Ion Chromatographic Analysis of Sulfur Species (S2−, SO32−, and S2O32−) in Natural Geothermal Water Samples

メタデータ	言語: English 出版者: 公開日: 2022-04-05 キーワード (Ja): キーワード (En): 作成者: Amin, Muhammad, Oktavia, Budhi, Anang, Sedyohutomo, Lim, Lee Wah, Nurdin, Muhammad メールアドレス: 所属:
URL	http://hdl.handle.net/10271/00004123

Ion Chromatographic Analysis of Sulfur Species (S^{2-}, SO_3^{2-}, and $S_2O_3^{2-}$) in Natural Geothermal Water Samples

Muhammad Amin[1,2,*], Budhi Oktavia[3], Anang Sedyohutomo[4], Lee Wah Lim[5], and Muhammad Nurdin[6]

[1]*Department of Chemistry Education, Faculty of Teacher Training and Education, Universitas Khairun, Jln. Bandara Babullah, Akehuda, Ternate 97723, North Maluku, Indonesia*
[2]*Basic and Integrated Laboratory, Universitas Khairun, Jln. Jusuf Abdulrahman, Gambesi, Ternate 97719, North Maluku, Indonesia*
[3]*Department of Chemistry, Faculty of Mathematic and Natural Sciences, Universitas Negeri Padang, Jln. Prof. Dr. Hamka, Air Tawar, Padang 25131, West Sumatera, Indonesia*
[4]*Department of Chemistry, Hamamatsu University School of Medicine, 1-20-1 Handayama, Higashi-ku, Hamamatsu, Shizuoka Prefecture 431-3122, Japan*
[5]*Department of Chemistry and Biomolecular Science, Faculty of Engineering, Gifu University, 1-1 Yanagido, Gifu 501-1193, Japan*
[6]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Halu Oleo, Jln. HEA Mokodompit Kampus Hijau Bumi Tridharma, Anduonohu, Kendari 93232 – Southeast Sulawesi, Indonesia*
** Email: muh_amin@unkhair.ac.id*

Abstract

A practical ion chromatography (IC) method has been developed for the analysis of sulfur species (S^{2-}, SO_3^{2-}, and $S_2O_3^{2-}$) contained in natural geothermal water samples. All species were separated by the combination of 6.0 mM dipotassium hydrogen phosphate as the mobile phase and TSKgel IC-Anion-PW column as the stationary phase at a flow rate of 1.0 mL/min. The UV detection instrument was set at 210 nm to analyze the standard and all the real samples. The chromatograms show the sulfur species were completely analyzed in less than 10 min. The detection limits at S/N=3 were 0.045, 0.386, and 0.049 μM for S^{2-}, SO_3^{2-}, and $S_2O_3^{2-}$, respectively, whereas the repeatability values were below 2.34%, 4.21%, and 3.74% for retention time, peak height, and peak area, respectively. The practical method was successfully applied to the determination of sulfur species concentration in natural geothermal waters obtained from Jailolo, North Maluku Province, Indonesia. To evaluate the performance of method, the all samples were then collected in two main sample points: close to- and a little far from- the beach.

Keywords: *Ion chromatography, Anions, Sulfur species, Geothermal water, Jailolo*

1. Introduction

The development of ion chromatography (IC) techniques in analyzing qualitatively and quantitatively a number of anions and cations in various types of water samples have been developed [1]–[7]. As generally known, river water, pond water, lake water, and including geothermal water are examples of various types the surface waters. The various types of anions and cations in geothermal water samples have become a deep concern for scientists in revealing their content and its health benefit to human's life [8], [9].

Geothermal is a source of heat energy contains hot water, vapour, and rocks with associated minerals and other gases which are all inseparable in a geothermal system

[10]–[14]. Geothermal products can include energy, steam and hot water, and mineral content. Over centuries, geothermal water has been well known can be used directly such as for goals of heating, tourism, bathing and treatment. In many countries in the world, geothermal water therapy has become a part of routine medical treatments, and even as well as treatment as a prevention of diseases [15], [16].

