

# Fabrication of SO<sub>4</sub><sup>2-</sup>-ISE based on Copolymer of Methyl methacrylate-butyl acrylate (MB28) Thin-film and Graphite Pencil Electrode (GPE)

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**Abstract.** The SO<sub>4</sub><sup>2-</sup>-ISE sensor fabrication process based on MB28 and GPE membranes has been successfully implemented. In this study, the MB28 membrane was prepared using the photo-polymer technique on the surface of a polypyrrole with KCl as a dopant layer previously coated on the GPE surface. In this study, the optimum composition of the MB28 membrane consisted of 1 mg of lipophilic salt TDDACl and a 1:2 mole ratio sulfate ionophore, where the resulting slope approached the Nernstian number with a linear range between 0.1 -10<sup>-6</sup> M. Meanwhile, selectivity tests were carried out using the FIM, where SO<sub>4</sub><sup>2-</sup>-ISE provides good selectivity to I<sup>-</sup>, Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> ions. This fabricated sensor can work for 12 days at pH 3-9 and provides performance comparable to the gravimetric method according to SNI 19-6964.5-2003.

## 1 Introduction

The sulfate ion (SO<sub>4</sub><sup>2-</sup>) is one of natural waters' main anions. This becomes very important in public water supplies because if the sulfate content in water is high, it will disturb the humans who consume it [1,2]. WHO recommends that the concentration of SO<sub>4</sub><sup>2-</sup> ions in water not exceed 250 mg/L[3].

Sulfate in water can be present scientifically or from human activities, such as industrial waste, including sulfur gas from factories discharged into the air to form acid rain and laboratory waste [2,4, 5,6] . Scientifically, sulfate usually comes from dissolving minerals containing S. The high sulfate concentration in water is generally caused by natural leaching from magnesium sulfate deposits (Epsom salt) or sodium sulfate[1,2]. Besides that, quite a significant contribution to the presence of SO<sub>4</sub><sup>2-</sup> ions in waters comes from detergent waste, which generally contains S atoms in its structure[7].

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Sulfates are of concern and deserve consideration because they are responsible for two serious problems often associated with wastewater treatment, namely their odor and their corrosive nature, as a result of the reduction of sulfates to hydrogen sulfide under anaerobic conditions. Sulfates irritate the gastrointestinal tract when mixed with magnesium or sodium. The amount of  $\text{MgSO}_4$  that is not too large can cause diarrhea. Sulfate in boilers causes deposits (hard scales) as well as in heat exchangers[1,5].

Given the significant environmental impact, the presence of  $\text{SO}_4^{2-}$  ions needs to be monitored regularly. The most commonly used method is the gravimetric method through which  $\text{BaCl}_2$  reagent forms  $\text{BaSO}_4$  precipitates[8,9]. Besides, the gravimetric method, other methods are turbidity testing, spectrophotometry, ICP, and ion chromatography[10]. However, these methods generally have drawbacks, including requiring many samples, being expensive, requiring special treatment, and large and complicated equipment. This condition certainly feels less practical when applied to field needs that require work that is more practical, inexpensive, and fast[8,11].

An alternative form of testing for  $\text{SO}_4^{2-}$  ions is to use a potentiometric technique, where this technique will measure the potential difference between the ion-selective electrode (ISE) as the working electrode and the reference electrode[8,12,13]. The ISE used generally has a thin membrane layer that is highly selective in the presence of target ions, in this case, the  $\text{SO}_4^{2-}$ -ion[12]. This method is efficient; the size can be reduced as needed, has a wide measurement distance, is not affected by turbidity, and has a fast response time, so it is very suitable for field applications[14,15]. The ISE membrane is generally based on polyvinyl chloride (PVC); however, this polymer has weaknesses that can affect the fabrication process and ISE performance. Some of the weaknesses of PVC are that it takes a long time for the solvent to evaporate and requires additional materials such as plasticizers, which automatically increase fabrication costs. Besides that, another weakness is the weak adhesion of the membrane to the membrane surface, which requires a complicated clamping process, especially for ISE with a small size[16,17].

