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Chemical analysis of sulfur species in geothermal waters

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ABSTRACT

Analytical methods have been developed to determine sulfur species concentrations in natural geothermal waters using Reagent-Free^{TM} Ion Chromatography (RF^{TM}-IC), titrations and spectrophotometry. The sulfur species include $SO_4{}^{2-}$, $S_2O_3{}^{2-}$, and $\sum S^{2-}$ with additional determination of $SO_3{}^{2-}$ and $S_xO_6{}^{2-}$ that remains somewhat semiquantitative. The observed workable limits of detections were $\leq$0.5 μM depending on sample matrix and the analytical detection limits were 0.1 μM. Due to changes in sulfur species concentrations upon storage, on-site analyses of natural water samples were preferred. Alternatively, the samples may be stabilized on resin for later elution and analysis in the laboratory. The analytical method further allowed simultaneous determination of other anions including F^-, Cl^-, dissolved inorganic carbon (DIC) and $NO_3{}^-$ without sample preservation or stabilization. The power of the newly developed methods relies in routine analysis of sulfur speciation of importance in natural waters using techniques and facilities available in most laboratories doing water sample analysis. The new methods were successfully applied for the determination of sulfur species concentrations in samples of natural and synthetic waters.

1. Introduction

The chemistry of sulfur redox compounds is very important to many geochemical and biogeochemical processes [1–4]. The distribution of sulfur species often depends on kinetics rather than thermodynamics, resulting in difficulties in sample preservation and accurate determination of the respective species. Geothermal waters ambiguously contain sulfur as one of the main components. The most common oxidation states include sulfide ($\sum S^{2-}$) and sulfate ($SO_4{}^{2-}$) but other species such as sulfur dioxide (SO_2) and elemental sulfur (S^0) are associated with volcanic hydrothermal fluids. In contrast to thermodynamic considerations, metastable intermediate sulfur species such as sulfite ($SO_3{}^{2-}$), thiosulfate ($S_2O_3{}^{2-}$) and polythionates ($S_xO_6{}^{2-}$) may also be present in measurable and sometimes significant concentrations both in geothermal waters as well as cold sulfide-rich natural waters including estuarine sediments and tidal flats [5–11]. Thus, it is crucial, but non-trivial, to analyze the species concentrations of importance, either on-site or on preserve samples until analyzed in the laboratory.

Many analytical methods have been developed and used for sulfur species determination. Wet chemical procedures can be applied to analyze most sulfur species. They are, however, time consuming and interferences may be a problem [12–14]. UV–vis spectrophotometry has also been applied to low concentrations (~10^{-6} M), however, the technique is usually only applicable in solutions only containing sulfur species [13–16]. Polarography and voltametry have been used with success to very low concentrations (~10^{-8} M) [17,18]. Infra-red (IR) and Raman spectroscopy has also been applied at ambient to elevated temperatures [19–22] these techniques not being very sensitive (>10^{-4} M). Ion chromatography (IC) and capillary electrophoreses (CE) have been particularly successful in determining multiple sulfur species in a given run to low concentrations (~10^{-7} M) [23].

Sulfur is among the major components in geothermal waters. Dissolved sulfate and sulfides are most common but other intermediate species have also been identified including polysulfides, thiosulfate, polythionates and sulfite [6,7,10,24,25]. The true sulfur speciation in geothermal waters is difficult to preserve for laboratory analysis. Most previous studies have either not considered this problem and used geothermal waters for matrix purpose only or preserved the species concentrations by chemical stabilization, freezing or using ion-exchange resin [7,11,24–32]. In many cases, however, preservation is difficult and may lead to analytical difficulties later on. Instead, it may be simpler to perform analysis immediately on-site. In this study, routine analytical methods were developed and applied for on-site determination of sulfur species

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concentrations in dilute geothermal waters. The analytical scheme allowed for simultaneous determination sulfur speciation including SO_4^{2-} and $S_2O_3^{2-}$, with additional analysis of other species of interest including F, Cl, CO_3^{2-} and NO_3^- and of SO_3^{2-} and $S_xO_6^{2-}$ that remains somewhat semiquantitative using ion chromatography. Total dissolved sulfides ($\sum S^{2-}$) were further analyzed by titration and/or spectrophotometrically.

2. Methods

2.1. Sample collection

Samples of natural geothermal waters including hot springs, acid-sulfate pools, mud pots and well discharges were collected and analyzed on-site within ~5 min from sampling for sulfur species concentrations. For comparison, samples were also collected and stabilized onto a resin and into amber glass bottles for laboratory analysis. All samples were filtered on-site through 0.2 μm filter (cellulose acetate) into pre-cleaned bottles. High temperature two-phase (steam and water) well discharges were collected using a Webre separator [33] and the liquid sample fraction was cooled and filtered for sulfur species analysis.

