

Cross-verified Measurement of Sulfide Concentration in Anaerobic Conditions Using Spectroscopic, Electrochemical, and Mass Spectrometric Methods

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Sulfide concentrations critically affect worker safety and the integrities of underground facilities, such as deep geological repositories for spent nuclear fuel. Sulfide is highly sensitive to oxygen, which can oxidize sulfide to sulfate. This can hinder precise measurement of the sulfide concentration. Hence, a literature review was conducted, which revealed that two methods are commonly used: the methylene blue and sulfide ion-selective electrode (ISE) methods. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used for comparison with the two methods. The sulfide ISE method was found to be superior as it yielded results with a higher degree of accuracy and involved fewer procedures for quantification of the sulfide concentration in solution. ICP-OES results can be distorted significantly when sulfide is present in solution owing to the formation of H₂S gas in the ICP-OES nebulizer. Therefore, the ICP-OES must be used with caution when quantifying underground water to prevent any distortion in the measured results. The results also suggest important measures to avoid problems when using ICP-OES for site selection. Furthermore, the sulfide ISE method is useful in determining sulfide concentrations in the field to predict the lifetime of disposal canisters of spent nuclear fuel in deep geological repositories and other industries.

Keywords: Sulfide, Ion-selective electrode, Deep geological repository, Titration, Methylene blue, Inductively coupled plasma optical emission spectroscopy

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1. Introduction

Deep geological repositories are considered to be the final step of the nuclear fuel cycle in most countries (e.g., South Korea, Sweden, Finland, USA, Japan) [1, 2]. Generally, a deep geological repository should be constructed 400–700 m underground [3]. At this distance from the surface, the conditions are anaerobic, because oxygen does not penetrate this deep underground. Due to the anaerobic conditions, canisters of spent nuclear fuels may be corroded by sulfide, and most countries analyze sulfide as the dominant corrosive agent of canisters [4, 5]. Thus, measuring the concentration of sulfide within a deep geological repository is critical.

Sulfide ions are quite problematic because they form hydrogen sulfide, which is highly toxic, flammable, and corrosive. A low concentration of hydrogen sulfide is toxic [6], and thus, numerous workers in wastewater treatment facilities have been injured or killed [7]. The quantification of sulfide ions in waste is crucial not only in a deep geological repository, but also in other industries and the field of public health.

A considerable amount of research has focused on measuring sulfide within potential sites of deep geological repositories, particularly in Sweden and Finland, Canada and South Korea is in the same situation [8-10]. In addition, laboratory-scale corrosion studies of canisters (spent nuclear fuels) also require the quantification of the sulfide concentration, because sulfide is very sensitive to oxygen.

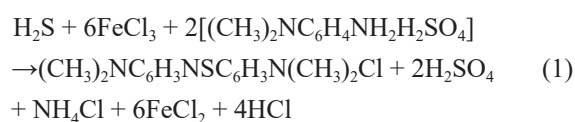
A reliable method of measuring the concentration of sulfide is required. However, there was no research comparing the sulfide ion-selective electrode (ISE) and methylene blue methods. Herein, the authors review the literature concerning the measurement of sulfide and demonstrate one of the most reliable methods, which uses an ion-selective electrode (ISE) to measure the sulfide concentration. Four studies were conducted to demonstrate the quantification of sulfide in the field and laboratory. The first study demonstrates the measurement of a sulfide solution under

aerobic conditions, with the results compared to those obtained using inductively coupled plasma-optical emission spectroscopy (ICP-OES). The second study demonstrates the low-cost, rapid measurement of a sulfide solution in the laboratory. In the third study, methylene blue method was conducted to demonstrate to show how to measure concentration of sulfide in solutions and compared the peak of wavelength and molar absorption coefficient with the reported data from another research group. In the last study, the sulfide ISE titration method, methylene blue method, and ICP-OES were conducted to measure the concentration of sulfide in the sulfide solution and cross-checked the results.