In addition to using a PVC membrane, in the ISE fabrication process for testing  $\text{SO}_4^{2-}$  ions, an acrylate-based membrane is used, such as methyl methacrylate-butylacrylate copolymer with a ratio of 2:8, which is commonly abbreviated as MB28. This membrane has advantages such as being easy to prepare, using the photo-polymer technique in minutes, not requiring a plasticizer, and having good adhesion to the ISE surface. These properties can cover the weaknesses shown in PVC-based ISE[18].

In addition to the membrane layer, the ISE has a transducer layer that converts chemical information from the sample into easily identifiable electrical information such as potential energy (mV)[14,19]. The commonly used transducers are based on  $\text{Ag}/\text{AgCl}$  electrodes[20]. Still, these electrodes are expensive, sensitive to light, and easily oxidised, which can reduce the sensor's ability[14,19]. Alternatively, a graphite-based transducer, such as a graphite pencil electrode (GPE) can be used. This electrode is very cheap and inert and has a good conductivity value of 5 ohms [21]. On the GPE surface a conducting polymer layer such as polypyrrole doped with  $\text{KCl}$  (PPy-Cl) will be given[18].

This study aims to optimize the composition of MB28 in fabricating  $\text{SO}_4^{2-}$ -ISE sensors based on GPE. Besides that, in this study,  $\text{SO}_4^{2-}$ -ISE performance testing, selectivity, pH effect, lifetime, and validation tests will be carried out using the SNI 19-6964.5-2003 method.

## 2 Materials And Method

## 2.1 Transducer preparation

The transducer is provided by making a Polypyrrole layer doped with KCl (PPy/Cl) on the graphite pencil electrode's (GPE) surface. Before the PPy/Cl coating, The GPE electrodes were characterized using the CV method in a KCl 0.1 solution. Furthermore, on the surface of the GPE electrode, the PPy/ Cl coating process was carried out using a mixture of 0.5 M Py solution and 0.1 M KCl for 10 cycles. After the PPy/Cl layer was formed, the PPy/Cl transducer was characterized by the CV technique in 0.1 M KCl solution and by testing the SEM techniques.

## 2.2 Optimations and MB28 deposited (sensing layer)

A total of 1 ml of methyl methacrylate and butyl acrylate monomer (2:8 ratio) mixed with 1  $\mu$ l of HDDA. Furthermore, as much as 100  $\mu$ l of the MB28/HDDA mixture was added to the variation of Tetradodecyl ammonium chloride (TDDACl) weight between 0.8-1.2 mg to get the optimum TDDACl and 1 mg DMPP. Next, the mixture was shaken until homogeneous. After homogeneity, as much as 5 ml of the mixture is dropped on the surface of the PPy/Cl transducer and placed on the UV box in N<sub>2</sub> gas flow. Furthermore, the photopolymer process is carried out for 3.5 minutes so the surface of the PPy/Cl transducer electrode will form a transparent film layer. After that, the ISE electrodes were immersed in 0.01 M Na<sub>2</sub>SO<sub>4</sub> solution for 15 minutes for hydration.

Furthermore, the ISE is connected to a Potentiostat device together with the double junction of the Ag/AgCl reference electrode. After connecting to the Potentiostat device, the potential value in various Na<sub>2</sub>SO<sub>4</sub> solutions was measured with a concentration range between 0.1 - 10<sup>-8</sup> M. The resulting potential value is then plotted on the calibration curve to obtain the optimum Nernstian number value. While, Ionophore optimization is the same process, where the ionophore composition used is 1: 1, 1: 2, 1: 3 and 1: 4 to the optimum TDDACl weight.

## 2.3 SO42--ISE characterizations

The optimum of SO42-- ISE is provided for LOD and selectivity testing. In the LOD test, the SO42--ISE was rinsed with ion-free water and connected to a Potentiostat device with a double junction of the Ag/AgCl reference electrode. After connecting to the Potentiostat device, the measurement of the potential value in various Na<sub>2</sub>SO<sub>4</sub> solutions with a concentration range of 0.1 - 10<sup>-8</sup> M. Next, extrapolation of the intersection point between linear and non-linear regions of the x v's y graph plot. Meanwhile, selectivity testing is carried out using Interfering ions, where the types of Interference ions used include ions Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, I<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and HPO<sub>4</sub><sup>2-</sup>. The selectivity test was carried out using the FIM method, where the concentration of the interfering solution used was 0.1M.

