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Use of ion chromatographic pulsed amperometric method (IC-PAD) for measuring aqueous sulfide in synthetic and real domestic wastewater

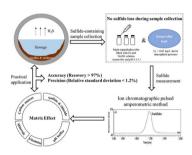
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HIGHLIGHTS

- · A sample collection method without sulfide antioxidant buffer is designed.
- A low detection limit of 3 µg/L sulfide is achieved by IC-PAD method.
- Matrix effect of wastewater samples during IC-PAD sulfide measurement is studied.
- The sulfide recovery in real domestic wastewater is higher than 97%.
- The RSD of sulfide measurement in real domestic wastewater is <1.2%.

GRAPHICAL ABSTRACT



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ABSTRACT

Sulfide detection in domestic wastewater is widely demanded, as sulfide induces odour nuisance and wastewater assets corrosion. However, traditional sulfide detection methods are usually plagued by the limited detection range or interference from impurities. To address these constraints, this study improved the ion chromatographic pulsed amperometric method (IC-PAD) and tested its validity for use in domestic wastewater. Prior to sulfide detection, sulfide-containing sample collection usually requires the use of sulfide antioxidant buffers (SAOB) to minimize sulfide loss. Different sample matrixes require different SAOB recipes, which increases complexity and uncertainty when measuring different environmental samples. Therefore, this study also developed a more convenient and generic sample collection method without the addition of SAOB. The results indicated that the proposed SAOB-free sample collection method could minimize the sulfide loss during sample collection. The IC-PAD method showed a wide linear detection range up to 10 mg-S/L. The detection limit was 3 µg-S/L. Matrix effect studies showed that 1 g/ L glucose, formate, acetate, methanol, ethanol, propionate, butyrate, lactate, or sulfate had no evident interference on sulfide measurement. However, 5 mM phosphate buffer led to interference, but reducing the KOH eluent concentration from 62 to 30 mM avoid this interference. Wolfe's vitamin mixture and Wolfe's modified mineral mixture could cause diminutive interference equivalent to $2.53 \pm 1.32 \, \mu g$ -S/L sulfide. Moreover, the interference caused by chloride indicated that the IC-PAD method is more applicable for measuring sulfide in low-chloride wastewater. To this end, the IC-PAD method showed high accuracy and precision in the real domestic wastewater samples with chloride concentration of 68 mg/L. The recovery was higher than 97% and the relative standard deviation (RSD) was lower than 1.2%. This study demonstrated the potential use of IC-PAD method for measuring sulfide in real domestic wastewater and possible interference from the solution matrix to be considered.

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1. Introduction

Hydrogen sulfide is commonly present in the transportation and treatment system of domestic wastewater, such as sewer systems and wastewater treatment plants (WWTP) (Jiang et al., 2017). The presence of sulfide in domestic wastewater not only causes odour nuisance but also leads to corrosion of wastewater assets (Jiang et al., 2017). In the United States, the direct costs of managing corrosion of national drinking water and sewer systems is estimated to be 36 billion US dollars per year (Koch et al., 2002). Several practical solutions and scientific insights are under development to solve this issue; however, an accurate and efficient quantification of aqueous sulfide (i.e. $\rm H_2S$, $\rm HS^-$ and $\rm S^{2-}$ in the liquid phase) in domestic wastewater is still required and has become increasingly important.

Quantification of aqueous sulfide requires proper sample collection and accurate measurement method. Collecting aqueous sulfide-containing sample is challenging, as aqueous sulfide has a highly reduced state and can be rapidly oxidized when exposed to oxygen. Keller-lehmann (Keller-Lehmann et al., 2006) indicated that, if 45 μL of air bubbles are dissolved in a 2 mL sample, theoretically 8 mg-S/L of sulfide can be oxidized in a short time. Besides sulfide oxidation, sulfide emission could also lead to sulfide loss during sample collection. When the pH is lower than 10, aqueous sulfide could, in theory, transfer to the gas phase in the form of gaseous H_2S . Therefore, prior to aqueous sulfide measurement, stabilizing the aqueous sulfide and avoiding aqueous sulfide loss during sample collection is of great importance.

Thus far, sulfide antioxidant buffer (SAOB) is commonly applied to minimize aqueous sulfide loss during sample collection. SAOB is usually composed of a reducing agent and complexing agents, which are dissolved in a caustic solution (Lawrence et al., 2000). Different sample matrixes require different SAOB recipes (Lawrence et al., 2000), which creates complexity and uncertainties in measuring aqueous sulfide in different environmental samples. This calls for the development of a more convenient and generic sulfide-containing sample collection method, especially for measuring aqueous sulfide in complex real environmental samples.