2.2. Standards and reagents

Standard solutions of $\sum S^{2-}$, SO_3^{2-}, $S_2O_3^{2}$, $S_xO_6^{2-}$ and SO_4^{2-} were prepared gravimetrically using deionized water (MilliQ 18 MΩ) the respective salts $Na_2S{\cdot}9H_2O$ (Sigma–Aldrich), Na_2SO_3 (Riedel-de Haen, puriss), $Na_2S_2O_3{\cdot}H_2O$ (Merck, p.a.), $K_2S_4O_6$ (Sigma–Aldrich), and SO_4 commercial standard solution (CertiPUR) in prewashed bottles, respectively. Deionized water used for SO_3^{2-} and $S_4O_6^{2-}$ solutions was boiled for >30 min and cooled under Ar-atmosphere. Tetrathionate standards were made in acid solutions of 0.01 M HCl. Thiosulfate and sulfite solutions were standardized using iodometric titration or as SO_4^{2-} after oxidation by H_2O_2 in the presence UV-light. For preparation of sulfide solution free of other species, washed and dried crystals were dissolved into deionized water that was boiled and cooled as described previously. Sulfide solution was standardized by precipitation titration using 0.001 M Hg–acetate solution (Sigma–Aldrich) and dithizone (Sigma–Aldrich, puriss) as an indicator [33]. For determination of $\sum S^{2-}$ by methylene blue method reagents were freshly prepared [34].

2.3. Determination of sulfoxy anions by RF™-IC

Dionex-2000 Reagent-Free™ Ion Chromatography (RF™-IC) system was used to determine the sulfoxy-anion species concentrations including SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, and $S_xO_6^{2-}$. The instrumental set-up consisted of IonPac® AG16 guard and AS16 analytical columns, KOH eluent that was degassed by vacuum and produced automatically in-line elecrochemically, ASRS-ULTRA suppressor and conductivity cell. Data collection was carried out with the Chromeleon computer program. The run conditions were optimized with the aid of Virtual Column software in Chromeleon and standard solutions tests to allow determination of sulfur species and major anions with good separation in reasonably short run duration, with main emphasis being on SO_4^{2-} and $S_2O_3^{2-}$. Run duration was 35 and 15 min with and without the incorporation of polythionates, respectively. Ramped eluent concentration was used with 18 mM (0–7 min), 18–45 mM (7–8 min) and 45 mM (8–35 min) KOH at flow rate 1 ml min^{-1}. For analysis of natural geothermal water, run conditions were varied if necessary to achieve better peak separation. Injection loop volume used was typically 25 μl but ranged between 10 and 100 μl to improve detection. Filtered samples were injected by hand using 1 ml PP syringes. Alternatively, the same set-up with IonPac® AG11 guard and AS11 analytical columns and isocratic 17 mM KOH eluent concentration was used with total runtime of 22 min to allow better separation of SO_3^{-2} and SO_4^{-2} compared to the columns AG16 and AS16.

Standard curves and synthetic samples were made and analyzed in the laboratory whereas samples of natural geothermal waters were analyzed within ~5 min of sampling on-site if not otherwise indicated.

Several water samples were collected on to anion exchange resin. The resin used was Bio-Rad™ (AG2-X8) previously shown to be appropriate for quantitative absorption of $S_2O_3^{2-}$, SO_4^{2-} and $S_xO_6^{2-}$ [35]. The resin units were prepared in the laboratory by packing slurry of resin and deionized water into 4 ml resin holder, with PP frits inserted at bottom and top and the column closed with plastic caps. The resins were activated using 0.1 M KOH. In the field, 10–60 ml of filtered (0.2 μm) sample was pumped through the column at the speed of 1–2 ml min^{-1} followed by wash with deionized water at the end of sampling to prevent side reactions upon storage. The sample volume was measured based on weight. The resin has a binding capacity of 1.2 meq l^{-1}. Thus the resin and sample volume have to be chosen in order to avoid saturation of the resin. Fully packed 4 ml resin column was found to be suitable for 100 ml of 10 mM SO_4 and S_2O_3 with 1% throughput of the sulfur species. The sulfoxyanions were subsequently eluted at 1.5 ml min^{-1} in the laboratory using 0.5 M KCl for sulfate and thiosulfate and 4 M KCl solutions for polythionates, followed by dilution to 0.1 M KCl. The concentrations of the sulfoxyanions were analyzed using the RF™-IC method described previously.

2.4. Sulfide analysis

Total dissolved sulfide was determined by precipitation titration with mercury (Hg)–acetate on-site [33], colorimetrically after formation of methylene blue complex on-site [34] or using direct UV–vis spectrophotometry in the laboratory [15,16]. Titration of sulfide with Hg–acetate solution is based on precipitation of HgS(s) in alkaline acetone–water solution using dithizone as the end-point indicator. After all S^{2-} have been precipitated, excess Hg^{2+} complexes with dithizone forming a pink complex. Alkaline conditions are to minimize degassing of sulfide, whereas acetone is needed to dissolve dithizone. Sample volume ranged between 0.1 and 50 ml depending of dissolved sulfide concentrations.

For spectrophotometric analysis of dissolved sulfide, methylene blue complex was formed on-site [34]. The sample volume ranged between 0.1 and 7.5 ml and was matched up with deionized water to give total of 7.5 ml when appropriate. The samples were stored in the dark and determined in the laboratory using UV–vis spectrophotometer at wavelength of 664 nm using 1 cm cuvette. Standards were freshly prepared prior to analysis. The method is sensitive to pH, and thus care has to be taken when it is applied to acidic waters due to protonation of the methylene blue complex, that shifts the absorbance from 664 nm to lower wavelengths. The pH can either by adjusted by the addition of 0.1 M NaOH or using a small sample volume.