## 2.4 Validation test

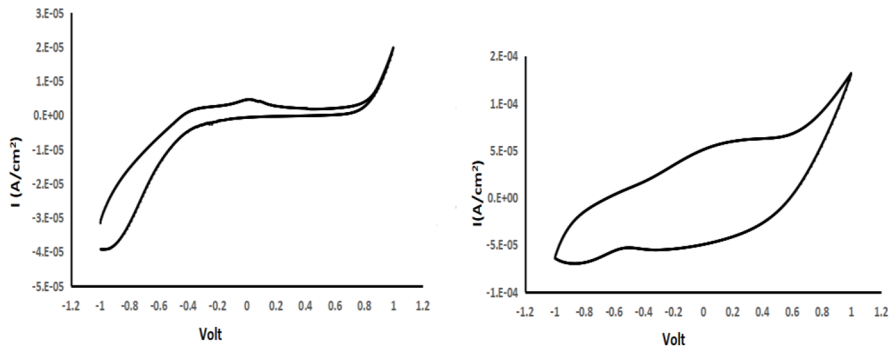
The optimum of the SO42--ISE provides for validation testing. The validation process is carried out by comparing the measurement results of the SO42--ISE sensor and the gravimetric measurement technique. In this measurement, artificial solutions with concentrations of 5 and 25 ppm were used while using real sample solutions from swimming pool, rainwater, and tap water.

3 Results and Discussion

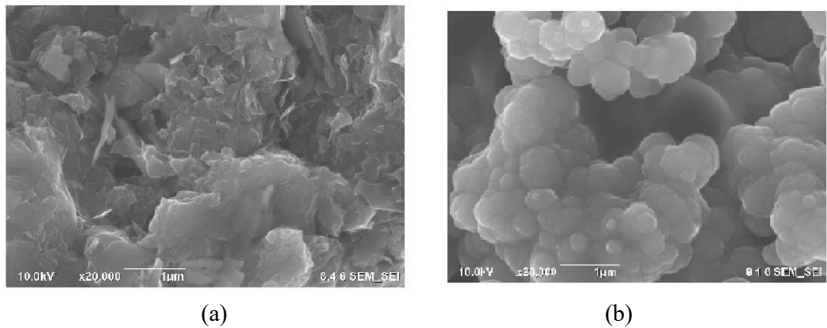
3.1 Fabrication of transducer

The transducer is a very important component in the fabrication process of a sensor, including ISE type sensors[19,20,21]. In this study, the transducer used was a polypyrrole doped with KCl (PPy-Cl), where PPy-Cl was coated on the surface of a GPE. The selection of GPE in transducer fabrication is based on several advantages such as the fact that this electrode is very cheap, easy to modify, size can be adjusted, easy to integrate with other components and has low resistance. The transducer's role is to convert chemical information into an easily recognizable electrical signal so that the concentration of a substance can be measured in the presence of electrical changes such as potential energy in potentiometric testing cases[18,21]. Therefore, the existence of a transducer is very important in the fabrication of ISE type sensors, including SO42--ISE. Meanwhile, PPy-Cl was chosen as the transducer because the electrical signal provided was relatively stable, the PPy-Cl structure did not change quickly due to the presence of dissolved oxygen in the sample. In addition, the PPy-Cl coating process on the GPE surface is relatively easy, cheap and fast[22,23].

In this study, transducer characterization was carried out using cyclic voltammetry (CV) testing in 0.1 M KCl solution and a scanning electrode microscope (SEM) device. The CV and SEM testing results can be seen in Figures 1 and 2.



