Monitoring of saline fluids from geothermal plants: Special aspects of sampling, sample preservation and analysis

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ABSTRACT

Sampling and analysis of saline fluids requires experience and from time to time also an adaptation, optimisation or substitution of methods. Some hundreds of different saline fluids were sampled and analysed by the authors during the last decade. Based on examples some issues in order to find the actual composition of saline fluids are presented.

In detail, for determination of cations and elements inductively coupled plasma mass spectrometry (ICP-MS) is used. By this method both, major and minor, cations can be analysed. Based on the example of Ca analysis the matrix effect resulting in an overestimation of the concentration is demonstrated. In consequence, analysis with standard addition was performed. Another possibility is to substitute the method. In this case atomic absorption spectroscopy (AAS) can be the alternative method, for the determination of heavy metals a voltammetric method can be applied. A special method was used for analysis of sulphide: the polarography. Anions were analysed by ion chromatography based on standardised methods. Based on the examples of co-elution of fluoride with organic acids and thiosulfate with iodide it is shown that the fluid composition is complex and the procedure to analyse it can diverge from standardised methods. Radionuclide analysis in saline fluids using gamma ray spectrometry is complicated by the occurrence of radioactive disequilibria. A mathematical treatment of the analytical results is necessary to achieve correct concentrations for the date of sampling.

1. INTRODUCTION

Monitoring of saline fluids is one essential tool for a correct operation of geothermal plants. Saline fluids from different aquifers varies among others concerning its total salt content, its chemical composition, its radionuclide inventory, its content of suspended particles, its gas composition and temperature. Depending on these variables sampling techniques, pre-treatment and preservation require an individual adaption.

Moreover, several techniques or applications for analysis of the saline fluids vary in dependence on the composition of the fluid. For characterisation of saline fluids standard methods, their adaptation and modification are presented.

2. METHODS

Cations and elements were determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS; Element 2, Thermo Fisher Scientific) according to DIN EN ISO 17294-2. The accumulated ions are separated by a magnetic and electrostatic field with subsequent detection by a multiplier.

Metrohm Ion chromatography systems (882 Compact IC plus, 930 Compact IC flex) with both, conductivity and UV detection, were used for determination of dissolved anions according to DIN EN ISO 10304-1 (D 20). Analysis was performed on Metrosep A Supp 5 columns of different length at a temperature of 30°C using a mixture of $NaHCO_3/Na_2CO_3$ (1 mM, 3.2 mM) as eluent.

Sulphide was determined polarographically by 797 VA Computrace (Metrohm) according to Metrohm Application Bulletin 199/3d.

Pb, Zn, Cu, Cd were analysed by a voltammetric method according to DIN 38406 E16 using the 797 VA Computrace (Metrohm) as well.

Gamma ray spectrometry measurements were performed in the underground laboratory Felsenkeller (Niese et al 1998) on several low-level spectrometry systems using HPGe detectors of 20 ... 90 % relative efficiency.

3. ANALYSIS OF MAJOR CATIONS AND ANIONS – DILUTION OF THE SAMPLES

Saline fluids from geothermic sources are characterised by high concentration of sodium, chloride and calcium. These main components are accompanied by a multitude of other elements and ions. As the number of components is diverse and their concentrations differ considerably (see Tab. 1) the analysis of saline fluids is complex and needs an adaption to the fluid composition.

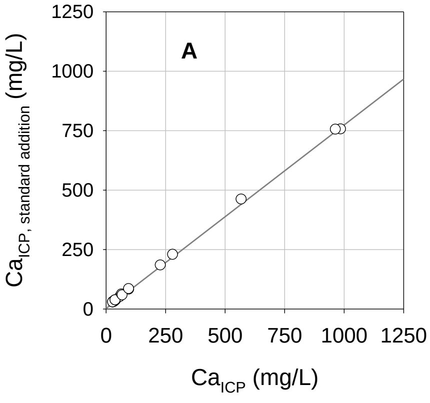
Table 1: Concentration range for components of saline fluids.

Components	examples	Concentration (mg/L)	
		minimum	maximum
major	Na, K, Cl^-, SO_4^{2-}	-	up to 10^5
minor	Cu, Ni, Hg	$< 10^{-3}$	-

Working ranges of the methods lie mostly in the range of micrograms per litre. Highest concentrations are more than 100 g/L. Thus, saline fluids have to dilute up to 1 : 10^6 in order to match the working range of the methods. By contrast, minor components have low concentrations. Hence, analysis of these components is often performed using the original samples with the consequence of interferences elicited by other components.

