or lanthanide-element specific resins (TRU.spec, Ln.spec) from eichrom (eichrom Technologies LLC, USA) which are used by Pin *et al.* [22]. In order to accelerate these processes, an automated preconcentration system [14] or an ICP-MS coupled with flow injection (FI) has been developed [23-25]. The latter implies a faster rate of the measurements and introduces lower sample volumes into the ICP-MS thus resulting in fewer deposits. For both alternatives, many components like peristaltic pumps, three-way valves and additional software are necessary. The acquirement of these components is rather expensive. Therefore, a method of analysis for highly saline samples up to 5 M NaCl has been developed. Reprogramming the auto sampler for short injection steps and measuring the resulting transient signals allows the use of the existing ICP-MS instrumentation unaltered.

## 2 Experimental

### 2.1 Chemicals and standards

Milli-Q deionised water (18.2 MΩ cm) was used to prepare all solutions. All used chemicals are at least “analytical reagent grade” and were purchased from Merck KGaA (Darmstadt, Germany). For the preparation of 1, 3 and 5 M NaCl solution NaCl with Emsure® quality was used. As 1000 mg L<sup>-1</sup> stock standard solution, the single element ICP-standards of Eu, U and Ho with Certipur® quality were used. To adjust the pH value perchloric acid (70 %, p.a.) and 1 M NaOH (p.a.) were used. Opalinus clay (BLT 14) samples from the Mont Terri Rock Laboratory in Switzerland were used for the sorption experiments. The bore cores were taken by the Federal Institute for Geosciences and

Natural Resources (BGR), and the OPA powder homogenate ( $< 500 \mu\text{m}$ ) was kindly provided by our project partners from Karlsruhe Institute for Technology, Institute for Nuclear Waste Disposal (KIT-INE). As plasma gas Argon 5.0 (Praxair, Germany) was used. As reference and test solutions one set of samples was prepared with 10 mM NaCl ionic strength.

## 2.2 Preparation of calibration samples

Calibration measurements for every analyte are necessary in order to derive concentration values from the measured values. In the case of lower metal concentrations calibration solutions from 0.1 to  $1 \mu\text{g L}^{-1}$  were used, and for higher metal concentrations solutions from 1 to  $100 \mu\text{g L}^{-1}$  were prepared. For this purpose, 6.36 mL MilliQ water was spiked with 300  $\mu\text{L}$   $\text{HNO}_3$  (65%, suprapure) and 10  $\mu\text{L}$  of a  $10 \text{ mg L}^{-1}$  holmium solution as internal standard (IS). The nitric acid prohibits metal ion sorption onto the tube surface and the IS was added to correct the time dependant sensitivity variation of the ICP-MS system. Based on a  $1 \text{ g L}^{-1}$  metal standard for every matrix an additional stock solution with a metal concentration of  $1 \text{ mg L}^{-1}$  and 3%  $\text{HNO}_3$  was necessary. For every calibration point the required amount was added to the mixture of ultrapure water, nitric acid and IS. The calibration standards were made up to 10 mL with the used matrix (0.01, 1 or 5 M NaCl solution).

## 2.3 Preparation of reference samples

For comparison between default and transient method several samples with higher (1 and 5 M NaCl) and lower (0.01 M NaCl) salinity were prepared. The metal concentration should be in the range of analyte concentration to be expected after sorption experiments. For such experiments the matrix solutions were spiked with different metal concentrations ( $0.8$  to  $80 \mu\text{g L}^{-1}$ ) using a  $1 \text{ mg L}^{-1}$  metal stock solution. For the transient ICP-MS measurements all samples were diluted 1:3. For the default ICP-MS measurement samples with lower salinity were diluted 1:3, too. Samples with higher salt content needed a dilution up to 1:100. Similar to the preparation of the calibration samples, 6.36 mL MilliQ water, 300  $\mu\text{L}$  nitric acid and 10  $\mu\text{L}$  of internal standard were mixed. For a 1:3 dilution 3.33 mL of the samples were added, for a 1:100 dilution only 100  $\mu\text{L}$  of the sample and 3.23 mL of MilliQ water were added.

## 2.4 Sample preparation

For sorption experiments at different pH values, 40 mg of homogenised Opalinus clay was weighed in a 15 mL centrifuge tube. 10 mL of 10 mM sodium chloride or sodium chloride solution with increased salinity (1, 3 or 5 M) were added. The samples were mixed in a HLC thermo mixer (MHL 23, DITABIS Biotech, Pforzheim, Germany) for 72 h at 25°C (100 % short mix, 500 vibrations per minute). After this equilibrating step, europium ( $0.66 \mu\text{mol L}^{-1}$ ) or uranium ( $0.35 \mu\text{mol L}^{-1}$ ) was added. The pH values from 2 to 12 were adjusted with 1 M NaOH and  $\text{HClO}_4$ , respectively. The samples were equilibrated for another 72 h at 25°C. The phase separation was performed in an Eppendorf centrifuge (Centrifuge 5804 R, Eppendorf, Hamburg, Germany) with 10,000 rpm for 10 minutes at 25°C. The supernatant was removed from the centrifugate.