2. Methods of Measuring Sulfide Ions

2.1 Methylene Blue Method

The methylene blue method is quite well-known and has been widely used to measure sulfide concentrations in various effluents for over a century [11, 12]. This method uses the following reaction between sulfide and N,N-dimethyl-p-phenylenediamine:



where sulfide is oxidized by FeCl_3 (oxidizing agent) [11]. Reaction (1) produces a deep blue color, and researchers may quantify the sulfide in their solutions based on the development of this blue color. A light or deep blue color indicates a low or high concentration of sulfide, respectively.

The color development may be analyzed using two methods: visual comparison with a reference solution or ultraviolet-visible (UV-Vis) spectroscopy [12]. Visual comparison is very handy and rapid in establishing the concentrations of sulfide in solutions. Hence, this method is very

useful in field studies, such as the verification of groundwater with mineral deposits. In contrast, UV-Vis spectroscopy is able to quantify the concentration more accurately than the naked eye. However, UV-Vis spectrometers are not very handy and hard to use in field studies.

The methylene blue method exhibits a disadvantage in field measurements of the sulfide concentration, as it requires preconditioning procedures to prevent interference in the measurement. Thiosulfate, iodide, and metals (i.e., Hg, Cd, and Cu) prevent or retard color development during measurement [12]. Additionally, ferrocyanide also produces a blue color using this method. Interference is removed via precipitation with zinc acetate and redissolution in deaerated pure water. Therefore, obtaining correct data without preconditioning is challenging.

2.2 Sulfide Ion-Selective Electrode

A sulfide ion-selective (-specific) electrode measures the concentration of sulfide in a solution using an ion-selective membrane [13]. The sulfide ion-selective membrane is a solid membrane composed of a single crystal lattice. Theoretically, this membrane enables the permeation of only sulfide ions, and the diffused sulfide ions change the measured potential by altering the activity of sulfide in the solution. However, cyanide and silver may be transported, too, and cyanide may interfere with the measurement, yielding an overestimated concentration of sulfide [14, 15]. Nevertheless, the sulfide ion-selective method displays an advantage in terms of preconditioning because the interfering species (except cyanide) of the methylene blue method do not penetrate the ion-selective membrane.

An ISE may be used to measure sulfide ions via the titration of a test solution with a lead (II) perchlorate solution or extrapolation based on reference sulfide solutions. Titration with lead perchlorate is quite accurate in measuring the sulfide in a solution, which reacts with the lead perchlorate, with lead sulfide precipitating. The concentration of sulfide ions is reduced in the test solution, which may be measured

via the potential. The extrapolation method uses reference sulfide solutions to plot a calibration curve of the measured potential of the electrode as a function of $-\log$ (concentration of sulfide ions). At any sulfide concentration range, titration should be conducted for accurate measurement.

2.3 Comparing the Methylene Blue and ISE Methods

The ISE measures a wider range of concentrations compared to that of the methylene blue method. The ISE and methylene blue method may measure from 1×10^{-7} to 1 M (pH range: 2–12) [14] and from 1.13×10^{-6} to 1×10^{-3} M [11], respectively. In addition, the methylene blue method requires calibration curves with several standard solutions of sulfide in various concentration ranges [11]. In preparing the standard solutions accurately, the methylene blue method requires extra chemical agents and equipment, and sulfide titration should be conducted. In summary, the ISE measures a wider range of concentrations of sulfide solutions, and the sulfide standard solutions may be prepared without extra chemical agents and equipment. Moreover, the methylene blue method exhibits considerable interference. Therefore, the authors used the sulfide ISE in this study as the primary method to measure sulfide concentration and also methylene blue method was conducted to compare with sulfide ISE results.