Besides sample collection method, the current aqueous sulfide measurement methods are also hampered by several problems. Current aqueous sulfide measurement methods are mainly based on either the iodometric method (Pawlak and Pawlak, 1999) or the methylene blue method (Okumura et al., 1999). The iodometric method is the representative of classical sulfide measurement method, which requires no sulfide standard. It quantifies the aqueous sulfide by adding iodine to convert sulfide into elemental sulfur (Pawlak and Pawlak, 1999). This method tends to underestimate the free sulfide concentration in wastewater, as a HCl acid-iodine solution is used that can partially oxidize sulfide to sulfate and interfere the measurement (Pawlak and Pawlak, 1999). The methylene blue method is the most widely used method for sulfide measurement. With the assistance of small amounts of ferric ions, the aqueous sulfide reacts with dimethyl-p-phenylenediamine to form methylene blue (Cassella1 et al., 1999). Methylene blue has a maximum light adsorption at \approx 670 nm and can be quantified by using a UV/visible spectroscopic technique (Kubaáň et al., 1992). The disadvantages are that the absorbance relates non-linearly to the sulfide concentration, and that the measurement range is relatively small (0.03-2 mg-S/L) (Keller-Lehmann et al., 2006), while aqueous sulfide concentration can reach up to 13 mg-S/L in real domestic wastewater (Jiang et al., 2013). An alternative measurement technique, i.e. the ion chromatographic pulsed amperometric method (IC-PAD), has been developed, which combines electrochemical and chromatographic principles for measuring aqueous sulfide (Cheng et al., 2005). The detection of aqueous sulfide by IC-PAD method equipped with the disposable silver electrode is based on the phenomenon that the oxidation of silver to free silver ions could be facilitated in the presence of sulfide ions. The free silver ions could react with sulfide ions and form silver salts (e.g., Ag₂S). The precipitation of formed silver salts removes the free silver ions from

the electrochemical equilibrium, thus decreasing the free energy differential and also the required driving electrochemical potential. The generated electric current of anodic silver oxidation is then used to determine the sulfide concentration (Cheng et al., 2005). This approach offers a measurement range of 1 µg-S/L to 100 mg-S/L, which is much broader than the methylene blue procedure, and has a linear relationship between electric current response and sulfide concentration. Moreover, compared to iodometric method, IC-PAD method takes advantage of the analytical column in the ion chromatography to separate sulfide from other compounds and thus minimizes possible interferences. Though being promising in offering a more reliable and sensitive sulfide measurement method, IC-PAD method has not been widely used for measuring aqueous sulfide in samples from complex natural environments, because samples from these environments (e.g., drinking water production, wastewater treatment and oil gas industries) usually contains various non-sulfide compounds in their matrixes that could compromise or interfere with the measurement of sulfide. These so-called matrix effects may hinder the extensive application of this technique, which has not yet been thoroughly examined.

This study aims therefore to develop an improved aqueous sulfide measurement method (via ion chromatographic pulsed amperometric; IC-PAD) and a corresponding sample collection method for measuring aqueous sulfide within complex chemical matrixes in environmental samples. First of all, a more widely applicable sample collection method without the addition of SAOB has been developed and tested. After that, the focus has been put on the matrix effect of the IC-PAD method. The potentially interfering compounds have been tested, namely: (1) common organic carbon substrate in environmental samples, (2) common anions in real domestic wastewater including sulfate and chloride, (3) phosphate naturally occurring or externally added as pH buffer agent (4) micronutrients including vitamins and trace minerals. In the end, the analytical performance of IC-PAD method to measure aqueous sulfide in synthetic and real domestic wastewater was evaluated.

2. Materials and method

2.1. Chemicals

Six matrixes were prepared and used for the preparation of sulfide-containing samples. The composition of each matrix is shown in Table 1. Milli Q water was produced by Milli-Q® IQ 7005 Water Purification System (Merck) and was used to prepare all the solutions. All the chemicals were obtained from Sigma-Aldrich. 10 mM NaOH solution was prepared from NaOH pellets with a purity $\geq 97\%$. Sodium sulfide nonahydrate analytical standards with a purity of 99.99% (Na₂S·9H₂O) were used to prepare sulfide-containing samples (Sigma-Aldrich 431,648). 50 mM phosphate buffer (pH 7.4) was prepared and diluted 10 times by 10 mM NaOH to obtain 5 mM phosphate buffer. The 50 mM phosphate buffer used in this study contains 1.36 g/L KH₂PO₄ and 5.67 g/L Na₂HPO₄. The recipe of Wolfe's vitamin and Wolfe's modified mineral solution was obtained from Wolin (Wolin et al., 1963). In this

Table 1
Composition of six matrixes tested in this research, all of which contains no sulfide except as otherwise indicated.