Sulfur is the major components contained in geothermal waters that has potential as a medium for the treatment of skin diseases, relaxation, freshness [17]–[19]. Sulfur species such as sulfide, sulfite, and thiosulfate have been widely identified as forms of inorganic compounds containing sulfur. By determining these compounds means that the total of sulfur in the sample can be estimated, so that it can be maximally utilized for this purpose. A number of developed analytical methods are available for the determination of sulfur species, including spectroscopy-based analytical techniques [20], high performance liquid chromatography [21], and IC [22]–[24]. However, the mentioned IC methods sacrifice extra time and required additional pre-treatments until the sulfur species signals are obtained. This paper describes a practical ion chromatographic method to analysis sulfur species anions in natural geothermal water samples. This method was based on direct UV detection and without any additional pre-treatment in their procedures, except filtering prior injection to the IC system.

2. Experimental

2.1. Materials and Methods

The pure reagent-grade salts employed were purchased from Nacalai Tesque (Kyoto, Japan). The standard solution of sulfur anions was prepared by dissolving sodium sulfide (Na_2S), sodium sulphite (Na_2SO_3), and sodium thiosulfate ($Na_2S_2O_3$) with deionized Milli-Q water (18.2 MΩ/cm) and kept for about 15 min in ultrasonic bath. The standards were prepared at concentration in 1.0 mM for each sulfur anion. The prepared standards were then stored in polyethylene containers and kept under refrigeration at 4^oC.

The ion chromatograph was performed on a 880-PU HPLC pump (Jasco, Tokyo, Japan), a Rheodyne 5095 injector equipped with a 20-μL sample loop (Cotati, CA, USA), a UV-1570 detector (Jasco, Tokyo, Japan), and a CDS plus Ver 5.0 chromatography data system (Tokyo, Japan). The analytical column as stationary phase employed for sulfur anion separation was a Tosoh TSKgel IC-Anion-PW (50 mm×4.6 mm I.D.) column.

2.2. Mobile Phase

The mobile phase used for analysing sulfur species was 6.0 mM dipotassium hydrogen phosphate. In order to optimize the performance of the mobile phase, it was prepared just before using with deionized Milli-Q water (18.2 MΩ/cm) and homogenized at ultrasonic bath for about 15 min.

2.3. Natural Geothermal Water Collection

The samples were collected from some points located in Jailolo district, a source of geothermal water in North Maluku Province. Table 1 shows the coordinates and positions of geothermal waters were determined by using Global Positioning System (GPS). For comparisons, the samples were collected by 2 categorizes: close to the beach and a little far from the beach points. All collected samples in the fields were acidified with 5 mM nitric acid until pH 3 to avoid any loss of anions and kept at a cool box. The samples were then stored in a refrigerator at 4^oC and filtered all the samples with a 0.45-μm membrane filters (Merck) prior injection to the chromatographic system.

Table 1. The Latitude, Longitude, and Temperature of Study Areas

Locations	Latitude (N)	Longitude (E)	Temperature (°C)
Arugasi	01°03.289'	127°23.571'	76
Bobo	01°03.360'	127°24.367'	46
Payo	01°03.700'	127°25.611'	50

3. Results and Discussion

3.1. Selection of Mobile Phases

In this study, the number of inorganic compounds such as carbonates, phosphates, and salts were examined as the mobile phase for the analysis of sulfur species (S^{2-}, SO_3^{2-}, and $S_2O_3^{2-}$). The mobile phases were sodium hydrogen carbonate, ammonium hydrogen carbonate, disodium carbonate, potassium hydrogen phosphate, dipotassium hydrogen phosphate, sodium hydrogen phosphate, sodium chloride, and potassium chloride.

The performances of these inorganic mobile phases were compared in terms of the retention times, selectivity, and peak shapes of sulfur species anions. Among the examined mobile phases, it was found that only dipotassium hydrogen phosphate (K_2HPO_4) provided complete separation of the three sulfur anions. Moreover, K_2HPO_4 mobile phase gave better peak shapes including SO_3^{2-} and good selectivity for all sulfur anions.