3. Methods

3.1 Materials

De-ionized Milli-Q water ($> 18.2 \text{ M}\Omega\cdot\text{m}$, Millipore-Sigma, Burlington, MA, USA) was used in the study. ACS grade lead (II) perchlorate was used to prepare a 0.1 M lead perchlorate solution for use in titration with sulfide using the sulfide ISE. Sulfide antioxidant buffers (SAOBs) were purchased from Thermo Fisher Scientific (Waltham, MA,

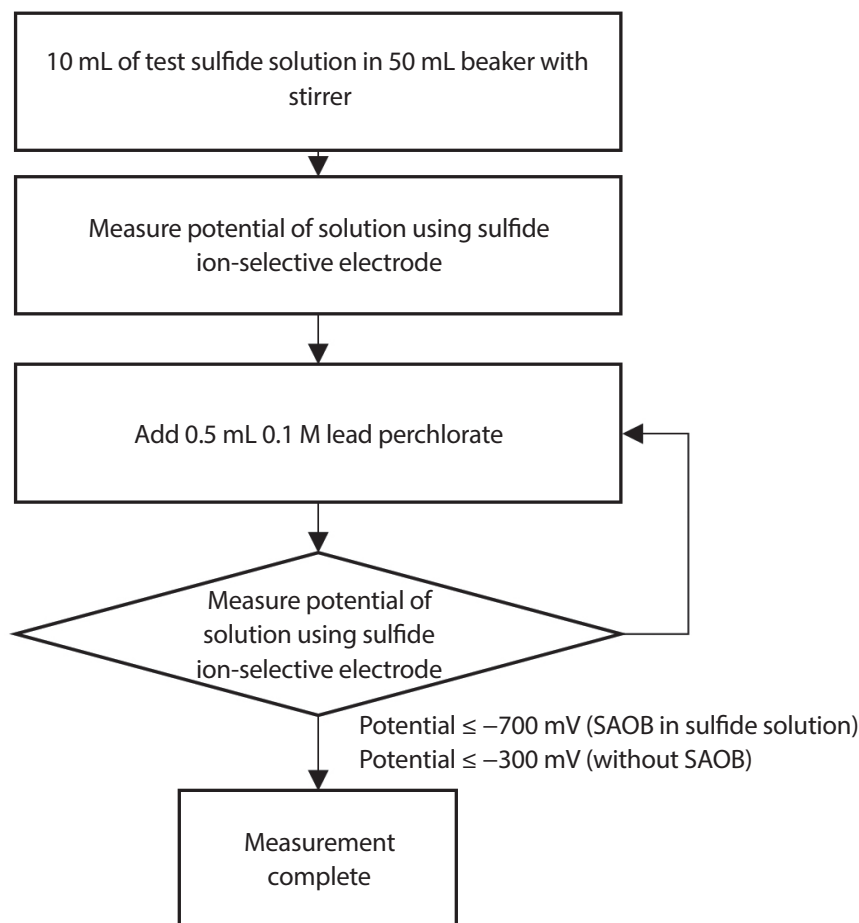


Fig. 1. Titration procedure to measure the sulfide concentration in a test solution using the sulfide ion-selective electrode.

USA), and a 1,000 mgL⁻¹ sulfur standard was purchased to prepare standard solutions for use in ICP-OES. The following five standard solutions were used in ICP-OES: 0, 700, 800, 900, and 1,000 mgL⁻¹. Mixed diamine solution was prepared using ACS grade ferric chloride, 6 M HCl, and N,N-Diethyl-p-phenylenediamine sulfate for the methylene blue method.

All sulfide solutions were prepared using a stock sulfide solution (1 M), which was prepared in a glove box (O₂ < 1 ppm) using 100 mL of deaerated water and 7.804 g of anhydrous sodium sulfide. Using the stock solution, all sulfide solutions were prepared in the glove box using micropipettes.

3.2 Analytical Instruments

An Orion silver/sulfide electrode was used in the first and second study with an Orion Star A214 pH/ISE benchtop meter. A 720 ICP-OES system (Agilent Technologies, Santa Clara, CA, USA) was used to measure the concentration of sulfur in the test solution via ICP-OES at the Korea Advanced Institute of Science & Technology Analysis Center for Research Advancement (Daejeon, South Korea). A QUINTIX precision balance (Sartorius, Göttingen, Germany) was used to measure the mass of sodium sulfide used in the stock solution. A SPECORD 200 PLUS UV-Vis spectrometer was used to measure the absorption spectrum of

sulfide solutions in the third study.