**Fig. 1.** Cyclic voltammogram of GPE (a) before PPy-Cl deposited (b) after PPy-Cl deposited in KCl 0.1 M.



**Figure 2.** (a) GPE surface before PPy-Cl deposited (b) after PPy-Cl deposited.

Based on CV 1a above, it can be seen that GPE does not show sufficient oxidation and reduction peaks between -1 to 1 V, except in the 0.05 V area, small and wide oxidation peaks are visible. The peak comes from impurities found in GPE, where GPE is a mixture of graphite carbon and clay as a binder. Meanwhile, in Figure 1b, you can see the changes in

the CV graph after polypyrrole coating, where you can see an oxidation peak in the area of 0.13 V and a reduction peak in the area of -0.89 V. This is inseparable from the fact that the GPE surface has been covered by the Ppy-Cl layer formed on it, where one of the properties of PPy-Cl is conductive, so it will easily undergo redox reactions. The results obtained are also following the results of research conducted by previous researchers[18].

This is also reinforced by data from Figure 2, where Figure 2a shows the micro-structure with enlargement of the GPE surface in the form of piled flakes, a typical form of the GPE surface[24]. Meanwhile, in Figure 2b, the micro-structure changes to a shape like grape balls, a typical particle shape of PPy-Cl, which is also consistent with the results of previous studies[25]. This indicates that the PPy-Cl layer has sat covering the surface of the GPE. Thus, the resulting GPE/PPy-Cl transducer can be used for SO42--ISE sensor fabrication.

3.2 Optimizations of MB28 compositions

One of the most important things in the fabrication of an ISE sensor, including for SO42--ions, is the composition of the membrane layer used. The membrane's composition will affect the ISE's performance [26,27]. In this study, the composition optimization process was carried out first to determine the amount of TDDACl used as a lyphophilic salt to extract negative ions entering the MB28 membrane layer [12]. The optimum concentration of TDDACl is 1 mg as shown in Figure 3 and Table 1 below.

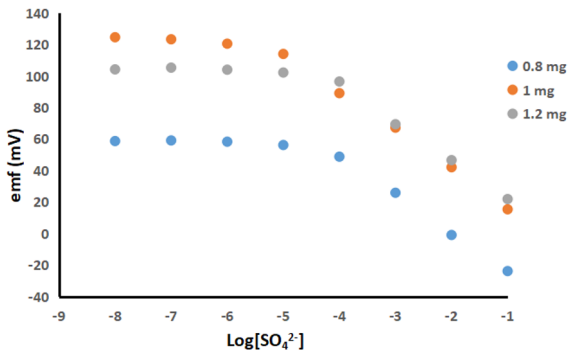


Figure 3. Response of SO42--ISE in various concentrations of SO42- solutions.

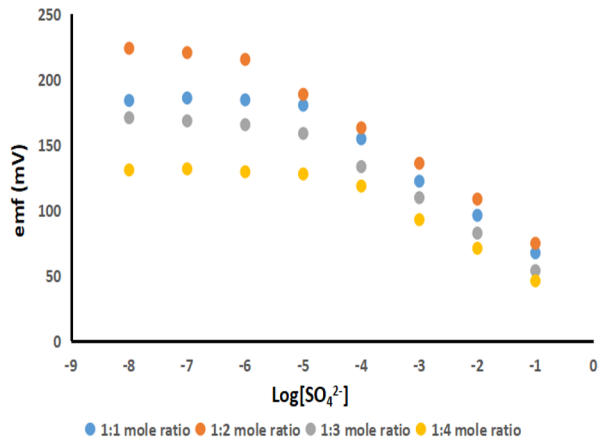
Table 1. The SO42--ISE performance was measured with various concentrations of TDDACl.

TDDACl (mg)	Slope (mV/dec)	Linear Range(M)	LoD (M)	r <sup>2</sup>
0.8	-24.5	0.1 -10 <sup>-4</sup>	4.47 x 10 <sup>-5</sup>	0.9990
1.0	-24.4	0.1-10 <sup>-5</sup>	4.07 x 10 <sup>-6</sup>	0.9989
1.2	-24.7	0.1-10 <sup>-4</sup>	4.89 x10 <sup>-5</sup>	0.9989