Similar to the reference samples, for the ICP-MS measurements, 6.36 mL of Milli-Q water was put into a sample tube and 300  $\mu\text{L}$  of  $\text{HNO}_3$  (65%, suprapure®) and 10  $\mu\text{L}$  internal standard were added. Finally, a volume of 3.33 mL of the sample supernatant was added to a total volume of 10 mL thus resulting in a total sample dilution of 1:3.

## 2.5 The ICP-MS System

For the transient measurement a commercial ICP-MS from Agilent (7500cx, Santa Clara, USA) with a Cetac auto sampler (ASX 500) was used. Additionally, a high matrix introduction system for higher salt concentrations (HMI, Agilent) was installed. The ICP Mass Hunter workstation software (vers. B01.01, Agilent) has been used as analysis software for the ICP-MS measurements. The software allows the user to select different acquisition modes for measurements. The default method is the spectrum acquisition mode with data processing based on signal height and continuous introduction of liquid sample during measurement. The conditions of this default method are described elsewhere [26]. A further acquisition mode is the time resolved mode which produces a transient signal that appears as intensity versus time. In this case, data processing is based on peak area.

For the transient measurements the obtained peak area should be directly proportional to the element concentration and with a calibration by linear regression the concentration of the analyte can be calculated. To obtain such a transient signal the ICP-MS system was slightly modified. The auto sampler was externally controlled with the program HyperTerminal which is included in the Windows® (Microsoft Corporation, Redmond, USA) operating system. The sample should be injected only for a few seconds. As a result, the highly saline samples are injected only for a very short time period to avoid the introduction of sizeable amounts of salt into the ICP-MS system. Further information concerning the measurement and instrumental details can be found in the Supplementary material. The isotopes were measured with mass scanning at the mass centre. The integration time of every isotope per measurement iteration was 0.1 sec.

## 2.6 Programming the autosampler with HyperTerminal

As mentioned above, the autosampler was controlled with the software HyperTerminal (Microsoft Corporation, Redmond, USA). As first part of the preparations, a sequence has to be programmed and loaded into the autosampler memory. A programmed sequence consisting of the size of the sample holder and the amount of samples has to be defined. After this, the position of the sample vial in the tray, needle depth and injection time must be specified. The sample uptake is followed by two cleaning steps; first, in a rinse station an external cleaning of the needle takes place and then a purging of the inside tubing with a diluted nitric acid as cleaning solution. These cleaning steps prevent cross contamination and eliminate memory effects. This described procedure is executed for each sample and a complete sequence allows for the measurement of six samples before the autosampler's memory limit of 1,000 bytes is reached.

The time for sample uptake was fixed to 10 seconds. The duration of the second cleaning step depends on the salt concentration in the samples. Generally, lower concentrations are rinsed out faster compared to higher analyte concentrations. A minimal cleaning time period of 60 seconds is required due to the relatively high internal standard (Ho) concentration of  $10 \mu\text{g L}^{-1}$ . In the case of higher Eu and U concentrations ( $> 10 \mu\text{g L}^{-1}$ ), a maximum cleaning time period of 90 seconds was used to wash out all elements quantitatively. A flow chart of the sequence is given in the Supplementary material. With one autosampler run 6 samples could be measured within 11 minutes. Due to the necessary triplicate measurements for every sample nearly 6 minutes are necessary. In comparison to the default method this is more time-consuming. However, in comparison with other alternative methods for seawater samples like the described method of Worsfold *et al.* [27] this running time for transient measurement is tolerable.

## 2.7 Modification of ICP-MS components

An uptake of air during the travel time of the autosampler needle between the sample vial and the rinse position leads to an instable aerosol formation and a strongly fluctuating analyte signal. To minimise this, a second tube was connected that continuously delivers make-up solution (diluted nitric acid, 1-5 %). Sample and make-up are mixed after the peristaltic pump using a cross piece. This approach enhances the nebulisation of the sample strongly and a disruption of nebulisation was reduced.

The tubing for the make-up needs an inside diameter which provides a stable flow to the nebuliser. Therefore, a tubing with an inside diameter of 1.07 mm was used for make-up addition. The sample tubing diameter should be smaller than the make-up tubing for achieving a sufficient dilution of the matrix. Additionally, the sample tubing diameter must be adequate to get a high



sensitivity and a low detection limit. As best alternative, a sample tube with an inside diameter of 0.57 mm was used. The application of two different tubing diameters has some advantages. By reducing the inside diameter of the sample tube the air suction during the travel time of the autosampler was reduced too. The minimisation of air uptake leads to a stabilisation of the analyte signal. Furthermore, with the settled tube diameters, a sample dilution of almost 1:4 was achieved. The inner diameter of the waste tubing is 1.66 mm to guarantee that the sample and make up flows are smaller than the waste flow.