In addition, the concentrations of HS^-, SO_3^{2-} and $S_2O_3^{2-}$ were measured in synthetic samples in the laboratory by direct UV–vis spectrophotometry and applying the Beer–Lambert Law, $A = l\sum \varepsilon_i c_i$, where A is the total absorbance, l is the path length (1 cm), and ε_i and c_i are the molar absorbtivities and concentration of the ith species, respectively. The maximum absorption band at 230 nm was used for HS^- (ε, 7800 l cm^{-1} mol^{-1}) after correction for absorption caused by the presence of $S_2O_3^{2-}$ (ε, 2250 l cm^{-1} mol^{-1}) and SO_3^{2-} (ε, 500 l cm^{-1} mol^{-1}) [36]. The SO_3^{2-} and $S_2O_3^{2-}$ concentrations were determined simultaneously using the RF™-IC method described previously.

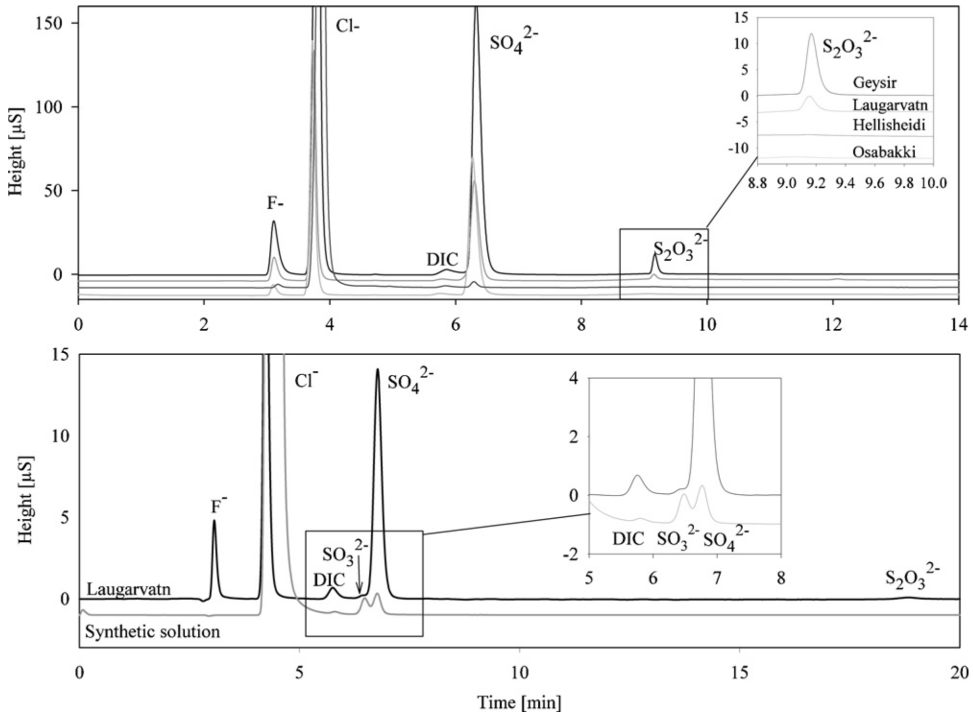

Fig. 1. Ion chromatogram of representative geothermal water samples using Dionex RF^{TM}-IC with (a) IonPac® AG16 and AS16 columns, 16–35 mM KOH eluent and 25 µl loop size. Samples from hot springs Geysir, Laugarvatn, and hot water well at Ósabakki in the Southern Lowlands, Iceland, and two-phase well discharge from two-phase well 17 at Hellisheidi. (b) IonPac® AG11 and AS11 columns, 17 mM KOH eluent and 10 µl loop. Sample from hot spring at Laugarvatn and synthetic solution containing Cl^-, SO_3^{2-} and SO_4^{2-}. Intensities were subtracted to allow better comparison of various chromatograms. DIC stands for dissolved inorganic carbon.

3. Results and discussion

3.1. Determination of sulfoxy-anions by RF^{TM}-IC

The sulfoxy-anions SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$ and $S_4O_6^{2-}$ were determined within 5 min of sampling using RF^{TM}-IC. In addition, other major anions were analyzed simultaneously using the same run including F^-, Cl^- and CO_3^{2-}. Typical chromatograms are shown in Fig. 1 for natural geothermal waters. The analytical detection limits were 0.1 µM based on 3σ of blank sample and the working detection limits indicating the concentration limit above which the results were reproducible within ±3%, were observed to be