It can be seen from Table 1 that all variations of TDDACl give a similar Nernstian number value, which is around -24 mV/dec, and this corresponds to the standard Nernstian number value for a two-charged ion, which is -29 ± 5 mV/dec [18]. However, Figure 3 shows that for TDDACl with an amount of 1 mg, gives a longer linear range of 0.1-10<sup>-5</sup>M. This is because, at an amount of 0.8 mg, TDDACl is not strong enough to force the SO42- -ions in the sample to diffuse into the MB28 membrane[28]. Meanwhile, at an amount of 1.2 mg, the amount of TDDACl will be very large, so the MB28 membrane will be too rich in favourable charge spots. This makes all the negatively charged ions in the sample easier to enter in excess. This

causes the ion balance in the MB28 membrane to be disrupted, ultimately pushing the ions in the MB28 membrane to move back into the sample[12].

Furthermore, the SO42--ISE sensor with 1 mg TDDACl was chosen to optimize the variation of the sulfate ionophore used. The results of optimizing variations in the amount of sulfate ionophore used can be seen in Table 2 and Figure 4 below.



**Fig. 4.** Response of SO42--ISE with variations in the mole ratio of TDDACl:Sulfate Ionophore in various concentrations of SO42- -ion solutions.

**Table 2.** Response of SO42--ISE with variations in the mole ratio of TDDACl: Sulfate Ionophore in various concentrations of SO42- -ion solutions (TDDACl = 1 mg).

Mole ratio	Slope (mV/dec)	Linear range (M)	LoD (M)	r <sup>2</sup>
1:1	-28.4	0.1 - 10 <sup>-5</sup>	6.46 x 10 <sup>-6</sup>	0.9989
1:2	-27.7	0.1 - 10 <sup>-6</sup>	4.79 x 10 <sup>-7</sup>	0.9978
1:3	-26.1	0.1 - 10 <sup>-5</sup>	2.75 x 10 <sup>-6</sup>	0.9987
1:4	-23.9	0.1 - 10 <sup>-4</sup>	1.51 x 10 <sup>-5</sup>	0.9991

Based on Figure 4 and Table 2 above, the addition of sulfate ionophore shows a change in the sensitivity value of the SO42--ISE sensor, where the optimum composition is obtained at a mole ratio of 1:2, which is -27.7 mV/dec and with a linear range between 0.1 to 10-6 M. The sensitivity of -27.7 mV/dec corresponds to the standard Nernstian number for divalent ions of -29 5 mV/dec [18]. Meanwhile, the composition of mole ratios 1:1 and 1:3, even though they have a sensitivity close to the Nernstian number, the resulting linear range is shorter. At a 1:1 ratio, the addition of ionophore sulfate is not enough to capture SO42- -ions that enter the membrane, although the sensitivity is better without sulfate ionophore as shown in Table 1. Sulfate ionophore functions as a neutral carrier that precisely recognition with SO42- -ions, wherein the SO42- -ions will be brought to the surface of the transducer and then read the potential changes that occur on the surface of the transducer[26,27].

Meanwhile, at a ratio of 1:3 and 1:4, the sensitivity tends to decrease because the amount of sulfate ionophore has increased, resulting in the Donnan effect. In this event, the charge balance in the MB28 membrane is uneven, so some of the charge and ion membrane components will migrate into the sample[29].

3.3 Coefficient selectivity study

In this study, selectivity testing was carried out using the fixed interfering method (FIM) as recommended by IUPAC [30]. This test is very important because it will show the extent to which the ability of the SO42--ISE sensor is not affected by the presence of foreign ions in a

sample, bearing in mind that in reality, in general, real samples will always have more than one ion, and this certainly has the potential to cause interference[18,23,25,30]. The results of the selectivity test can be shown in Table 3 below.

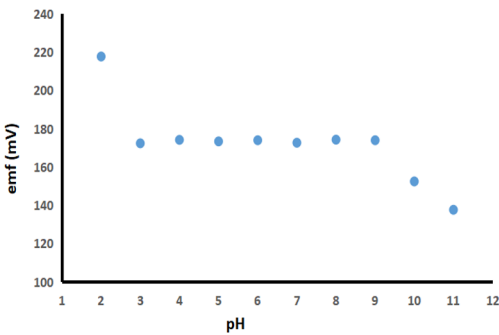
**Table 3.** Comparison of the selectivity coefficient (LogK<sub>pota,b</sub>) with several previous studies.