The peristaltic pump rotates with 0.1 rounds per second (rps) and has a radius of 2 cm corresponding to a perimeter of 12.6 cm. With a tube inside diameter of 0.57 mm in 10 seconds nearly 30  $\mu\text{L}$  of the sample was injected. In order to calculate the relative standard deviations between repeated measurements every sample was measured in triplicates. Altogether during these three injections a total sample volume of 90  $\mu\text{L}$  was injected into the ICP-MS. In contrast, during a measurement using the default method where the sample was continuously injected for some minutes due to the higher inside diameter of the sample tubing, longer sample uptake, several stabilisation processes and repeated measurements in total between 1 and 2 mL of the sample were injected for triplicate measurements. In this way for the transient method a reduction of the injected sample volume of more than 10 to 20 times compared to the default method was implemented.

### 3 Results and Discussion

#### 3.1 Analytical figures of merit for the transient measurement method

Usually, certified reference materials (CRMs) are applied in order to validate an analytical method. Unfortunately, it was difficult to obtain CRMs with a comparable matrix and salinity up to 5 M NaCl. To assess the accuracy of the new method, experiments similar to the standard addition method Duan *et al.* applied in their work [28]. Based on this example, calibration measurements with europium and uranium were performed to validate our transient method. Typically, all signals of Eu and U are normalised with a normalisation factor which is calculated from the Ho signal and the factor 100,000. This factor fluctuated in the range of 1.5 to 3.5 depending on ionic strength of the sample, running time of the ICP-MS (usual time dependant sensitivity variation of the instrument) and the time since the last cleaning or replacement of cones and ion lenses. For each metal two series with artificial matrix (1 and 5 M NaCl) were prepared. The first, for small concentrations in the range of 0.1 to 1  $\mu\text{g L}^{-1}$  (0.1, 0.3, 0.5, 0.8, 1  $\mu\text{g L}^{-1}$ ), and the second for higher concentrations (1, 5, 10, 50 and 100  $\mu\text{g L}^{-1}$ ). All calibration curves for both metals show a good linearity and a direct proportional relation between metal concentration and peak area. Using the example of 1 M NaCl solution the linear function of the calibration curve for low Eu concentrations is  $y = 5953.4x + 33.8$

and for low U concentrations it is  $y = 7991.6x - 49.2$ . The linear functions for high metal concentrations are for Eu  $y = 6153.8x + 415.7$  and for U  $y = 7612.2x + 1256.7$ . In both cases the slope of uranium is clearly higher than the slope of europium mainly due to the isotopic abundance which is nearly 100 % for uranium-238 in comparison to 52 % for europium-153.

The linear coefficients of determination ( $R^2$ ) are for higher metal concentrations 0.9998 (U) and 0.9995 (Eu) and for lower metal concentrations 0.9992 (U) and 0.9990 (Eu). All values are close to 1.0000 and confirm the linear relation between concentration and peak area. Variations in the peak height do not allow using the peak height for quantification of the metal concentration. The calibration data of high and low metal concentrations with linear fit equations are shown in the Supplementary material. Additionally, the minimum concentration of a substance which could be distinguished from the absence of the substance in the sample (limit of detection, LOD, based on the mean of the blank  $|x_B|$  and the standard deviation of the blank  $s_B$ ; see eqn. 1 with  $n=30$ ) and which could be quantitatively analysed with defined accuracy (limit of quantification, LOQ, see eqn. 2 with  $n=30$ ) have been determined [29, 30]. For europium samples with high salinity (5 M NaCl), a LOD of  $20 \text{ ng L}^{-1}$  and a LOQ of  $66 \text{ ng L}^{-1}$  has been determined. With decreasing ionic strength the LOD and LOQ improve (0.01 M NaCl LOD =  $4 \text{ ng L}^{-1}$ ; LOQ =  $13 \text{ ng L}^{-1}$ ). The values for uranium are in the same order of magnitude.

$$\text{LOD} = |x_B| + 3 \cdot s_B \quad (1)$$

$$\text{LOQ} = 3.3 \cdot \text{LOD} \quad (2)$$

Due to the continuous liquid uptake by non-stop working of the peristaltic pump (including needle movement from wash to sample vial and back to wash vial) the volume of the sample in the sample tube and therefore the liquid filling level is an important parameter. The measured counts for the analyte are dependent on the filling volume of the sample vial. After Ho normalisation of the analyte counts this dependency is eliminated, compare Supplementary material for further details.

In summary, the relative standard deviation (RSD) of the transient measurements are clearly lower by Ho normalisation of the analyte signal and especially at higher analyte concentrations ( $> 10 \text{ } \mu\text{g L}^{-1}$ ), the RSD is lower than 1%.