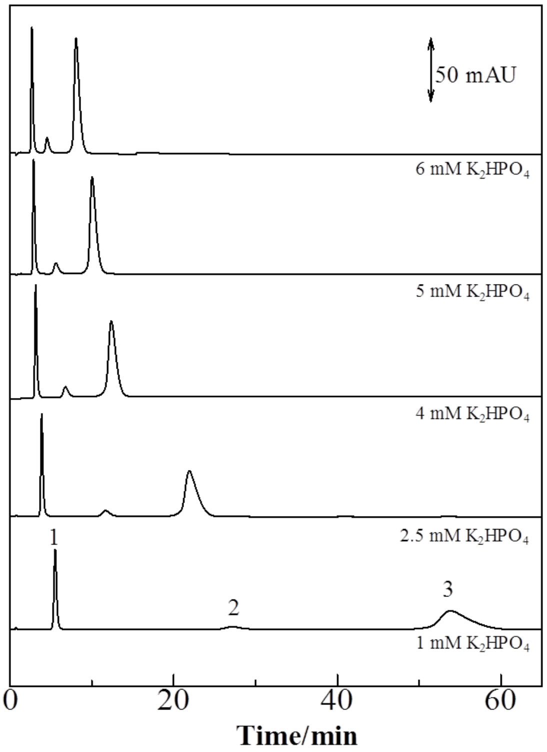

Figure 1. The differences of chromatographic profiles on retention time for sulfur anions by the variation of mobile phase concentration. Mobile phase: 1.0-6.0 mM K_2HPO_4. Column: TSK_{gel} IC-Anion-PW (50 mmx4.6 mm I.D.). Mobile phase flow rate: 1.0 mL/min. Column temperature: 35°C. Injection volume: 20-µL. Sulfur anions: 1=Sulfide, S^{2-}; 2=Sulfite, SO_3^{2-}; 3=Thiosulfate, $S_2O_3^{2-}$.

3.2. Effects of Dipotassium Hydrogen Phosphate Mobile Phase

In order to evaluate the optimum concentration of the mobile phase, various concentrations containing K_2HPO_4 was used to check the effect of analyzing sulfur anions (S^{2-}, SO_3^{2-}, and $S_2O_3^{2-}$) on retention time. The concentration of mobile phase was in the range of 1.0-6.0 mM.

Figure 1 shows the chromatograms of the three sulfur anions of interest at different mobile phase concentrations. The mobile phase concentration increased as retention time values of sulfur anions decreased. In addition, higher mobile phase concentration than 6.0 mM (i.e., 7.0 mM) was done to check the performances of S^{2-} and SO_3^{2-} particularly in term of selectivity, and it seems overlapped due the time, and worried when these two ions contained much more in real samples.

In this study, a TSKgel IC-Anion-PW (50 mm×4.6 mm I.D.) was selected as the polymer-based anion-exchange column. It showed that the retention behaviour of analysis was also influenced by hydrophobic absorption of the anion-exchange resins and the pH of mobile phase. The mobile phase's pH gradually increases with increasing K_2HPO_4 mobile phase concentration, and the pH at 6.0 mM mobile phase was 8.23. The order of these sulfur anions was occurred by different of their ion charge and interaction with anion-exchange as the stationary phase, therefore the elution order was $S^{2-} < SO_3^{2-} < S_2O_3^{2-}$. Considering of the above results, 6.0 mM of the mobile phase concentration was recommended in subsequent analysis.

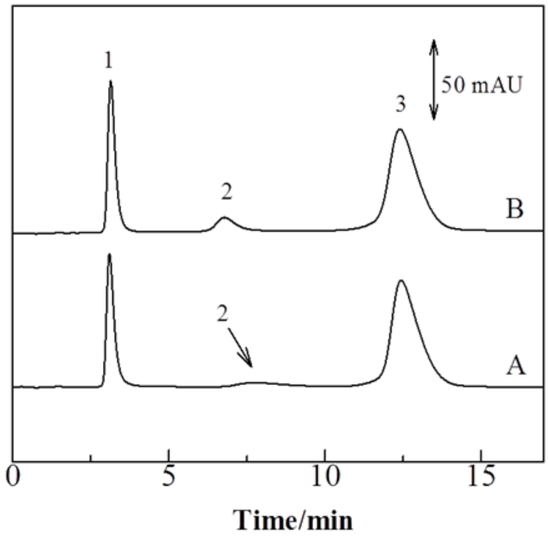

Figure 2. Comparison of two chromatograms of sulfur anions using (A) un-fresh and (B) freshly mobile phases. Mobile phase: 4.0 mM K_2HPO_4. Anions (concentration in 1.0 mM of each): 1=S^{2-}, 2=SO_3^{2-}, and 3= $S_2O_3^{2-}$. Other operating conditions, as in Figure 1.