Matrix	Composition						
	Milli Q	NaOH solution (mM)	phosphate buffer (mM)	Wolfe's vitamin mixture (mL/L)	Wolfe's modified mineral mixture (mL/L)		
A	+						
В	+	10					
C	+	10	5				
D	+	10	5	0.1			
E	+	10	5		0.1		
F	+	10	5	0.1	0.1		

study, Wolfe's vitamin mixture and Wolfe's modified mineral mixture were 10 times concentrated. Wolfe's modified mineral mixture contained (in g/L) Na₂SeO₃, 0.1; NiCl₂·6H₂O, 0.1; Na₂WO₄·2H₂O, 0.1; nitrilotriacetic acid, 15; MgSO₄, 30; MnSO₄, 5; NaCl, 10; FeSO₄, 1, CaCl₂, 1; CoCl₂, 1; ZnSO₄, 1; CuSO₄, 1; AlK(SO₄)₂, 0.1; H₃BO₃, 0.1; Na₂MoO₄, 0.12. Wolfe's vitamin mixture contained the following vitamins (in mg/L): biotin, 20; folic acid 20; pyridoxine hydrochloride, 100; riboflavin, 50; thiamine, 50; nicotinic acid, 50; pantothenic acid, 50; vitamin B₁₂, 1; p-aminobenzoic acid, 50; thioctic acid, 50. Before use, the Milli Q water, 10 mM NaOH and 50 mM phosphate buffer were flushed with nitrogen gas for 1 h and transferred to an anaerobic tent to reach an anaerobic state.

2.2. Instrumentation

The sulfide concentration was quantified by ion chromatography (Dionex IC-S6000) equipped with a Dionex IonPac AS17-C 2 mm IC analytical column and a 2 mm guard column. The sample was injected by autosampler (DionexTM AS-AP Autosampler), and the injection volume was 10 µL. The stationary phase of the column (which consists of cationic resin) allowed separation between the components at 30 °C. The eluent for separation was isocratic 30- or 62-mM potassium hydroxide solution at a flow rate of 0.25 mL/min, which was automatically generated with Dionex ICS-6000 eluent generator. These separated components were then detected by Dionex ICS-6000 Electrochemical Detector (ECD). ECD was composed of a pH-Ag/AgCl reference electrode (P/N 071,879, ThermoFisher scientific) and a Certified Disposable Silver (Ag) working electrode (P/N 063,003, ThermoFisher scientific). The waveform of Disposable Silver (Ag) working electrode was (in time/ potential vs Ag/AgCl reference electrode): 0 ms/-100 mV, 200 ms/-100 mV, 900 ms/-100 mV, 910 ms/-1000 mV, 930 ms/-300 mV, 1000 ms/-300 mV (Cheng et al., 2005). The measurement time of each sample was 5 min (62 mM eluent) or 10 min (30 mM eluent), and the data was processed by Dionex Chromelon software 7.3.

2.3. Sample collection method development

2.3.1. Sample collection method procedure

A new sample collection method without the addition of SAOB was proposed and studied. The sulfide-containing sample need to be diluted 10 times by 10 mM NaOH solution, and an anaerobic tent (O $_2 < 0.03$ mg/L and at atmospheric pressure) was used to minimize the sulfide loss during sample collection at room temperature. The detailed procedure is shown below.

Step I. (anaerobic)

9 mL of anaerobic 10 mM NaOH solution was added into a 10 mL glass tube (Macherey-Nagel) in the anaerobic tent. The glass tube was then capped with Butyl/PTFE molded septa (Septa N20 butyl/PTFE grey 3 mm, Macherey-Nagel) and aluminum crimp seal (Crimp closure, N 20, alu., center hole, no liner, Macherey-Nagel) in an anaerobic tent using the electronic capper (Crimping tool for 20 mm aluminum caps, electronic, battery-powered, Macherey-Nagel) to keep the content in the glass tube under anaerobic conditions. The crimp setting of the electronic capper was first set at 58% closing strength and then to 63% to ensure the capped glass tube was airtight. The appearance of a capped glass tube was shown in Fig.S1.

Step II. (aerobic)

1 mL of sample was taken out from the reactors by using 1 mL plastic syringes (Syringe 3-parts 1 mL Tuberceline, Becton Dickinson) with a needle (Microlance3 needles 23 G 1'' RB Thin (Blue), BD) and was then immediately added into the capped glass tube (assembled in Step I) by puncturing through the Butyl/PTFE molded septa (Septa N20 butyl/PTFE grey 3 mm, Macherey-Nagel).