3.3 First Study: Sulfide and SAOB

Using the stock solution, the test solution used in the first study was prepared via serial dilution. First, a 0.1 M sulfide solution was prepared by adding 10 mL of sulfide stock solution to 10 mL of SAOB and 80 mL of deaerated water in a 100 mL volumetric flask. Second, the prepared 0.1 M sulfide solution was diluted to the final test solution.

This final test solution was sampled three times to measure the concentrations of sulfide and sulfur via the titration method and ICP-OES (10 mL used in each method). The sampled solution was titrated under atmospheric conditions. The sulfide ISE (Thermo Fisher Scientific) and an Orion Star A214 meter were used to measure the potentials of the test solutions. A hot plate and magnetic stirrer were used to maintain the temperature at 25°C and accelerate the precipitation reaction within the solution. The sulfide ISE was placed in the test solution and then 0.5 mL of 0.1 M lead (II) perchlorate solution was added dropwise (Fig. 1). Subsequently, the stabilized potential was recorded. The titration proceeded until the potential decreased significantly (> 200 mV).

The significant decrease in potential represents the end of the sulfide precipitation reaction with lead (II) perchlorate. Hence, this point is used to calculate the sulfide concentration in the test solution using the following equation:

$$C_{sulfide} = C_{pb} \cdot V_{pb} / 1000 \cdot V_{sample} / 1000 \quad (2)$$

where $C_{sulfide}$ is the calculated concentration of sulfide, [M]; C_{pb} is the concentration of the lead (II) perchlorate solution, [M]; V_{pb} is the volume of the lead (II) perchlorate solution used at the end point of sulfide precipitation, [mL]; and V_{sample} is the volume of the sample solution used in the titration, [mL]. In this study, the concentration of the lead perchlorate solution (C_{pb}) and volume of the sample solution used in titration (V_{sample}) are fixed at 0.1 M and 10 mL.

3.4 Second Study: Sulfide Without SAOB

All procedures were the same as those described in Section 3.3 (Fig. 1), except the test solutions. In this study, the test solution was prepared without SAOB and the titration was conducted inside the glove box. Moreover, the test solution was prepared via a single dilution from the stock solution, using 15 mL of stock solution with 85 mL of deaerated water in a 100 mL volumetric flask.

3.5 Third Study: Methylene Blue Method

The same stock solution was used to prepare the following four standard samples for methylene blue method: 0.216, 0.316, 0.416 and 0.509 mM of sulfide. The standard solutions were mixed with mixed diamine reagent (MDR) as suggested in Reese et al. 2011 (Cline method) [11]. All these solutions were left undisturbed for over 2 hours to ensure color development within the solutions and measured via UV-Vis spectroscopy at 667 nm wavelength. The wave path length was fixed at 1 cm with cuvettes. All the data was recorded by Aspect Plus software.

Absorption spectroscopy for methylene blue method obey Beer-Lambert's law in the following equation:

$$A = \epsilon l c \cdot \alpha \quad (3)$$

where A is absorbance, [unitless]; ϵ is molar absorption coefficients, [$\text{Lmol}^{-1} \cdot \text{cm}^{-1}$]; l is path length of light, [cm]; c is concentration of solution, [M]; α is dilution factor, [unitless] [16]. The dilution factor represents the diluted ratio of samples (sulfide solutions).

3.6 Fourth Study: Comparison of ISE and Methylene Blue Method

The same stock solution was used to prepare 0.5 mM of sulfide solution to compare sulfide ISE and methylene blue with UV-Vis spectroscopy. All the procedures are same

Table 1. Concentrations of sulfide measured via titration using the sulfide ion-selective electrode (ISE) and the concentrations of sulfur measured via inductively coupled plasma spectroscopy with a reference solution

Sample number	Sulfide ion-selective electrode	Inductively coupled plasma spectroscopy
1	0.0229 M	0.0215 ± 0.0006 M
2	0.0229 M	0.0228 ± 0.0004 M
3	0.0229 M	0.0214 ± 0.0003 M

as in Section 3.3 for titration of sulfide with sulfide ISE, except using 0.01 M of lead perchlorate solution. For the methylene blue with UV-Vis spectroscopy, all the procedures were same as in Section 3.5. In the case of ICP-OES, the same 0.5 mM of sulfide solution (including SAOB) was used to measure concentration of sulfur in the solution. Sulfide ISE and methylene blue method were conducted three times to measure the concentration of the prepared 0.5 mM of sulfide solution. ICP-OES measured three times after 1 week, and a single time after 1 month of 0.5 mM of sulfide solution in SAOB.