Interfering Ion	[31]	[32]	[33]	[34]	This study
I <sup>-</sup>	-1.6	-2.5	-3.6	-	-1.8
NO <sub>3</sub> <sup>-</sup>	-1.9	-2.8	-2.5	1.8	-2.3
Cl <sup>-</sup>	-1.2	-2.0	-2.3	-0.1	-1.6
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	-0.4	-	-	-	-0.8
HPO <sub>4</sub> <sup>2-</sup>	-0.4	-	-	-	-1.3

Based on data from Table 3, it can be seen that the resulting coefficient selectivity is comparable to several previous studies where the greatest disturbance was given by H<sub>2</sub>PO<sub>4</sub>-ions. This is inseparable from the order of the Hoffmiester series, which shows that SO<sub>4</sub><sup>2-</sup> ions are adjacent to H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and HPO<sub>4</sub><sup>2-</sup> thus its ability to associate with the sulfate ionophore is almost as strong[31].

3.4 pH effect

In this research, a study of the effect of pH was also carried out. This is important because the presence of SO<sub>4</sub><sup>2-</sup> in the environment is influenced by pH [31,32,33,34]. In practice, the test uses a solution containing SO<sub>4</sub><sup>2-</sup> ions, and the pH is adjusted in the range 2-11, where the results can be seen in Figure 5 below.



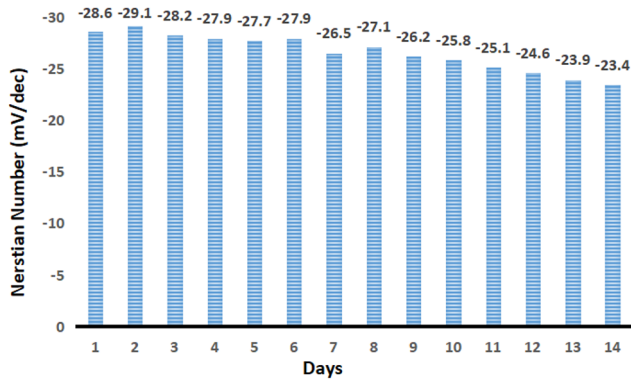
**Figure 5.** Response SO<sub>4</sub><sup>2-</sup>-ISE in SO<sub>4</sub><sup>2-</sup> solution with variations in pH.

Based on Figure 5, it can be seen that the response of the SO<sub>4</sub><sup>2-</sup> -ISE sensor is also influenced by pH. Where the pH is less than 3, the SO<sub>4</sub><sup>2-</sup> -ISE gives a high potential value response. This is inseparable from the fact that at a pH of less than 3, some of SO<sub>4</sub><sup>2-</sup> changes form to HSO<sub>4</sub><sup>-</sup>. Of course, this will decrease the concentration of SO<sub>4</sub><sup>2-</sup> ions in the sample, whereas, at low concentrations, it will provide a higher mV value for anion detection using ISE [32]. Meanwhile, at pH 3-9, the ISE response was stable at 172-174 mV. At a pH above 9, more OH<sup>-</sup> ions in the sample are formed, thus disturbing the reading of the SO<sub>4</sub><sup>2-</sup>-ISE sensor [33,34].

3.5 Lifetime study

Lifetime testing is one of the tests that is of concern in this study. This test aims to determine the performance of SO<sub>4</sub><sup>2-</sup>-ISE can still work well for a certain period. In this test,

measurements were made using a solution containing  $\text{SO}_4^{2-}$  ions with a concentration of  $0.1 \cdot 10^{-6} \text{ M}$ , which is the linear range of the  $\text{SO}_4^{2-}$ -ISE sensor [35]. Data collection is carried out once a day with one measurement, where the measurement results can be seen in Figure 6 below.