Figure 2 shows a comparison of two chromatograms of sulfur anions using un-fresh and freshly mobile phases. Broke peak of SO_3^{2-} was obtained when using un-fresh mobile phase. SO_3^{2-} known is very unstable compounds along other sulfur anions. The analysis of SO_3^{2-} was disturbed by the presence of un-fresh phosphate of mobile phase resulting decreased analytical precision of SO_3^{2-} is another possible reason. Hence, it is suggested that the preparation of K_2HPO_4 mobile phase just before using.

Figure 3 reports the linear relationship between the logarithm of retention factor of sulfur anions and the logarithm of K_2HPO_4 mobile phase concentrations. The slope value obtained by the ratio of analyte and mobile phase ionic valances. Therefore, the slopes for these sulfur anions were −0.502, −1.146, and −1.150 for S^{2-}, SO_3^{2-}, and $S_2O_3^{2-}$, respectively. As shown in Figure 3 assumed that the retention time for S^{2-} and SO_3^{2-} ions were overlapped due the time, whereas SO_3^{2-} and $S_2O_3^{2-}$ were almost constant.

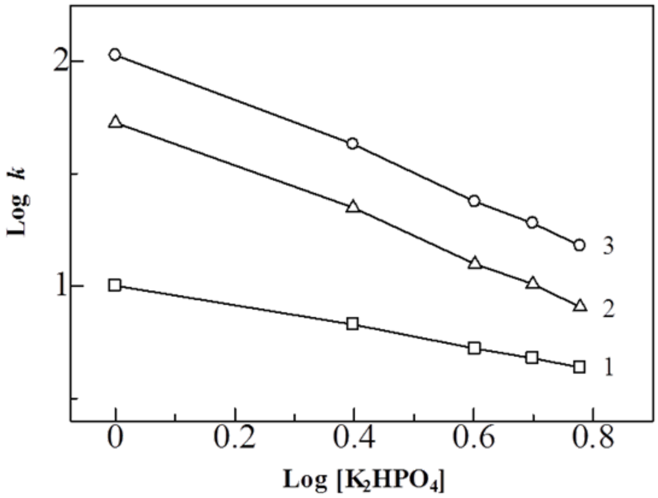

Figure 3. The logarithm of the retention factor versus the logarithm of K_2HPO_4 concentration of sulfur anions. Mobile phase: 1.0-6.0 mM K_2HPO_4. Plot lines: 1=S^{2-}; 2=SO_3^{2-}; 3= $S_2O_3^{2-}$. Other operating conditions, as in Figure 1.

3.3. Analysis of Sulfur Anions using Standard Samples

In the chromatogram in Figure 4, the three sulfur species anions (S^{2-}, SO_3^{2-}, and $S_2O_3^{2-}$) completely eluted within 10 min. All peaks were nicely analysed and symmetrical. Although, the SO_3^{2-} peak gave lower peak in height compared to other but could give good quantitative analysis.

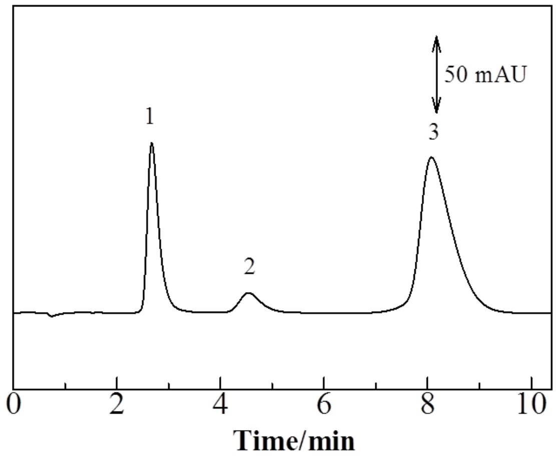

Figure 4. Chromatogram of sulfur anions using standard sample. Mobile phase: 6.0 mM K_2HPO_4. Sulfur anions (concentration in 1.0 mM of each): 1=S^{2-}, 2=SO_3^{2-}, and 3=$S_2O_3^{2-}$. Other operating conditions, as in Figure 1.