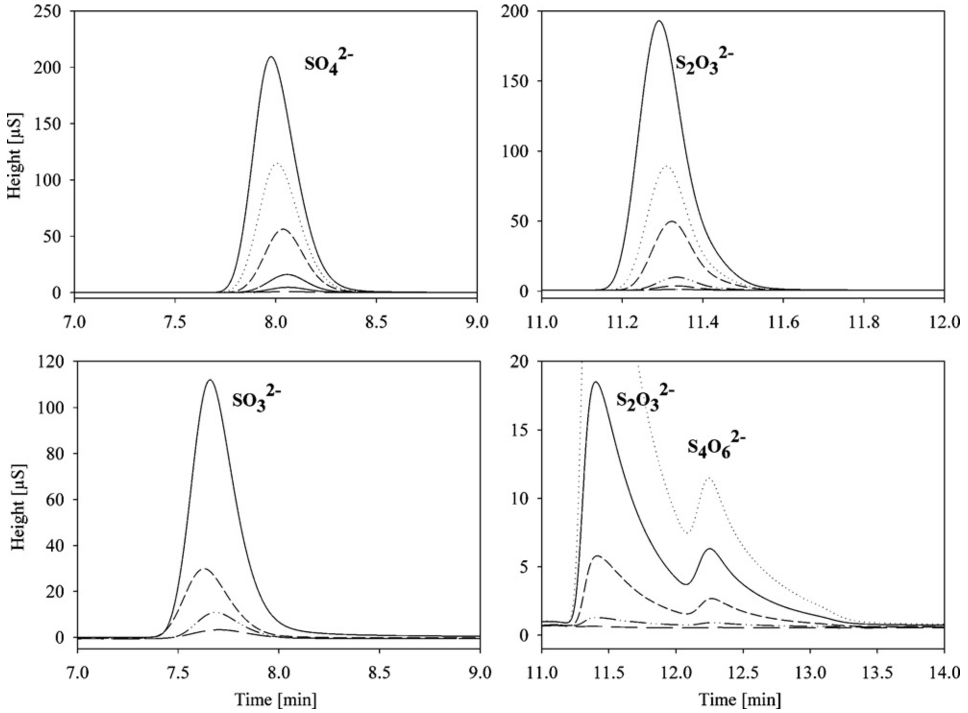

Fig. 2. Shapes and positions of sulfoxyanion peaks by Dionex RF^{TM}-IC using IonPac® AG-16 and AS-16 columns (loop size 25 µl, 18–45 mM KOH eluent).

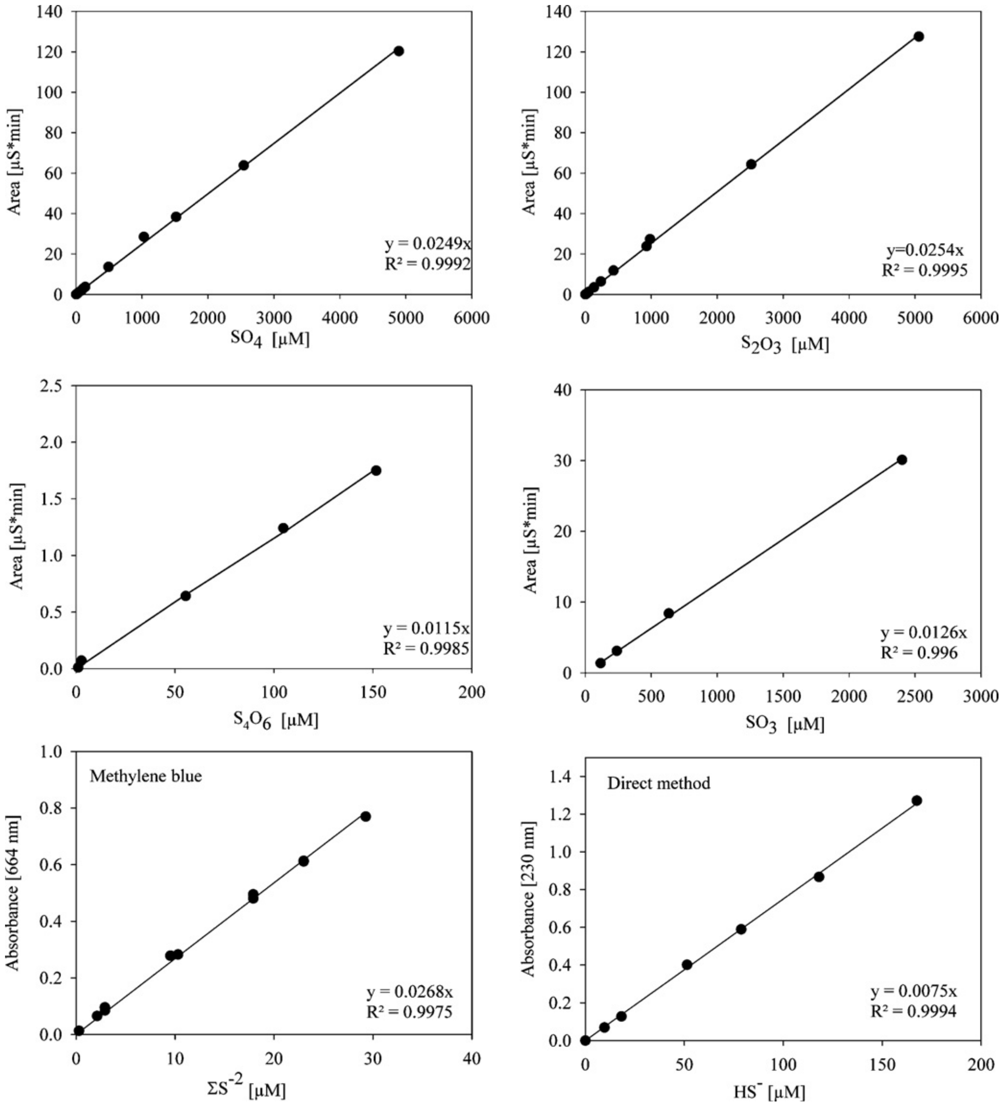

Fig. 3. Examples of calibration curves for sulfoxyanions determined by Dionex RF^{TM}-IC using IonPac® AG16 and AS16 columns (loop size 25 µl, 18–45 mM KOH eluent) and sulfide determination by methylene blue method and direct UV–vis spectrophotometry with 1 cm path length.

$\leq$0.5 µM depending on sample matrix. The detection limit is sufficient for detection of the major sulfur species in most natural geothermal waters down to the $\sim 10^{-7}$ M concentration level.