4. Results and Discussion

4.1 First Study: Field-applicable Titration Method (with SAOB)

Fig. 2 shows the potentials in the prepared solutions, as measured using the sulfide ISE. All measured solutions exhibit almost identical decreases in magnitude of potential from -950 to -700 mV, indicating that the measurements are quite successful. The potential of -950 mV indicates the presence of sulfide in the solution and that of -700 mV indicates that almost all sulfide is precipitated by the lead (II) perchlorate solution, with only the SAOB agents remaining in the solution.

The measured potentials may be converted to their second derivatives to establish the inflection points, as shown in Fig. 2. The inflection points occur at approximately 2.29 mL of 0.1 M lead (II) perchlorate solution. Using equation

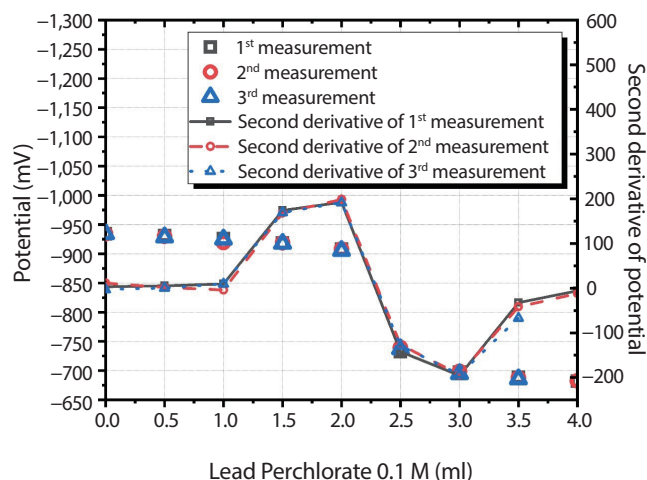


Fig. 2. Potentials (with sulfide antioxidant buffer) measured via titration of sulfide with lead (II) perchlorate using the sulfide ion-selective electrode and the second derivatives of the measured potentials as functions of the total amount of lead (II) perchlorate added.

(2), the concentrations of sulfide are calculated and shown in Table 1 for comparison with the results of ICP-OES, which was used to measure the total sulfur concentrations.

The measured concentration of sulfide, based on all three measurements using the sulfide ISE, is 0.023 M. The results of ICP-OES are 0.021, 0.023, and 0.021 M sulfur. The maximum measurement error of the sulfide ISE is 0.1%, which is mostly due to the preparation of the 0.1 M lead perchlorate solution. The measurement errors (relative standard deviations) of ICP-OES are 2.86%, 1.61%, and 1.5% (Table 1). The measured errors are quite small and reveal that all measurements were conducted well. The measured concentrations of sulfide and sulfur are quite consistent, indicating that the experimental conditions

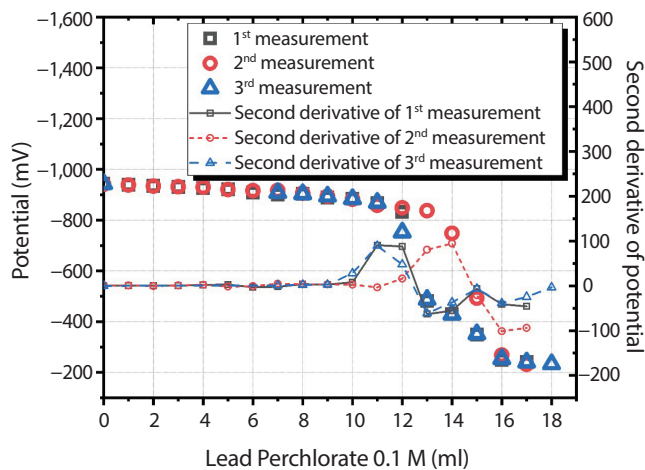


Fig. 3. Potentials (without sulfide antioxidant buffer) measured via the titration of sulfide with lead (II) perchlorate using the sulfide ion-selective electrode and the second derivatives of the measured potentials as functions of the total amount of lead (II) perchlorate added.