It is generally known that with increase in salinity the instrument sensitivity is depressed. This effect should affect both the analyte and its internal standard to the same extent. In order to proof this and to exclude additional matrix effects, calibration data with different salt concentrations (0.01, 1 and 5 M) have been created (Table S6 and S7 in Supplementary material). As expected, no differences were observed between the chemically very similar europium and holmium (both trivalent lanthanides with similar masses). The comparison between the heavier and divalent

uranium and the trivalent holmium as internal standard has shown that the signal intensity of uranium was stronger depressed than the chosen internal standard but nevertheless the linear dependency was given. This shows that the choice of the internal standard is very important and for every analyte a suitable internal standard is necessary. For uranium an internal standard with a more similar mass e.g. bismuth would be useful. In cases where it is impossible to use a perfect internal standard that shows identical chemical behaviour and mass it is crucial to prepare the calibration standards with the same matrix as the samples (matrix matching). The signal of the internal standard is stable for equal salinities during a long period of data acquisition. The calculated standard uncertainty for peak area measurements of the internal standard was usually  $\leq 3\%$ .

### 3.2 Comparison of default and transient ICP-MS measurements with europium and uranium

It is necessary to compare the congruency of the default method with the transient method to find out if the transient method provides consistent results. In the first experiment, samples with 0.01, 1 and 5 M sodium chloride and known concentrations of uranium and europium (0.8, 3, 8, 15, 30 and 80  $\mu\text{g L}^{-1}$ ) were prepared. These samples have been measured in spectrum and time resolved mode. For the transient ICP-MS measurement all samples are diluted 1:3 (see section "Preparation of reference samples"). With the default measurement only the 0.01 M could be diluted 1:3, the samples of 1 and 5 M NaCl had to be diluted 1:100 before ICP-MS measurements due to the high salt concentration. During the default measurement matrix concentrations between 0.033 and 0.05 M entered the ICP-MS. During the transient measurement and with the online dilution due to the make-up solution and different tube diameter the salinity which entered the ICP-MS is in the range of 0.00074 and 0.37 M. The results of this test series are shown in Table 1.

The default method shows good recoveries for samples with low matrix influence and a small dilution. For samples with higher dilution (1:100) the recovery decreases with increasing salinity mainly in the range of low metal concentration (e.g. 0.8  $\mu\text{g L}^{-1}$ ). In most cases, the determined concentrations are lower than the added metal concentration. At metal concentrations of 0.8  $\mu\text{g L}^{-1}$  the difference to the added concentration is very high mainly due to the high dilution and the resulting low metal concentration measured. For europium the recovery is only 30 %. For uranium, the recovery is clearly better due to the higher isotopic abundance which is for U-238 99.3 % and for Eu-153 52.2 %. With a 1:100 dilution a concentration of 8 ng  $\text{L}^{-1}$  resulted. This concentration is in the range of the LOQ of the default ICP-MS measurement. Additionally, the resulting counts per second (CPS) are in the range of the blank measurements. However, the dilution of 1:100 is necessary due to the high salinity and the used concentration of 0.8  $\mu\text{g L}^{-1}$  is a reasonable metal concentration after sorption experiments. The strong differences between 1 and 5 M NaCl are caused by the lower sensitivity due to signal suppression by the higher matrix concentration. The internal standard yields

an inaccurate correction of the signal probably due to the strong concentration differences between internal standard ( $10 \mu\text{g L}^{-1}$ ) and analytes ( $8 \text{ ng L}^{-1}$ ). For measurements in this concentration range the concentration of the internal standard has to be matched. Consequently, for the default method optimisation steps would be necessary whereby measurements in the range of the LOD are not preferred. At higher metal concentration the recovery for all analytes improves to nearly 100%.

**Table 1** Comparison of the europium and uranium recoveries (%) for different metal concentrations added ( $0.8 - 80.0 \mu\text{g L}^{-1}$ ) in 0.01, 1 and 5 M NaCl sample matrix determined by the default and transient ICP-MS method.

Default measurements						
$C_{\text{Me added}}$	0.01 M NaCl		1 M NaCl		5 M NaCl	
	(1:3 dilution)		(1:100 dilution)		(1:100 dilution)	
	Eu	U	Eu	U	Eu	U
0.8	93.8	98.8	47.5	73.8	27.5	60.0
3.0	96.7	100.0	90.0	93.3	86.7	93.3
8.0	98.8	97.5	100.0	96.3	95.0	95.0
15.0	98.7	98.0	98.0	98.0	94.7	96.7
30.0	98.7	99.3	98.7	99.3	98.3	96.7
80.0	99.3	100.0	99.1	99.6	100.4	98.6
Transient measurements						
$C_{\text{Me added}}$	0.01 M NaCl		1 M NaCl		5 M NaCl	
	(1:3 dilution)		(1:3 dilution)		(1:3 dilution)	
	Eu	U	Eu	U	Eu	U
0.8	101.3	105.0	97.5	106.3	98.8	108.8
3.0	100.0	96.7	100.0	100.0	100.0	100.0
8.0	100.0	100.0	98.8	101.3	100.0	98.8
15.0	100.0	100.0	98.7	99.3	94.7	99.3
30.0	100.3	100.0	99.7	99.7	99.0	96.0
80.0	100.3	99.6	99.9	99.4	98.9	99.1

Due to the short injection time of the samples for the transient measurement the samples need a clearly lower dilution during sample preparation than the samples for the default measurement. As a consequence, the analyte concentration is less strongly diluted but the matrix exerts a greater influence. In comparison to the default method, the matrix is partly 7-fold higher. Nonetheless the transient method provides results in good agreement with the added metal concentration. All recoveries are close to 100% even at lower metal concentrations.