3.4. Validation of the Method

The limit of detection (LOD) of the method were determined by injecting 20-µL volume of the sample standard solution and were calculated at S/N=3. The results are shown in Table 2. The LOD obtained by the method were 1.446-30.877 ppb. Sub-ppb level of analysis will be feasible using this method for the analysis of sulfur anions in the samples.

Table 2 shows the linear relationships between the signal response of peak heights and the anions concentrations were found for all sulfur species anions. The calibration curve of sulfur anions showed good linear correlations. From the Table, the coefficient of correlation, r^2>0.999 proved good linearity of the method.

Table 2. The Detection Limits, Correlation Coefficients, and Retention Times of Sulfur Anions using 6.0 mM Dipotassium Hydrogen Phosphate Mobile Phase

Sulfur anion	**LOD (S/N=3)**		**Correlation coefficient *(r^2)***	**Retention times *(t_R)*/min**
	µM	ppb		
S^2	0.045	1.446	0.9998	2.58
SO_3^{2-}	0.386	30.877	0.9993	4.54
$S_2O_3^{2-}$	0.049	5.538	0.9992	8.09

Table 3 shows the reproducibility of the signals (retention time, peak height, and peak area) for seven replicate measurements under the optimum chromatographic conditions, as in Figure 4. The reproducibility values were below 2.34%, 4.21%, and 3.74% for retention time, peak height, and peak area, respectively.

Table 3. The Reproducibility of Sulfur Anions Using 6.0 mM Dipotassium Hydrogen Phosphate Mobile Phase

Sulfur anion	**RSD (%), n=7[a]**		
	Retention time	**Peak height**	**Peak area**
S^{2-}	1.88	2.37	2.49
SO_3^{2-}	2.34	4.21	3.25
$S_2O_3^{2-}$	2.05	3.95	3.74

[a] *n=number of measurements*

3.5. Application to Natural Geothermal Water Samples

The method was applied to the analysis of sulfur anions natural geothermal water samples. The samples were collected from Jailolo, a district in the province of North Maluku, Indonesia. Figure 5 shows the points of samples collection were classified for comparison, close to the beach and a little far from the beach sample points. In avoiding an accidental contamination of the samples, all the samples were stored in a refrigerator at 4°C and filtered with a 0.45-µm membrane filter prior injection to the chromatographic system.

Good chromatograms for sulfur anions in natural geothermal water samples were achieved, as in Figure 6. All sulfur anions showed with good separation, although SO_3^{2-} was not satisfactory in samples obtained from close to the beach sample. It is assumed that this may be caused by interference ions contained in sea water. The concentrations of S^{2-}, SO_3^{2-}, and $S_2O_3^{2-}$ in all collected samples were analyzed to be 0.016-0.279 mM, 0.079-1.207 mM, and 0.119-0.190 mM, respectively, as summarized in Table 4.

Figure 5. Map of Jailolo, North Maluku showing the 3 sampling points: (●) Arugasi; (●) Bobo; (●) Payo