were well-controlled. In addition, ICP-OES may be used as a verification method to confirm the sulfide concentration in the test solution.

4.2 Second Study: Laboratory Titration Method (Without SAOB)

Fig. 3 shows the potentials measured during the titration of sulfide with lead (II) perchlorate without the SAOB in the test solutions. This was performed in the glove box, and thus, using SAOB to prevent sulfide oxidation was unnecessary. The measured potentials of the sulfide solutions are from -950 to -200 mV. The initial potential is the same as that observed using the SAOB (Fig. 2). In contrast, the final potential is -200 mV, which is a magnitude of approximately 500 mV less than that observed using the SAOB. The SAOB contains ions that may decrease the potentials due to the formation of high potential gradients across the ion-selective membrane. Therefore, in the laboratory-scale study, the concentration of sulfide ions may be measured in the glove box without SAOB, which may save time and costs.

As shown in Fig. 3, the inflection points are 12.5, 12.5, and 14.4 mL of 0.1 M lead (II) perchlorate solution. Based

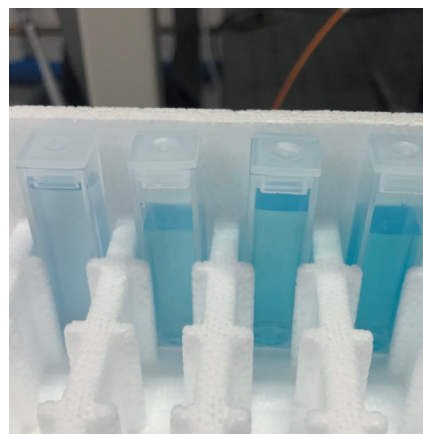


Fig. 4. Color development of mixed standard solutions and mixed diamine solution. Left to right: low concentration to high concentration.

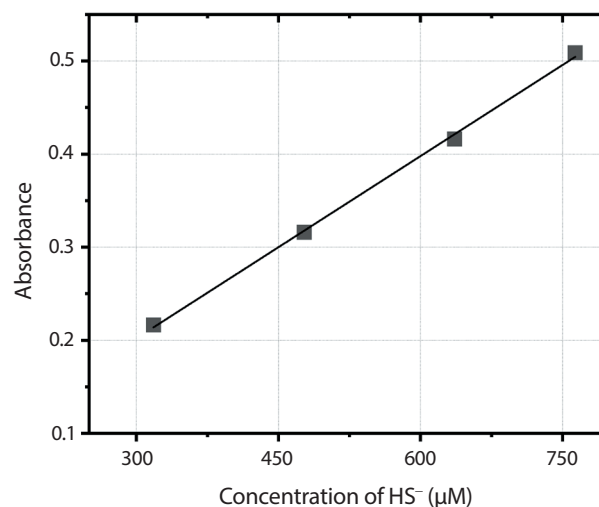


Fig. 5. Measured linear calibration curve for methylene blue method with four standard samples (0.216, 0.316, 0.416, and 0.509 mM).

on equation (2), the concentrations of sulfide ions are 0.125, 0.125, and 0.144 M. The first and third measurements are consistent, but the second measurement is quite different from the other two. The deviation should be due to the heterogeneous distribution of sulfide in the test solution. Unlike the first study (with SAOB), a much more concentrated sulfide solution was used in this study, and this solution displayed heterogeneous flow prior to measurement via the titration method. Therefore, the measured

Table 2. Concentrations of sulfide measured via titration using the sulfide ion-selective electrode (ISE) and methylene blue method with UV-Vis spectroscopy

Analytical method	Times	Measured value(mM)
Sulfide ion-selective electrode with titration	Immediately	0.442 ± 0.006
Methylene blue method with UV-Vis spectroscopy	Immediately	0.476 ± 0.002
Inductively Coupled Plasma Optical Emission spectroscopy*	Immediately	15.07 ± 2.57
Inductively Coupled Plasma Optical Emission spectroscopy**	After one month	0.719

*Measure sulfur element.