In solutions containing major anions and $S_2O_3{}^{2-}$, the analytical peaks were nicely separated and symmetrical (Fig. 2). This allowed for accurate linear calibration based on peak area (Fig. 3), reaching up to >5 mM. For lower concentrations (<1 mM), the separate calibration using the standards in the respective concentration range is recommended. Accurate determination of $SO_3{}^{2-}$, and $S_xO_6{}^{2-}$ was more complicated and their determination remains somewhat semiquantitative in natural geothermal waters due to appearance of $SO_3{}^{2-}$ peak immediately before $SO_4{}^{2-}$ and the instability and impurity of commercial $S_4O_6{}^{2-}$ standard giving rise to a series of peaks. The major peak arising from $S_4O_6{}^{2-}$ standard solution had retention time of 12.3 min and minor peaks (26.5 and 29.7 min, <5% of the area at 12.3 min) in addition to $S_2O_3{}^{2-}$ and minor $SO_4{}^{2-}$. These are considered to be due to $S_4O_6{}^{2-}$ and other polythionates, respectively.

Alternative run with columns AG and AS11 was set-up to better separate $SO_3{}^{2-}$ and $SO_4{}^{2-}$ in addition to F^-, Cl^-, and $S_2O_3{}^{2-}$. The determination of $SO_3{}^{2-}$ was disturbed by the presence of high concentrations of $CO_3{}^{2-}$ and $SO_4{}^{2-}$ and had to be treated as a rider peak, resulting resulted in increased detection limits and decreased analytical precision (Fig. 1). The calibration curves for $S_2O_3{}^{2-}$ and $SO_4{}^{2-}$ had the similar slope as in Fig. 3. Columns AG and AS-16 may, however, be preferred due to their ability to separate other species of interest including arsenic and selenium species [37,38], and better suitability for $S_xO_6{}^{2-}$ determination.

Sample stabilities were tested both on synthetic standards and on natural geothermal water samples collected in the field. Representative results are shown in Fig. 4. The concentrations of the sulfoxyanions in sulfidic waters changed rapidly upon storage in presence of atmospheric O_2. The oxidation and disproportionation reactions were found to depend on water pH [10]. In general, dissolved sulfide was found to oxidize to form $S_2O_3{}^{2-}$ and $SO_4{}^{2-}$ upon storage. In addition, synthetic solutions of $SO_3{}^{2-}$ and $S_4O_6{}^{2-}$ were found to be unstable. It results that for accurate sulfoxyanion determination samples need to be analyzed immediately upon preparation or sampling with the exception of waters only containing $SO_4{}^{2-}$ or $S_2O_3{}^{2-}$. This can be achieved either by sample stabilization on-site or direct analysis-on site.

3.2. Determination of dissolved sulfide

The concentrations of dissolved sulfide ($\sum S^{2-}$) were determined by three methods, by precipitation titration using

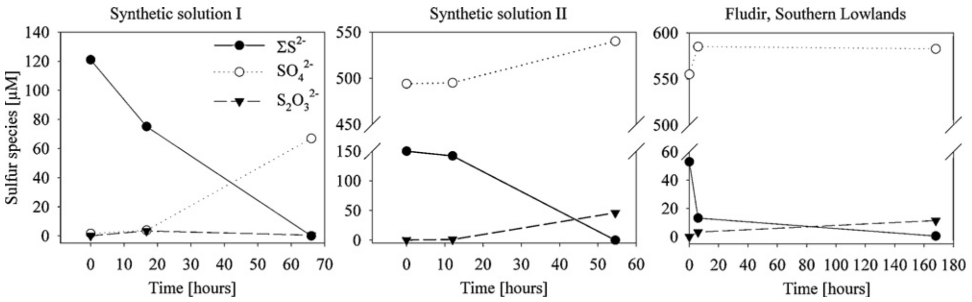

Fig. 4. Stability of synthetic laboratory solutions and natural geothermal water sample containing sulfide.

Hg–acetate and dithizone as an indicator [33], colorimetrically using the methylene blue method [34] and using direct UV–vis spectrophotometry [15,16,36]. Typical calibration (recovery) curves are shown in Fig. 3. The calibration curves for methylene blue method and direct UV–vis spectrophotometry using 1 cm path length start to curve off above 30 and 200 μM, respectively. Smaller cell path length can be used to extend the linear range to higher concentrations. The first two methods for the sulfide analysis are not specific for free sulfide and it is operationally defined as sulfide that is reactive upon Hg–acetate titration and the methylene blue complex. Methylene blue is considered to include S^{2-}, HS^-, H_2S, terminal sulfide in S_x^{2-} as well as acid reactive sulfides such as most MeS-type metal–sulfide complexes [39,40]. Hg–acetate titration includes sulfide that forms S^{2-} in alkaline conditions and reacts with Hg^{2+} to form HgS. However, it is not clear how polysulfides concentrations (S_x^{-2}) are affected by these methods. The UV–vis spectrophotometric method, however, is species sensitive. It utilizes the ion to solvent transitions and is capable of measuring individually HS^-, H_2S(aq) and some other sulfur species concentrations [10,15,16,36]. On the other hand, the direct determination