All experiments were repeated five times. That means all samples were prepared five times (replicates) to allow the deduction of a confidence interval. Additionally, every single sample was measured in triplicate in order to determine the relative standard deviations (RSDs) for the measurements. The confidence intervals of the different test series are very similar. The transient method shows at lower metal concentrations ( $0.8$  and  $3 \mu\text{g L}^{-1}$ ) a higher interval up to  $\pm 6\%$ . The confidence intervals for the other samples are lower ( $\pm 3\%$ ). In the case of the transient method the RSDs of the triplicates are calculated by 3 injections of the same sample. The RSDs are in the range of  $0.5$  to  $5\%$  depending on the metal concentration. With lower metal concentration the RSD increases strongly. The default method leads to comparable values for the RSDs which are calculated by the mass hunter software: For samples with  $1$  and  $5 \text{ M NaCl}$  matrices and low metal concentration ( $3 \mu\text{g L}^{-1}$ ) the RSD is in a range of  $2$  to  $7\%$ . For the samples with  $0.8 \mu\text{g L}^{-1}$  metal concentration and high matrix influence the RSD varied strongly and increase up to  $15\%$ . For higher analyte concentrations and all samples in  $0.01 \text{ M NaCl}$  solution the RSD is situated between  $0.2$  and  $2\%$ .

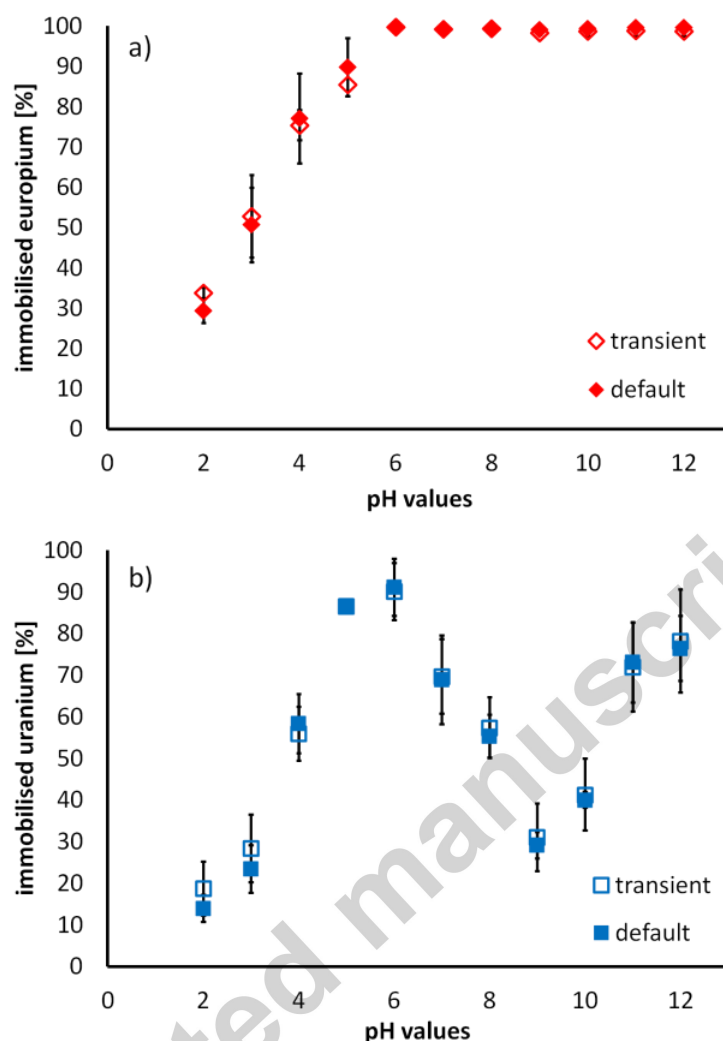
### **3.3 Comparison of default and transient ICP-MS measurements: Sorption experiments of europium and uranium onto Opalinus clay in sodium chloride**

In order to check the validity of the new transient measurement method in complex geochemical matrices, pH sorption edges of europium and uranium onto Opalinus clay in  $10 \text{ mM}$  sodium perchlorate solution were performed. Due to the low ionic strength in the sample matrix, these samples have been analysed undiluted both by the default as well as by the transient ICP-MS method presented here. Thus results of both applied methods can be compared to each other.