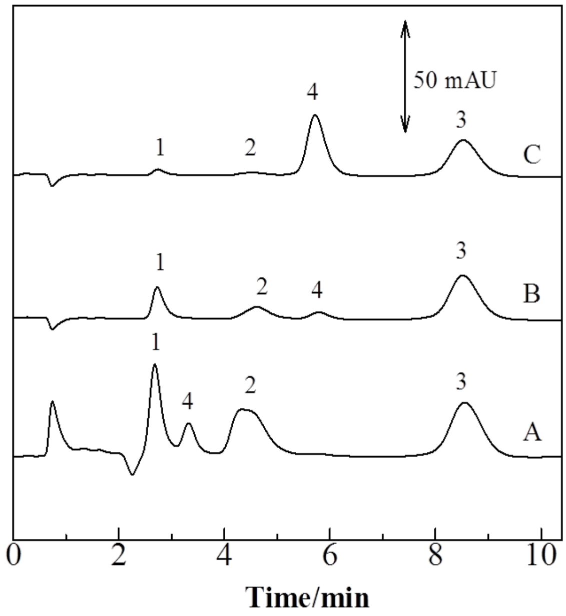

Figure 6. Chromatograms of sulfur species anions in natural geothermal water with the type of samples: (A) close to the beach and (B and C) a little far from the beach. Anions: 1=S^{2-}, 2=SO_3^{2-}, 3= $S_2O_3^{2-}$, and 4= unknown peak. Other chromatographic conditions, as in Figure 4.

Table 4. Analysis Results for Sulfur Species in Natural Geothermal Waters

Sulfur anion	**Sample location**					
	Arugasi (A)		**Payo (B)**		**Bobo (C)**	
	Mean value (mM)	RSD (%)	Mean value (mM)	RSD (%)	Mean value (mM)	RSD (%)
S^{2-}	0.279	2.87	0.099	3.16	0.016	2.49
SO_3^{2-}	1.207	2.21	0.298	2.83	0.079	2.84
$S_2O_3^{2-}$	0.190	3.91	0.154	2.78	0.119	2.98

4. Conclusions

The method using UV detection mode was achieved by the combination of 6.0 mM dipotassium hydrogen phosphate as the mobile phase and TSKgel IC-Anion-PW column as the stationary phase. In UV detection, it was possible to analysis the three target anions of sulfur species on the polymer-based anion-exchange column. It should be noted that this method potentially to be use for routine analysis, especially samples which contained higher concentration of sulfur species. However, the method should be improved in order to analysis another sulfur anions interests such as sulfate (SO_4^{2-}) and polythionates ($S_4O_6^{2-}$) and to increase the selectivity and sensitivity particularly for close to the beach sample.

Acknowledgments

This research was supported by funding of Incentive of National Innovation System Research (InSINAS) 2018, Ministry for Research, Technology, and Higher Education, Republic of Indonesia, with grant Recipient No. 128.

References

[1] A. Caliamanis, M. J. McCormick, and P. D. Carpenter, “Enhanced conductometric detection of cyanide in suppressed ion chromatography,” *J. Chromatogr. A*, vol. 884, no. 1–2, pp. 75–80, 2000.

[2] H. Small, “TS Stevens and WC Bauman,” *Anal. Chem*, vol. 47, p. 1801, 1975.

[3] J. C. Chow and J. G. Watson, “Ion chromatography in elemental analysis of airborne particles,” *Elem. Anal. airborne Part.*, vol. 1, pp. 97–137, 1999.

[4] T. Manickum, Tp. Kumalo, S. Qegu, “Validation of Rapid Test Method for the Quantification of Priority Anions in Drinking Water by Ion Chromatography-Suppressed Conductivity Detection,” *J Chromatogr Sep Tech*, vol. 10, no. 2, p. 1000418, 2019.

[5] A. Huseyin, A. Serife, A. Esra, A. Asude, S. Sezen, “Use of Ion Chromatography Method on the Determination of Some Anions in the Water Collected from Sakarya, Turkey,” *J. Chem. Metrol.*, vol. 13, no. 1, pp. 14–20, 2019.

[6] M. Amin, L. W. Lim, and T. Takeuchi, “Determination of common inorganic anions and cations by non-suppressed ion chromatography with column switching,” *J. Chromatogr. A*, vol. 1182, no. 2, pp. 169–175, 2008.

[7] P. E. Jackson, “Ion chromatography in environmental analysis,” *Encycl. Anal. Chem. Appl. Theory Instrum.*, 2006.

[8] J. W. Lund, “Balneological use of thermal and mineral waters in the USA,” *Geothermics*, vol. 25, no. 1, pp. 103–147, 1996.

[9] Z. Hamzah, N. L. A. Rani, A. Saat, and A. K. Wood, “Determination of hot springs physico-chemical water quality potentially use for balneotherapy,” *Malaysia J. Anal. Sci.*, vol. 17, no. 3, pp. 436–444, 2013.