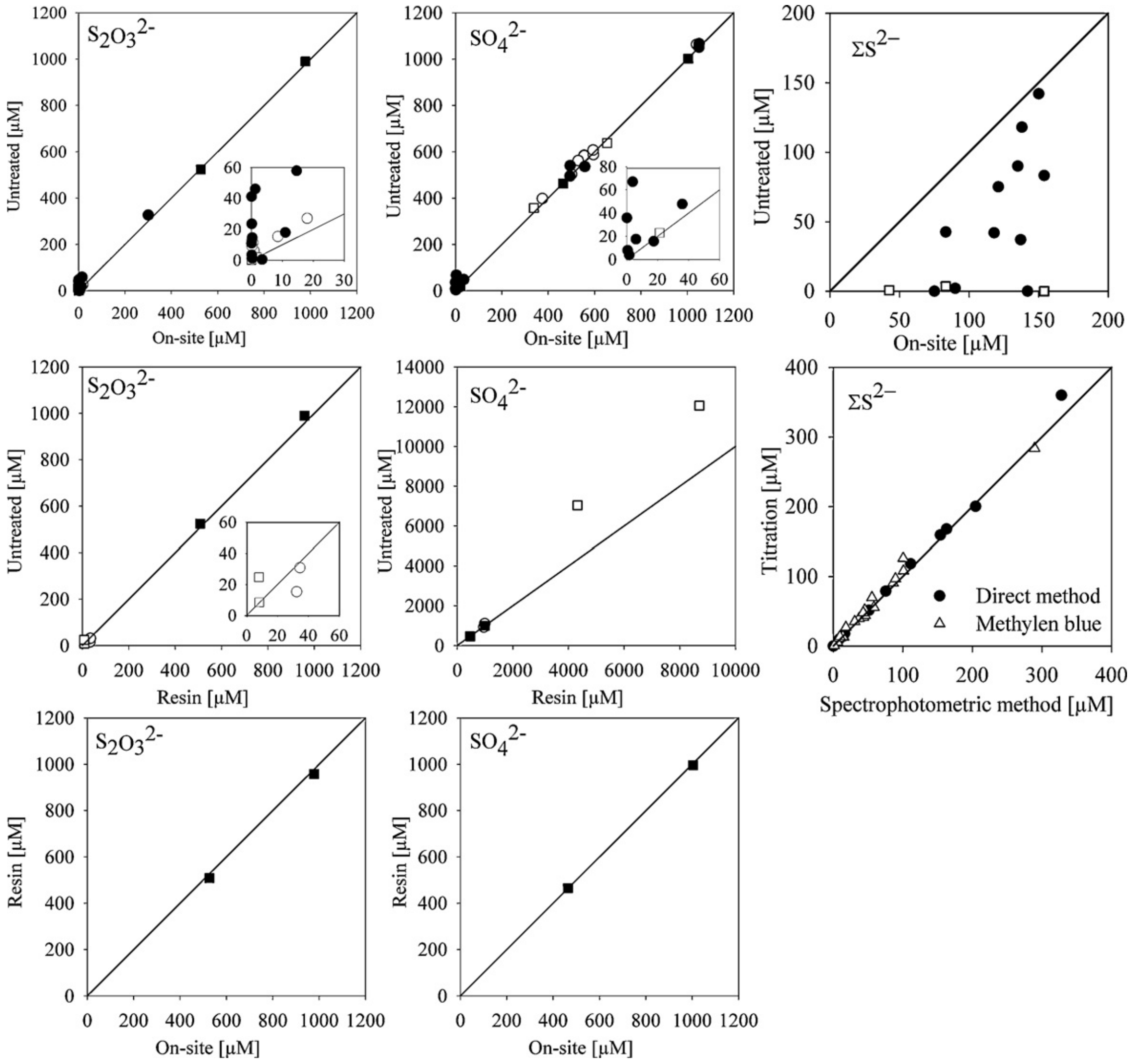

Fig. 5. Comparison of various analytical techniques for sulfur species determination for synthetic samples (black symbols) and geothermal water samples (white symbols). The samples that contained sulfide are indicated as circles and the sulfide free samples as squares. Sulfoxyanions were analyzed on-site or immediately after preparation of standard solution, analysis of untreated samples after 1–3 days in the laboratory and after sample stabilization onto resin followed by elution and IC analysis. Sulfide concentrations were determined by mercury acetate titration and methylene blue or direct UV–vis spectrophotometric method. The solid lines indicate 1:1 ratio.

Table 1

Comparison of analytical and sampling methods applied for sulfur species determination. Units are in μM.

#	Location	T (°C)	pH/°C	$\sum S^{2-}$				SO_4^{2-}				$S_2O_3^{2-}$				$S_xO_6^{2-}$			SO_3^{2-}		
				MB[a]	Titr.[b]	UV–vis[c]	Δ%	On-site[d]	Untr.[e]	Resin[f]	Δ%	On-site	Untr.	Resin	Δ%	On-site	Untr.	Resin Δ %	On-site	Untr. E	Resin Δ %
1	Otherrishola	97	8.25/97	101	108		6.5		930	955	2.6		15.3	32.3	52.6		<0.5	<0.5			
2	Blesi	92	8.41/92	43	48		10.4		1097	990	10.8		30.8	34.5	10.7		<0.5	<0.5			
3	Krýsuvík	100	2.58/21						7037	4327	62.6		8.5	8.3	2.4		0.5	<0.5			
4	Krýsuvík	100	2.59						12,052	8703	38.5		24.7	8.0	>100		0.5	<0.5			
5	Flúdir, 0.25 days	94	9.35/24	52.9				555	585		5.4	<0.5	3.3		>100	<0.5	<0.5				
6	Flúdir, 7 days	94	9.35/24	<1				555	583		5.0	<0.5	11.4		>100	<0.5	<0.5				
7	Ingolfsfjall	4	9.30/4	<1	<1			21.3	22.9		7.6	0	0		0	<0.5	<0.5				
8	Experimental solution	24	9.10/24		159	154	3.2	<0.5	35.8		>100	<0.5	11.0		>100				< 0.5	6.1	>100
9	Experimental solution	24	6.74/24			239		0.54	7.80		>100	<0.5	41.2		>100				< 0.5	2.2	>100

[a] MB, methylen blue spectrophotometric method.