In Figure 1 the pH edges for the sorption of uranium and europium onto Opalinus clay determined with the two different ICP-MS methods are shown for comparison. The sorption results for europium and uranium are very different from each other. Europium shows a constantly increasing sorption with an increasing pH value until a quantitative sorption onto the clay is observed. The low sorption at acidic pH values ( $\text{pH} < 5$ ) is caused by protons which are present in high excess and the mono- and especially divalent cations like calcium and magnesium that dissolve from the Opalinus clay.

The pH edges of uranium have two minima and maxima. From pH  $2$  to  $6$  an increasing of the sorption is observed due to the present  $\text{UO}_2^{2+}$  as dominant species. The positively charged uranium

species can be sorbed well onto the clay and only the high excess of protons and competing cations prohibit the sorption at acidic pH values.



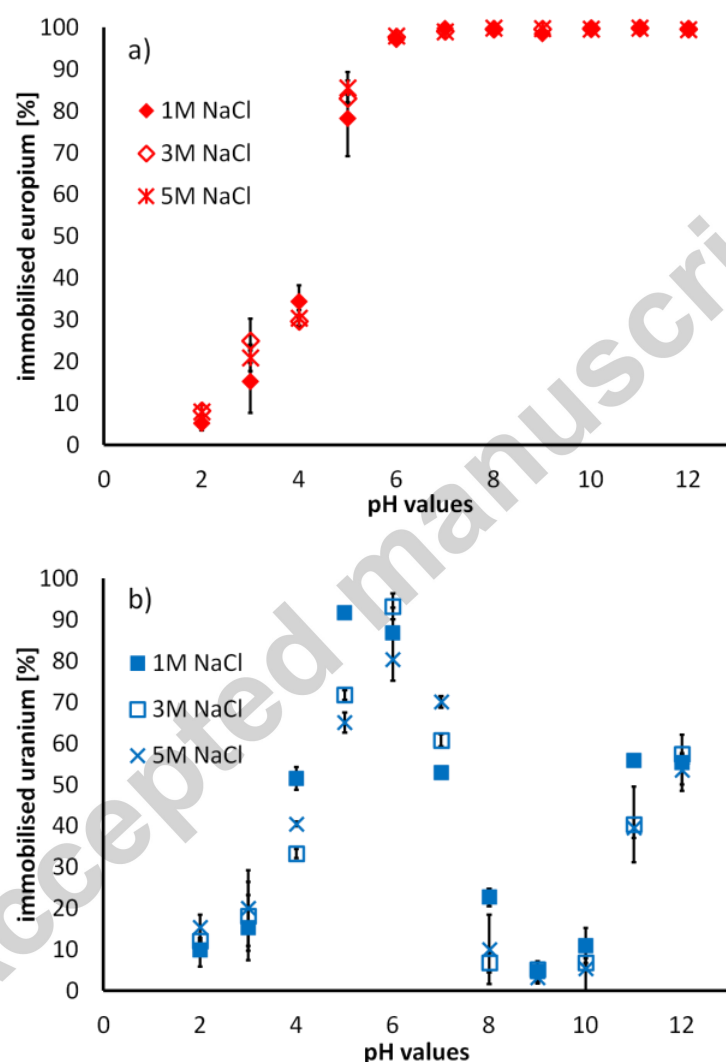
**Fig. 1.** pH-edges of europium (a) and uranium (b) onto Opalinus clay in 10 mM sodium chloride solution with default and transient ICP-MS measurements (n=5).

At higher pH values the amount of negatively charged uranium species in solution increases rapidly. These species exhibit lower sorption tendency. In the alkaline pH range more trivalent competing cations like aluminium are dissolved from the clay [20]. These cations could precipitate the uranyl-carbonato-species which therefore affect increasing sorption behaviour. If we compare the two different methods to each other, a good agreement of the transient ICP-MS measurement with the default method was found. In the case of uranium the deviations between the two measurement methods were smaller than the calculated standard deviations for each method and were in the range of 5 %. The results of europium sorption onto OPA show smaller variations

between the two measurement methods. At low pH values ( $\text{pH} < 5$ ) the deviations of the metal sorption data increase but do not exceed 4 %.

### 3.4 Application of the transient ICP-MS method for analysis of samples with high ionic strength

With the developed method, measurements in sample matrices with high ionic strength are possible. An example is given in Figure 2 which shows the pH edges of europium and uranium in 1, 3 and 5 M NaCl solutions.



**Fig. 2.** pH-edges of europium (a) and uranium (b) in 1 M, 3 M and 5 M sodium chloride solution with transient ICP-MS measurement ( $n=5$ ).