**Figure 6.** The  $\text{SO}_4^{2-}$ -ISE performance in daily measurements.

It can be seen from Figure 6 above that the sensor performance shows a decreasing trend of the Nernstian number, where until the 12th day, the Nernstian number is still following the standard  $-29 \pm 5 \text{ mV/dec}$  [18]. However, after the 12th day, the Nernstian's number exceeded the standard. This happened because, during the testing process, some of the water components also diffused into the membrane and were trapped in the MB28 membrane to form small pools or water trap. This situation also disrupts the membrane's charge balance and encourages leaching several components [36,37].The presence of a pool of water in the membrane will also cause changes in the pH of the ISE system, and, of course, this will change the performance of the ISE [38]. In addition, the formation of several small pools exerts pressure from within on the MB28 membrane to lift slightly. Of course, it has an impact on decreasing the adhesion of the membrane to the surface of the electrode and causing the edge areas of the MB28 membrane to begin to open, so that the membrane components are also leaching and foreign ions will more easily enter the membrane and cause interference [39].

3.6 Validation test

In this study, validation testing is important, as it aims to ensure that the  $\text{SO}_4^{2-}$ -ISE sensor that has been fabricated has the same reading ability as the standard method [18, 23]. In this validation process, two samples were used: an artificial solution with a known concentration of  $\text{SO}_4^{2-}$  ions and a real sample solution consisting of swimming pool samples, tap water, and rainwater. The standard method used is SNI 19-6964.5-2003 using the gravimetric technique, where the validation test results can be seen in table 4 below[40].

**Table 4.** Comparison of sample test results between  $\text{SO}_4^{2-}$ -ISE sensors and SNI 19-6964.5-2003 (n=3)

Samples	SO42--ISE	SNI 19-6964.5-2003
5 ppm (artificial)	4.8 ± 1.2	5.1 ± 0.8
25 ppm (artificial)	26.3 ± 0.7	25.9 ± 1.4
Swimming pool	27.6 ± 0.8	26.2 ± 0.8
Tap water	37.2 ± 0.3	37.9 ± 1.2
Rainwater	2.1 ± 0.6	1.9 ± 0.5



Based on Table 4 above, it can be seen that the results of the validation measurements do not show a difference between the  $\text{SO}_4^{2-}$ -ISE sensors and SNI 19-6964.5-2003. This indicates that the fabricated sensor can work properly. The sample testing results also showed that the  $\text{SO}_4^{2-}$ -ion concentration in the sample was still less than 50 ppm, which means that it is still following WHO standards, which require the presence of  $\text{SO}_4^{2-}$ -ions in water not to exceed 250 ppm [3]. The presence of  $\text{SO}_4^{2-}$ -ions in tap water and swimming pools is usually due to the addition of copper sulfate and aluminum sulfate as a disinfectant [41,42]. Meanwhile, sulfate is generally present in rainwater due to a reaction between water vapor and  $\text{SO}_2$  gas in the air, also known as acid rain. In this study, the rainwater samples were taken at the Mercubuana University campus in the Meruya area, Jakarta [43].

## 4 Conclusion

Based on the studies that have been carried out, there are four important points: transducer preparation, optimization of the composition of the MB28 membrane,  $\text{SO}_4^{2-}$ -ISE sensor performance testing, and validation tests. In the transducer preparation, the PPy-Cl layer was successfully formed on the surface of the GPE as indicated by the appearance of oxidation and reduction peaks on the CV test. In addition, an indication of the formation of a PPy-Cl layer was based on the results of SEM testing which showed the formation of spherical particles like grape balls on the GPE surface. Meanwhile, in the process of optimizing the composition of the MB28 membrane, the optimum amount of TDDACl was 1 mg and the mole ratio to sulfate ionophore was 1:2. With this composition, the  $\text{SO}_4^{2-}$ -ISE sensor provides values close to the Nernstian number of values for divalent ions and has a linear range between 0.1-10<sup>-6</sup> M. In performance testing, the  $\text{SO}_4^{2-}$ -ISE sensor showed selectivity values comparable to previous studies where the main interfering elements were dibasic and monobasic phosphate ions. The performance test results also show that  $\text{SO}_4^{2-}$ -ISE can function well in the pH range 3-9 and can function up to 12 days of use. The validation results show that the fabricated sensors give comparable results to the SNI 19-6964.5-2003 method.

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