[b] Titr., mercury acetate titration.

[c] UV–vis, direct UV–vis spectrophotometric method.

[d] Samples analyzed on-site in the field or immediately after preparation in the laboratory for synthetic samples.

[e] Untreated samples analyzed in the laboratory few hours to few days after sampling.

[f] Samples collected onto resin followed by analysis in the laboratory.

Table 2

Comparison of standard and analyzed concentrations of synthetic samples. Units are in μM.

	Solution	$\sum S^{2-}$					SO_4^{2-}					$S_2O_3^{2-}$					SO_3^{2-}					$S_xO_6^{2-}$				
		Std[a]	Titr.[b]	Δ %	UV–vis [c]	Δ %	Std	On-site[d]	Δ %	Resin[e]	Δ %	Std	On-site	Δ %	Resin	Δ %	Std	On-site	Δ %	Resin	Δ %	Std	On-site	Δ %	Resin	Δ %
1	$S_2O_3^{2-}$, SO_4^{2-}						1002	1004	0.2	996	0.6	990	978	1.2	958	3.2	0	<0.5		<0.5		0	<0.5		<0.5	
2	$S_2O_3^{2-}$, SO_4^{2-}						463	464	0.2	464	0.2	524	527	0.6	508	3.1	0	<0.5		<0.5		0	<0.5		<0.5	
3	S^{2-}, $S_2O_3^{2-}$, SO_4^{2-}	85.8	84.9	1.1			548	549	0.2			65.8	65.1	1.0			0	<0.5				0	<0.5			
4	S^{2-}, $S_2O_3^{2-}$, SO_4^{2-}	448	441	1.6			484	485	0.3			56.5	56.9	0.6			0	<0.5				0	<0.5			
5	S^{2-}, $S_2O_3^{2-}$, SO_4^{2-}	919	902	1.8			398	398	0.1			44.8	46.4	3.5			0	<0.5				0	<0.5			
6	S^{2-}	168			163	2.7	0	<0.5				0	<0.5				0	<0.5				0	<0.5			
7	S^{2-}		135				0	<0.5				0	<0.5				0	<0.5				0	<0.5			
8	$S_4O_6^{2-}$							0.99					106				0	<0.5				55	54	2.2		

[a] Std, standard concentration.

[b] Titr., Hg–acetate titration.

[c] UV–vis, direct UV–vis spectrophotometry.

[d] Analyzed immediately after preparation.

[e] Collected onto a resin.

of dissolved sulfide species concentration can only be made on simple samples only containing sulfur species and UV–vis inert compounds and is therefore not practical for dissolved sulfide analysis in natural samples.

3.3. Sulfur speciation in natural geothermal waters and synthetic samples

The performance of the various analytical methods was tested and compared with synthetic and natural geothermal waters. The results are shown in Tables 1 and 2 and Fig. 5.

The methods were compared using percent difference Δ % defined as:

$$\Delta\,\% = \frac{|c - c_{ref}|}{c_{ref}} \times 100$$

where c is the concentration determined by various methods and c_{ref} is the species concentration of the synthetic standard solution or on-site. The synthetic standard concentrations and immediately analyzed concentrations were in very good agreement in standard solutions and mixed standards, i.e. effectively it is standard solution concentrations typically within 3% (Table 2). However, the concentrations in natural samples and experimental solutions the various methods were found to depend on sulfur species present in the sample, sample preservation and analytical procedure (Table 1).

The three methods used for determining dissolved sulfide concentrations were in good agreement, usually with differences within 10% of the various methods (Tables 1, 2 and Fig. 5). However, with respect to the sulfoxyanions, this was not the case for solutions containing dissolved sulfide. Upon storage, $\sum S^{2-}$ was found to oxidize resulting in increased $S_2O_3{}^{2-}$ and $SO_4{}^{2-}$ with sample storage in untreated samples. On the other hand, reasonable agreement was observed between samples collected onto resin and analyzed in the laboratory and samples analyzed on-site with the exceptions of samples with elevated $SO_4{}^{2-}$ where oversaturation of the sample resins may have occurred (samples 3 and 4 in Table 1). However, the analytical detection and accuracy were found to be lower for resin samples close to the detection limit due to elevated Cl^- concentrations produced upon laboratory elution.

In addition to S^{2-}, $SO_4{}^{2-}$ and $S_2O_3{}^{2-}$, the method allowed for determination of $SO_3{}^{2-}$ and $S_xO_6{}^{2-}$ that were not commonly found in geothermal waters in Iceland. Due to problems arising from various sample matrixes and standard stability, their determination in natural waters may remain somewhat semiquantitative. Polythionates were only accurately measured on synthetic samples and usually not present in the geothermal waters except in very acidic samples where concentrations were close to analytical detection limits. Direct comparison of on-site analysis of natural geothermal waters and resin samples was therefore difficult.

Based on the above observations we conclude that for accurate sulfur species determination in sulfidic natural geothermal waters on-site analysis is preferred within few minutes of sampling. Alternatively, samples may be preserved using anion exchange resins, however, such treatment makes analysis by RF^{TM}-IC more difficult, less sensitive and accurate at low concentrations due to elevated Cl^- concentrations resulting from resin elution. However, concentrations of sulfur species will change within minutes to hours upon sample storage in untreated samples.