The pH edges for europium and uranium are typical for the respective elements which are shown in Figure 1. The present competing cations, in this case sodium, decrease the sorption of europium particularly in the acidic pH range ( $\text{pH} < 4$ ). At pH values higher than 6 the sorption of Eu was not

influenced by the ionic strength. For uranium the sorption decreased over the entire pH range. The present sodium cations influence the electrostatic interactions between uranium and the clay. The presence of such high concentration of cations can lead to a leaching of higher valent cations like calcium from the clay [26]. Therefore, the speciation of uranyl could change in the sodium chloride solution.

No relevant differences of the pH edges between 1 and 5 M NaCl can be observed. This could be explained by the high excess of sodium chloride. If we compare the results from 10 mM to 1 M NaCl ionic strength in the samples a 100-fold amount of sodium was present. An inhibition of the sorption was a consequence of the high sodium concentration. If we compare the results of 1 and 5 M NaCl ionic strength only a small difference for the metal sorption onto Opalinus clay is visible because only the 5-fold amount of sodium cations is present in solution when comparing 5 M NaCl with 1 M NaCl. As a further benefit of the transient measurement neither salt deposits on the cones nor relevant changes apart from time dependant sensitivity variation of the ICP-MS were observed even after 500 samples of uranium and europium in highly saline matrices.

#### 4 Conclusions

In summary, the herein presented transient ICP-MS method is very suitable for measuring metal ions such as europium or uranium in highly saline sample matrices. Employing series of measurements with 0.01 M NaCl, being measurable with both the default and the transient method, it was shown that the latter performs similarly well when compared to the default method. Additionally, the transient measurement allows the analysis of samples with high salinities up to 5 M NaCl without time-consuming sample clean-up prior to ICP-MS analysis or expensive online dilution or matrix removal systems and shows a high sensitivity due to the data processing based on the peak area. At the same time no increased salt depositions or matrix introduction in the ICP-MS system can be noticed even after a long time period of transient measurements of highly saline samples.

#### Notes and References

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Supplementary material available: [operating parameters for transient ICP-MS measurement; manual peak integration; time diagrams of calibration; linear calibration data; influence of different matrices]



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## References

- [1] E. C. Gaucher, C. Tournassat, F. J. Pearson, P. Blanc, C. Crouzet, C. Lerouge, S. Altmann, A robust model for pore-water chemistry of clayrock, *Geochim. Cosmochim. Acta*, 2009, 73, 6470-6487.
- [2] E. Tertre, A. Hofmann and G. Berger, Rare Earth Element sorption by basaltic rock : experimental data and modeling results using the “generalised composite approach”, *Geochim. Cosmochim. Acta*, 2008, 72, 1043-1056.
- [3] F. Z. El Aamrani, L. Duro, J. de Pablo, J. Bruno, Experimental study and modeling of the sorption of uranium(VI) onto olivine-rock, *Appl. Geochem.*, 2002, 17, 399-408.
- [4] E. Tertre, G. Berger, E. Simoni, S. Castet, E. Giffaut, M. Loubet, H. Catalette, Europium retention onto clay minerals from 25 to 150 °C: Experimental measurements, spectroscopic features and sorption modelling, *Geochim. Cosmochim. Acta*, 2006, 70, 4563-4578.
- [5] J. J. Katz, G. T. Seaborg, L. R. Morss, *The Chemistry of the Actinide Elements*, second ed., Chapman & Hall, New York, 1986.
- [6] A. B. Kersting, D. W. Efur, D. L. Finnegan, D. J. Rokop, D. K. Smith, J. L. Thompson, Migration of plutonium in ground water at the Nevada Test Site, *Nature*, 1999, 397, 56-59.
- [7] R. Kautenburger, Batch is bad? Leaching of Opalinus clay samples and ICP-MS determination of extracted elements, *J. Anal. At. Spectrom.*, 2011, 26, 2089-2092.
- [8] D. R. Fröhlich, S. Amayri, J. Drebert, T. Reich, Influence of temperature and background electrolyte on the sorption of neptunium(V) on Opalinus Clay, *Appl. Clay Sci.*, 2012, 69, 43-49.
- [9] L. R. Van Loon, B. Baeyens, M. H. Bradbury, The sorption behaviour of caesium on Opalinus Clay: A comparison between intact and crushed material, *Appl. Geochem.*, 2009, 24, 999-1004.
- [10] T. Pasinli, A. E. Eroglu, T. Shahwan, Preconcentration and atomic spectrometric determination of rare earth elements (REEs) in natural water samples by inductively coupled plasma atomic emission spectrometry, *Anal. Chim. Acta*, 2005, 547, 42-49.
- [11] M. Kyriakou, I. Pashalidis, Application of different types of resins in the radiometric determination of uranium in waters, *J. Radioanal. Nucl. Chem.*, 2011, 287, 773-778.
- [12] H. Takata, T. Aono, S. Uchida, K. Tagami, Determination of naturally occurring uranium concentrations in seawater, sediment, and marine organisms in Japanese estuarine areas, *J. Radioanal. Nucl. Chem.*, 2011, 287, 795-799.