**Measure sulfur element and measured only a single time.

solution was not mixed very well, inducing a deviation in the sulfide concentration.

4.3 Third Study: Methylene Blue Method

The mixed standard solutions with MDR show various color developments from light blue to dark blue (low HS⁻ to high HS⁻ concentration) as can be seen in Fig. 4. Fig. 5 shows the linearity of the measured five mixed standard solutions. As can be seen in Fig. 5, the R-square value is more than 0.999 which proved the mixed standard solutions were prepared well. Hence, the linearity was maintained for sulfide solutions in the 0.25 to 1 mM range. These standard solutions can be used to draw a calibration curve (Fig. 5) for measuring other sulfide samples from the laboratory.

In our data, we observed the peak of absorb wavelength at 667 nm which is similar to Cline 1969 and Reese et al. 2011 suggested values (670 and 667 nm) [11, 17]. Molar absorption coefficient is 32,617 L·(mol⁻¹·cm⁻¹) which is similar to 34,500 and 33,400 L·(mol⁻¹·cm⁻¹) from Reese et al. 2011 and Cline 1969, respectively [11, 17]. Herein, the authors used 1:50 dilution as suggested in Cline 1969 and Reese et al. 2011, and multiplied the dilution factor to calculate the molar absorption coefficient using equation (3) [11, 17]. Researchers, who want to use the methylene blue method with UV-Vis spectroscopy, have to keep in mind to multiply the dilution factor (50 here) to calculate the molar absorption coefficient value.

4.4 Fourth Study: Sulfide ISE and Methylene Blue Comparison

Table 2 shows average concentration of sulfide by sulfide ISE, methylene blue with UV-Vis spectroscopy, and ICP-OES. As mentioned earlier, each method (except the one month later of ICP-OES result) was conducted three times to measure the sample solutions. Compare the overall results (Table 2), the ICP-OES results (immediately measured the samples) are around 30 times higher concentration of sulfur among the three methods. The ICP-OES results show 15.07 ± 2.57 mM of sulfur concentration, meanwhile the sulfide ISE and the methylene blue results were reported 0.442 ± 0.006 mM and 0.476 ± 0.002 mM of sulfide concentration. However, after the one month, ICP-OES result shows 0.719 mM of sulfur concentration which is close to the results of sulfide ISE and methylene blue.

The huge difference from the ICP-OES results were originated from different behavior of sulfide and sulfate during the measurement of ICP-OES. Generally, sulfide is not stable under atmospheric conditions due to its high reactivity with O₂ in the air. That is the reason why there is no sulfide standard solution for ICP-OES and also theoretically there should be no difference between sulfide and sulfate measurement in ICP-OES. Because ICP-OES only counts the amounts of sulfur elements and does not related with each chemical form. However, this is not true for sulfide and sulfate cases. Sulfide can generate H₂S gas during the

measurement of ICP-OES (in nebulizer), in contrast, sulfate will be transported as aerosols form by nebulizer. This makes different transport speed of sulfur elements (H_2S gas and sulfate aerosols) which significantly alters the measured intensity of light in ICP-OES. The H_2S increase the intensity of signal by accelerating the transported rate of sulfur elements through gaseous form [18]. As can be seen in M. Colon et al. (2008) the calibration curve for sulfide and sulfate in ICP-OES results show huge different where sulfide solutions show much higher intensity and the much steeper slope in sulfide solutions [18]. Therefore, amounts of sulfur measured by ICP-OES immediately is overestimated due to H_2S gas formation during the ICP-OES measurement.