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References

[1] W. Stumm, J.J. Morgan, Aquatic Chemistry – An Introduction Emphasizing Chemical Equilibria in Natural Waters, second ed., Wiley, New York, 1981.
[2] P. Brimblecombe, in: H.D. Holland, K.K. Turekian (Eds.), Treatise on Geochemistry, vol. 8, Oxford, Pergamon, 2003, pp. 645–682.
[3] T.M. Seward, H.L. Barnes, in: H.L. Barnes (Ed.), Geochemistry of Hydrothermal Ore Deposits, third ed., Wiley, New York, 1997, pp. 435–486.
[4] D.J. Burdige, The Geochemisty of Marine Sediments, Princeton, Princeton, Oxford, 2006.
[5] B.B. Jørgensen, Science 249 (1990) 152.
[6] B. Takano, S. Ohsawa, R.B. Glover, J. Volcanol. Geotherm. Res. 60 (1994) 29.
[7] Y. Xu, M.A.A. Schoonen, D.K. Nordstrom, K.M. Cunningham, J.W. Ball, Geochim. Cosmochim. Acta 62 (1998) 3729.
[8] J. Gun, A. Goifman, I. Shkrob, A. Kamyshny, B. Ginzburg, O. Hadas, I. Dor, A.D. Modestov, O. Lev, Environ. Sci. Technol. 34 (2000) 4741.
[9] A. Kamyshny Jr., M. Zilberbrand, I. Ekeltchik, T. Voitsekovski, J. Gun, O. Lev, Aquat. Geochem. 14 (2008) 171.
[10] H. Kaasalainen, A. Stefánsson, Geochim. Cosmochim. Acta 75 (2011) 2777.
[11] J.G. Webster, Appl. Geochem. 2 (1987) 579.
[12] E. Blasius, G. Horn, A. Knochel, J. Munch, H. Wagner, in: G. Nickless (Ed.), Inorganic Sulfur Chemistry, 1968, p. 199.
[13] L. Szekeres, Talanta 21 (1974) 1.
[14] T. Koh, Anal. Sci. 6 (1990) 3.
[15] W.F. Giggenbach, Inorg. Chem. (1974) 1724.
[16] W.F. Giggenbach, Inorg. Chem. (1974) 1730.
[17] G.W. Luther III, T.M. Church, D. Powell, Deep-Sea Res. 38 (1991) S1121.
[18] E. Henneke, G.W. Luther III, G.J. De Lange, J. Hoefs, Geochim. Cosmochim. Acta 61 (1997) 307.
[19] S. Milicev, A. Stergarsek, Spectrochim. Acta A 45 (1989) 225.
[20] D.A. Holman, A.W. Thompson, D.W. Dennett, J.D. Otvos, Anal. Chem. 66 (1994) 1378.
[21] G.V. Bondarenko, Yu.E. Gorbaty, Geochim. Cosmochim. Acta 61 (1997) 1413.
[22] G.S. Pokrovski, L.S. Dubrovinsky, Science 331 (2011) 1052.
[23] J.W. O'Reilly, G.W. Dicinoski, M.J. Shaw, P.R. Haddad, Anal. Chim. Acta 432 (2001) 165.
[24] C.O. Moses, D.K. Nordstrom, A.L. Mills, Talanta 31 (1984) 331.
[25] A.A. Migdisov, A.Y. Bychkov, J. Volcanol. Geotherm. Res. 85 (1998) 153.
[26] Y. Xu, M.A.A. Schoonen, D.K. Nordstrom, K.M. Cunningham, J.W. Ball, J. Volcanol. Geotherm. Res. 97 (2000) 407.
[27] Y. Miura, Y. Yonemura, T. Koh, Nippon Kagaku Kaishi 8 (1991) 1083.
[28] M. Tsubamoto, T. Koh, Anal. Sci. 10 (1994) 595.
[29] Y. Miura, A. Saitoh, T. Koh, J. Chromatogr. A 770 (1997) 157.
[30] Y. Miura, K. Fukasawa, T. Koh, J. Chromatogr. A 804 (1998) 143.
[31] Y. Miura, A. Kawaoi, J. Chromatogr. A 884 (2000) 81.
[32] B. Takano, Watanuki, Talanta 35 (1988) 847.
[33] S. Arnórsson, J.Ö. Bjarnason, N. Giroud, I. Gunnarsson, A. Stefansson, Geofluids 6 (2006) 203.
[34] A.D. Eaton, L.S. Clesceri, W.R. Rice, A.E. Greenberg, M.A.H. Franson (Eds.), Standard Methods for the Examination of Water and Wastewater, American Public Health Association (APHA), American Water Works Association (AWWA) and Water Environment Federation (WEF), Washington, DC, 2005.
[35] G.K. Druschel, M.A.A. Schoonen, D.K. Nordstrom, J.W. Ball, Y. Xu, C.A. Cohn, Geochem. Trans. 4 (2003) 12.
[36] K.Y. Chen, J.C. Morris, Environ. Sci. Technol. 6 (1972) 529.
[37] D. Wallschläger, R. Roel, J. Anal. At. Spectrom. 16 (2001) 922.
[38] S. Stauder, B. Raue, F. Sacher, Environ. Sci. Technol. 39 (2005) 5933.
[39] H. Manolopoulos, Ph.D. thesis McMaster University, 2001.
[40] S.E. Mylon, G. Benoit, Environ. Sci. Technol. 35 (2001) 4544.