- [13] H. Takata, J. Zheng, K. Tagami, T. Aono, S. Uchida, Determination of  $^{232}\text{Th}$  in seawater by ICP-MS after preconcentration and separation using a chelating resin, *Talanta*, 2011, 85, 1772-1777.
- [14] Y. Sohrin, S. Urushihara, S. Nakatsuka, T. Kono, E. Higo, T. Minami, K. Norisuye, S. Umetani, Multielemental determination of GEOTRACES key trace metals in seawater by ICPMS after preconcentration using an ethylenediaminetriacetic acid chelating resin, *Anal. Chem.*, 2008, 80, 6267-6273.
- [15] P. O. Persson, P. S. Andersson, J. Zhang, D. Porcelli, Determination of Nd isotopes in water: A chemical separation technique for extracting Nd from seawater using a chelating resin, *Anal. Chem.*, 2011, 83, 1336-1341.
- [16] P. Pakalns, Separation of uranium from natural waters on chelex-100 resin, *Anal. Chim. Acta*, 1980, 120, 289-296.
- [17] A. O. Mykytiuk, D. S. Russel, R. E. Sturgeon, Simultaneous determination of iron, cadmium, zinc, copper, nickel, lead, and uranium in sea water by stable isotope dilution spark source mass spectrometry, *Anal. Chem.*, 1980, 52, 1281-1283.
- [18] D. H. Philipps, B. Gu, D. B. Watson, C. S. Parmele, Uranium removal from contaminated groundwater by synthetic resins, *Water Res.*, 2008, 42, 260-268.
- [19] T. Kiliari, I. Pashalidis, Simplified alpha-spectroscopic analysis of uranium in natural waters after its separation by cation-exchange, *Radiat. Meas.*, 2010, 45, 966-968.
- [20] T. Kiliari, I. Pashalidis, Simplified alpha – spectroscopic analysis of uranium in natural waters its separation by cation – exchange, *J. Radioanal. Nucl. Chem.*, 2010, 284, 547-551.
- [21] M. Efstathiou, T. Kiliari, I. Pashalidis, Uranium analysis in Cypriot groundwaters by total alpha-radiometry and alpha-spectroscopy, *Radiat. Meas.*, 2011, 46, 626-630.
- [22] C. Pin, J. F. S. Zalduegui, Sequential separation of light rare-earth elements, thorium and uranium by miniaturized extraction chromatography: application to isotopic analyses of silicate rocks, *Anal. Chim. Acta*, 1997, 339, 79-89.
- [23] I. S. Trujillo, E. V. Alonso, M. T. Cordero, J. M. C. Pavon, A. G. de Torres, On-line solid- phase chelation for the determination of six metals in sea-water by inductively coupled plasma mass spectrometry, *J. Anal. Atom. Spectrom.*, 2010, 25, 1063-1071.
- [24] N. Nicolai, C. Rosin, Y. Nicolai, Trace metals analysis in estuarine and seawater by ICP-MS using on line preconcentration and matrix elimination with chelating resin, *Talanta*, 1999, 50, 433-444.
- [25] E. P. Oliveira, L. Yang, R. E. Sturgeon, R. E. Santelli, M. A. Bezerry, S. N. Willie, R. Capilla, Determination of trace metals in high-salinity petroleum produced formation water by inductively coupled plasma mass spectrometry following on-line analyte separation/preconcentration, *J. Anal. Atom. Spectrom.*, 2011, 26, 578-585.

- [26] R. Hahn, N. Kunkel, C. Hein, R. Kautenburger, H. Kohlmann, Recovery rate and homogeneity of doping europium into luminescent metal hydrides by chemical analysis, *RSC Adv.*, 2015, 5, 9722-9726.
- [27] R. Clough, H. Sela, A. Milne, M. C. Lohan, S. Tokalioglu, P. J. Worsfold, Uncertainty contributions to the measurement of dissolved Co, Fe, Pb and V in seawater using flow injection with solid phase preconcentration and detection by collision/reaction cell-quadrupole ICP-MS, *Talanta*, 2015, 133, 162-169.
- [28] H. Duan, J. Lin, Z. Gong, J. Huang, S. Yang, Removal of high-salinity matrices through polymer-complexation-ultrafiltration for the detection of trace levels of REEs using inductively coupled plasma mass spectrometry, *Talanta*, 2015, 143, 287-293.
- [29] V. Thomsen, D. Schatzlein, D. Mercuro, Limits of detection in spectroscopy, *Spectroscopy*, 2003, 18, 112-114.
- [30] V. Barwick, E. Prichard, EURACHEM Terminology in Analytical Measurement – Introduction to VIM 3, 2011.

#### Highlights

Simple and effective modification of ICP-MS for transient measurements

Transient ICP-MS method for trace element analysis in complex matrices

Determination of trace elements in high saline samples without sample clean-up

graphical abstract