4. ANALYSIS OF CALCIUM – INTERFERENCES WITH THE SAMPLE MATRIX

Quantification of some components is often problematic as the analysis is interfered variously by the other ions. Consequently, measured values may be inaccurate and have to evaluate by alternative method or by the standard addition method. Thus, in order to detect and eliminate such effects standard addition method was used for determination of Ca in saline solutions (see Figure 1). Ca was determined by ICP-MS and AAS. Whereas Ca values measured by ICP-MS were considerably higher as determined by ICP-MS using the standard addition method (see Figure 1A) Ca values analysed by AAS were comparable to the ICP-MS results obtained with standard addition (Figure 1B). The slope of the regression line is closer to 1 for the relationship between Ca determined by AAS and ICP-MS standard addition method. In conclusion, when analysing Ca in this special saline matrix by ICP-MS the standard addition is the preferable method. Otherwise AAS can be used.



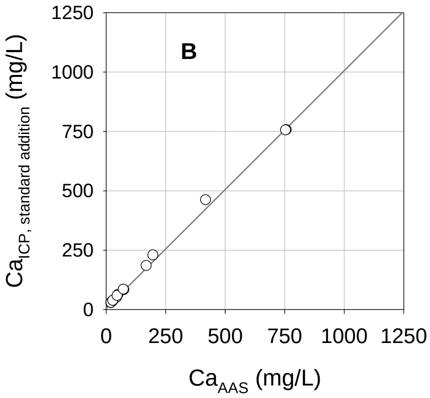


Figure 1: Analysis of Ca in saline fluids: A Determination by ICP-MS versus ICP-MS with standard addition. B Determination by AAS versus ICP-MS with standard addition. The slope as result of deming regression is 0.772 for A and 1.00 for B.

5. ANALYSIS OF TRACE ELEMENTS BESIDES THE MAJOR COMPONENTS – VOLTAMMETRIC DETERMINATION

An alternative method to analyse minor components, e.g. heavy metals, is offered by voltammetric measurements. The advantage of the method is that the high salt concentrations serves as electrolyte and may be beneficial to the analytical procedures.

Thus, for the analysis of lead and zinc a voltammetric procedure according to DIN 38406 E16 was applied (Figure 2). Concentrations were estimated by standard addition method.

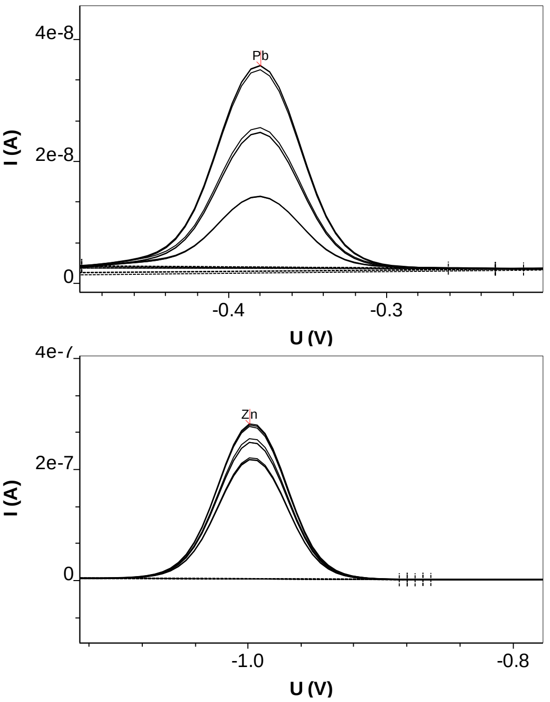


Figure 2: Voltammetric determination of zinc and lead in saline fluids.

6. INFLUENCE OF PRESERVATION, DILUTION AND FILTRATION OF SAMPLES

An important influence is attributed to an adequate pre-treatment of the samples, especially to the fact that the temperature of the fluid decreases during sampling. In general, samples for ICP-MS analysis have to be preserved by adding nitric acid in order to keep ions in solution. As earthy based ions tend to precipitate it is appropriate to dilute the samples directly after sampling. For analysis of sulphide an antioxidant reagent (SAOB) is added in order to avoid the oxidation of sulphide. As in sulphide-rich samples also sulphate concentration can be influenced, fluids for sulphate analysis have also to be fixed. Instead of SAOB the fluids are preserved by adding zinc acetate for analysing sulphate by ion chromatography. Further, fluids may contain suspended particles. By adding nitric acid parts of them can be solubilised. Consequently, only after filtration of the fluids the measured values of dissolved concentrations are accurate. For filtration cellulose acetate filters with pore size of 0.45 µm are used. On example concerning the influence of filtration is given by the comparison of selected ions (Table 2). The difference of measured values between filtered and unfiltered samples may exceed the uncertainty of the method for some elements considerable (see for example Cu). However, the difference can also be lower the uncertainty of the method (see for example Na, chloride).