This is proved by our experiment results as well in Table 2. The measured value of ICP-OES results of the same sample after a month show 0.719 mM of sulfur concentration. The reason of huge concentration changed was originated from oxidation of sulfide to sulfate by oxygen. For a month, the sample solution was stored in 10 ml of glass bottle and sealed with lead in a $4^\circ C$ of refrigerator. Most of sulfide was oxidized by oxygen and became sulfate, but still some minor amounts of sulfide can be remained due to SAOB in the solution. Therefore, a month later concentration of sulfur elements in solution show much lower value than the immediately measured value.

The cross-check between three different methods show important points for quantifying amounts of sulfur in sample solutions. As mentioned earlier, ICP-OES can be overestimate amounts of sulfur elements in fresh sulfide solution due to H_2S gas generation in the nebulizer of ICP-OES machine. To overcome this issue, either sulfide standard must be prepared by users of ICP-OES or precondition the samples to quantify the amounts of sulfide indirectly. The first method can be done by using SAOB in standard sulfide samples. In general, SAOB can maintain the concentration of sulfide in solution over a week without any significant loss of sulfide concentration in solution. For the second method, complete oxidation of sulfide or precipitation of sulfide can be used to indirectly measure the amounts of

sulfide through ICP-OES. The complete oxidation of sulfide means stored the sulfide solution under the air and let it fully oxidized to sulfate. But, this method requires a relative long time at least couple of weeks. The precipitation of sulfide can be done by adding excessive amounts of lead perchlorate solution. Then the amount of lead left in the solution, after filtering, can be quantified by ICP-OES which can recalculate the amounts of sulfide was in the solution by subtraction of added amounts of lead perchlorate with remained amounts of lead perchlorate.

In the results (Table 2), the measured concentration of sulfide is 0.034 mM higher in the methylene blue method with UV-Vis spectroscopy than the titration with sulfide ISE. Because the precision of methylene blue method relies on the prepared standard solution which should be corrected by other methods (such as titration) to make precise standard samples. The authors did not conduct to correct the standard samples for the methylene blue method. Hence, the methylene blue method was over measured the concentration of sulfide in the samples.

5. Conclusions

The authors demonstrated the experimental measurement of the sulfide concentration in a solution and compared the results with those of ICP-OES. The sulfide ISE could measure the concentration of sulfide quite accurately. Moreover, in the laboratory-scale study, the authors saved time and costs by not using the SAOB in the test solution. The measured potential of the test solution (sulfide) displayed the same initial potential of -950 mV, but the final measured potential, when sulfide was completely precipitated by lead perchlorate, was approximately -200 mV. This potential may be used to indicate the termination of the sulfide precipitation reaction.

Using the sulfide ISE, lower concentrations of sulfide of up to 1×10^{-7} M may be measured. In addition, the sulfide ISE could be used in two different methods: the titration

and calibration methods. The titration method was useful in preparing a precise standard sulfide solution, and the calibration method was useful in measuring numerous test solutions. Therefore, researchers may select the method of measuring their samples based on precision and time.

ICP-OES is not a good method to quantify the amounts of sulfur elements in sulfide solutions, however through the suggested methods (complete oxidation of sulfide or sulfide precipitation) can overcome the problem and be used for quantifying the concentration of sulfur in sulfide solutions. Hence, the ICP-OES can be used as a reference method to check the results of sulfide ISE method with cautions.

Examination or quantification of sulfur in underground water by ICP-OES must be conducted with care regarding the existing problem of overestimation of sulfur contents in underground water due to presence of sulfide. This can significantly distort the conditions of underground water and change the conditions for corrosion of canisters in deep geological repository. The overestimated amounts of sulfur contents in water can significantly reduce the predicted duration of canisters by corrosion.

The sulfide ISE method may be used as a preliminary method in evaluating the chemical environments of potential sites of deep geological repositories in the field, as the sulfide ISE could measure the sulfide concentration precisely without significant sulfide loss caused by oxygen. This method may be very useful in determining the sulfide concentration to predict the lifetimes of disposal canisters in the preliminary performance evaluation of deep geological repository systems.

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