[10] B. Sanjuan, J. Scheiber, F. Gal, S. Touzelet, A. Genter, and G. Villadangos, “Inter-well chemical tracer testing at the Rittershoffen geothermal site (Alsace, France),” 2016.

[11] P. Reimus, F. Caporuscio, O. Marina, and D. Janney, “Field demonstration of the combined use of thermally-degrading and cation-exchanging tracers to predict thermal drawdown in a geothermal reservoir,” *Geothermics*, vol. 83, p. 101712, 2020.

[12] C.-H. Kuo, S.-R. Song, P. Rose, and C.-M. Liu, “Reactive tracer experiments in a low temperature geothermal field, Yilan, Taiwan,” *Geothermics*, vol. 74, pp. 298–304, 2018.

[13] C. Marieni, J. Přikryl, E. S. Aradóttir, I. Gunnarsson, and A. Stefánsson, “Towards ‘green’geothermal energy: Co-mineralization of carbon and sulfur in geothermal reservoirs,” *Int. J. Greenh. Gas Control*, vol. 77, pp. 96–105, 2018.

[14] J. P. Maity, C. Y. Chen, J. Bundschuh, and P. Bhattacharya, “Investigation of arsenic contamination from geothermal water in different geological settings of Taiwan: Hydrogeochemical and microbial signatures,” in *Arsenic Research and Global Sustainability: Proceedings of the Sixth International Congress on Arsenic in the Environment (As2016), June 19-23, 2016, Stockholm, Sweden*, p. 84, 2016.

[15] B. Tomaszewska and M. Dendys, “Zero-waste initiatives–waste geothermal water as a source of medicinal raw material and drinking water,” *Desalin. WATER Treat.*, vol. 112, pp. 12–18, 2018.

[16] L. Rapolienė, A. Razbadauskas, and A. Jurgelėnas, “The reduction of distress using therapeutic geothermal water procedures in a randomized controlled clinical trial,” *Adv. Prev. Med.*, vol. 2015, 2015.

[17] E. Dotsika, I. Leontiadis, D. Poutoukis, R. Cioni, and B. Raco, “Fluid geochemistry of the Chios geothermal area, Chios Island, Greece,” *J. Volcanol. Geotherm. Res.*, vol. 154, no. 3–4, pp. 237–250, 2006.

[18] L. Rapolienė, “The Effect of Geothermal Water on Skin Condition and Body Fat,” *J. Adv. Med. Med. Res.*, pp. 1–13, 2016.

[19] K. S. Leslie, G. W. M. Millington, and N. J. Levell, “Sulphur and skin: from Satan to Saddam!,” *J. Cosmet. Dermatol.*, vol. 3, no. 2, pp. 94–98, 2004.

[20] P. Musagala, H. Ssekaalo, J. Mbabazi, and M. Ntale, “A spectrophotometric method for quantification of sulphite ions in environmental samples,” *J. Toxicol. Environ. Heal. Sci.*, vol. 5, no. 4, pp. 66–72, 2013.

[21] A. S. Casas, M. A. Armienta, and S. Ramos, “Sulfur speciation with high performance liquid chromatography as a tool for El Chichón volcano, crater lake monitoring,” *J. South Am. Earth Sci.*, vol. 72, pp. 241–249, 2016.

[22] Y. Miura and A. Kawaoi, “Determination of thiosulfate, thiocyanate and polythionates in a mixture by ion-pair chromatography with ultraviolet absorbance detection,” *J. Chromatogr. A*, vol. 884, no. 1–2, pp. 81–87, 2000.

[23] H. Kaasalainen and A. Stefánsson, “Chemical analysis of sulfur species in geothermal waters,” *Talanta*, vol. 85, no. 4, pp. 1897–1903, 2011.

[24] M. L. Chen, M. L. Ye, X. L. Zeng, Y. C. Fan, and Z. Yan, “Determination of sulfur anions by ion chromatography–postcolumn derivation and UV detection,” *Chinese Chem. Lett.*, vol. 20, no. 10, pp. 1241–1244, 2009.