Table 2: Range of selected components between filtered and unfiltered samples.

component	Range = Δ(variables)/mean(variables) (%)
Na	-0,4
Cl	-0,7
Cu	+140
Sr	+5,0
sulphate	-5,1

7. POLAROGRAPHIC DETERMINATION OF SULPHIDE

For determination of sulphide a polarographic method was applied. The method allowed the analysis of sulphide up to 250 µg/L, the detection of the method limit is 30 µg/L. In comparison to the photometric method this method is less time consuming.

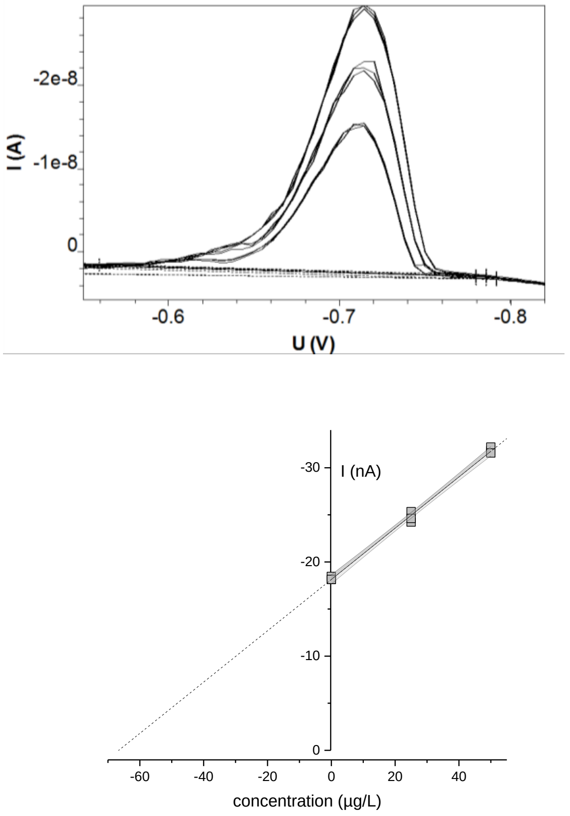


Figure 3: Polarographic determination of sulphide in saline fluids. Result of standard addition plot: 0.067 mg/L sulphide.

8. SPECIAL ASPECTS OF ION CHROMATOGRAPHIC DETERMINATION

Anions which are determined by ion chromatography standard methods are fluoride, chloride, bromide, iodide, nitrate, nitrite, sulphate.

Moreover, by the same method short-chain organic acids, namely formate, acetate and propionates, can be analysed. However, resolution of the peaks of these three ions is not complete when analysis is performed by the standard method for anions using a Metrosep A Supp 5 column (see Figure 4A). The elution within the range of retention times of organic acids is interfered by elution of fluoride. In order to analyse fluoride more precise the standard addition method is applied (not presented). For analysis of organic acids another method including the change of the column and the eluent can be used (see Figure 4B) resulting to a complete resolution of the peaks.

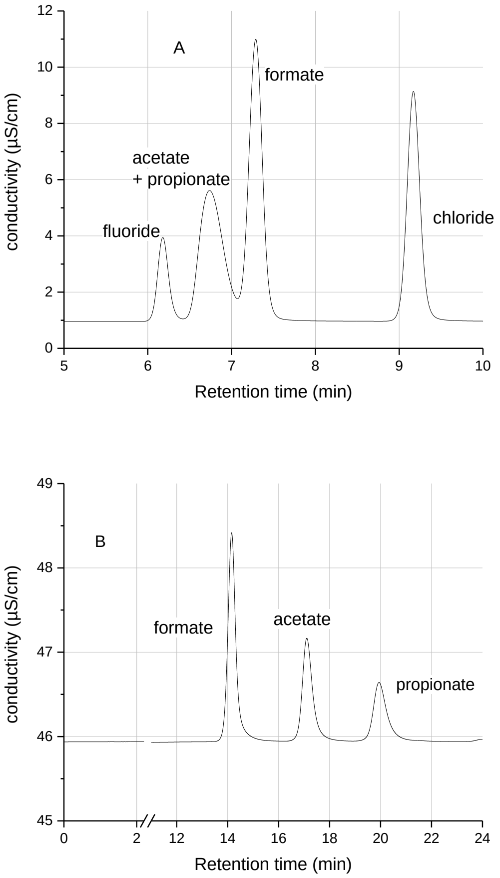


Figure 4: Ion chromatograms of a mixture of organic acids with anions. A Analysis with Metrosep A Supp 5. B Analysis with Metrosep Organic Acids.

For analysis of iodide it is important to test whether or not sample can contain thiosulphate. In this case a complete separation of iodide and thiosulphate is only possible by analysing with a column of 250 mm length (compare Figure 5A and 5B). By contrast, iodide and thiosulphate are overlapped when analysing with a shorter column (see Figure 5A).

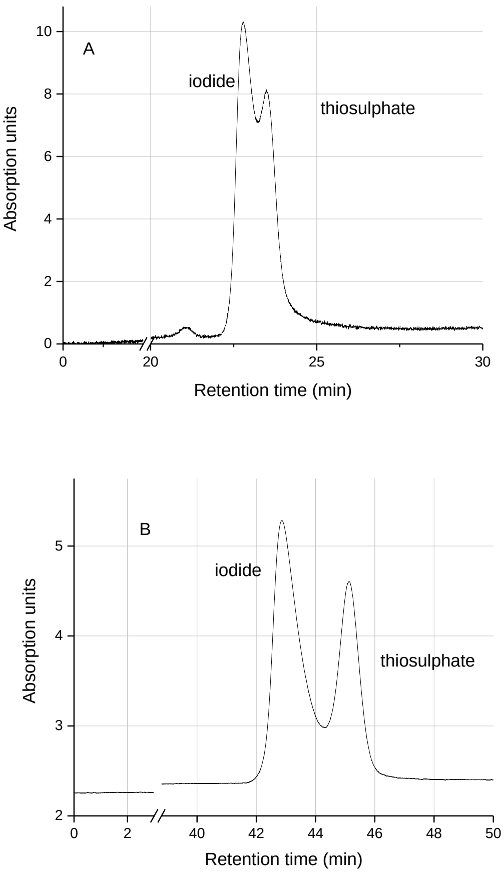


Figure 5: Ion chromatograms of fluids containing iodide and thiosulphate as well. Analysis with Metrosep A Supp 5: A length of the column 150 mm. B length of the column 250 mm.

9. RADIONUCLIDES IN SALINE FLUIDS

Deepwaters of high salinity often show enhanced levels of members of the natural decay chains, namely ^{226}Ra, ^{210}Pb (^{238}U decay series) and ^{228}Ra, ^{224}Ra (^{232}Th decay series) as well as the natural radioactive potassium isotope ^{40}K. Other members like all Uranium and Thorium isotopes lie below the detection limits (cf. Degering & Köhler 2009). The appearing members of the decay series are called “unsupported” because of the absence of their parent nuclides. As a consequence, strong radioactive disequilibria occur and result in a time dependence of the activity concentrations. To determine the concentrations at the moment of sampling simple exponential decay correction lead to erroneous results and must be replaced by a mathematical model reconstructing the time evolution of these disequilibria. This mathematical approach is described in detail by Degering & Köhler (2011).

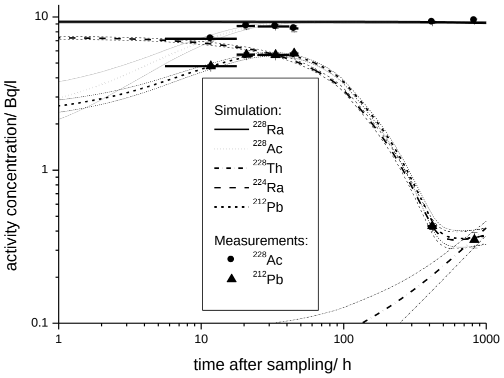


Figure 6: Time evolution of the radioactive disequilibrium in the ^{232}Th decay series in a fluid sample from a geothermal plant (from Degering & Köhler 2011).

Figure 6 gives an example of such a simulation based on six gamma spectrometric measurements on the fluid. At least three measurements are necessary for a complete reconstruction of the state at the time of sampling.

10. CONCLUSIONS

Analysis of saline fluids can be performed using common methods. However, based on examples it is demonstrated that these standard procedures do not always yield to unbiased results. Saline fluids are complex mixtures. In order to sample and analyse it, chemical and physical interactions should be taken into account. On the way to optimise the analysis various procedures have to be tested.

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