Step III. (anaerobic)

4 mL of solution was taken out from the capped glass tube and was filtered through a 0.2 μm filter (CHROMAFIL® Xtra. Typ: PES 20/25, Marcherey-Nagel, Germany) inside the anaerobic tent. After discarding the first 2 mL, around 0.8 mL of filtrate was directly added to the IC vial (Snap ring/crimp neck vial, N 11, 11.6 \times 32.0 mm, 0.7 mL, round bottom insert, Macherey-Nagel) and capped and taken out the anaerobic tent for measurement.

2.3.2. Examination of sample collection method performance

Possible interference from 10 mM NaOH solution was first determined by comparing the peak area in the chromatogram of Milli Q water and 10 mM NaOH solution (in triplicates). Afterwards, to test the performance of this sample collection method, sulfide-containing samples with the final concentrations of 10 $\mu g\text{-S/L}$ and 1 mg-S/L were prepared by Matrix C according to the sulfide sample collection method. 30 mM KOH was selected as the eluent for sulfide measurement. Relative standard deviation (RSD) and recovery of each concentration were determined to evaluate the precision and accuracy of this sulfide sampling method (in Quintuplicate), as described in Aydin et al., 2021 (Aydin et al., 2021).

2.4. Sulfide measurement method development

2.4.1. Analytical performance

To test the analytical performance of IC-PAD method, the linearity between peak area and sulfide concentration was investigated by establishing calibration curves with Matrix B; 21 samples containing different sulfide concentrations were prepared by Matrix B and tested by 30 mM eluent (0.001, 0.002, 0.004, 0.005, 0.01, 0.02, 0.04, 0.05, 0.1, 0.2, 0.4, 0.5, 1, 2, 4, 5, 10, 20, 40, 50, 100 mg-S/L sulfide). Limit of detection (LOD) of Matrix B was determined to evaluate the sensitivity of IC-PAD method. Each matrix without sulfide was tested in quintuplicate to determine the interference peaks of background noise. The LOD equaled to 3 of signal-to-noise ratio (Cheng et al., 2005; Shrivastava and Gupta, 2011). The accuracy and precision of this sulfide analysis method in Matrix B was evaluated by recovery and relative standard deviation (RSD) (Aydin et al., 2021). Recovery and RSD experiments were carried out in quintuplicate at sulfide concentrations of 10 μ g-S/L and 1 mg-S/L.

2.4.2. Matrix effect

Phosphate buffer is a pH buffer commonly added in synthetic domestic wastewater, especially in microbial or bioelectrochemical experiments. The commonly used concentration of phosphate buffer is usually less than 50 mM. Therefore, 50 mM phosphate buffer was chosen as a representative concentration in the sulfide-containing sample. In addition, to minimize the loss of sulfide during sample collection, the sulfide-containing sample need to be diluted 10 times with 10 mM NaOH to increase the pH value above 11.5 (see section 2.3.1). Therefore, the final concentration of phosphate buffer in matrix C was set at 5 mM. In order to determine the possible interference from the phosphate buffer, Matrix B without sulfide, Matrix C without sulfide and Matrix C with 4 or 10 μ g-S/L sulfide were prepared and tested in quintuplicate with 62 mM eluent. When the interfering peak of phosphate buffer appeared, the eluent concentration was decreased from 62 mM to 30 mM to separate the sulfide peak from the interfering peak.

Vitamins and minerals were essential in experiments related to microorganisms. Some vitamins such as thiamine, thioctic acid and biotin contained sulfur in molecular structure, which might interfere with the sulfide test based on the amperometric method. To determine the possible interference from Wolfe's vitamin mixture and Wolfe's modified mineral mixture, Matrix F without sulfide were prepared and the corresponding interference peaks of background noises were determined in triplicates with 30 mM eluent. When an interfering peak appeared after the addition of Wolfe's vitamin mixture and/or Wolfe's modified mineral mixture, 1 mg/L of each vitamin and mineral

compound was further measured individually.

Carbon sources served as electron donors was of great importance in biological formation of sulfide. The commonly used carbon sources for sulfate reduction were formate, methanol, ethanol, lactate, acetate, propionate, butyrate and glucose (Liamleam and Annachhatre, 2007). In order to determine the possible interference from carbon source, solutions containing 1 g/L formate, methanol, ethanol, lactate, acetate, propionate, butyrate or glucose were prepared by Matrix C and tested in quintuplicates with 30 mM eluent.

Besides carbon sources, the possible interference of sulfate and chloride on sulfide measurement by IC-PAD method were also investigated. Sulfate and chloride are the common anions in real domestic wastewater. Sulfate is the electron acceptor of biological sulfide formation. Chloride has similar retention time to sulfide in ion chromatography (Keller-Lehmann et al., 2006; Ohira and Toda, 2006). However, whether chloride interferes with IC-PAD sulfide measurement by interacting with electrochemical detector (pulsed amperometric detection) has not been investigated. To determine the possible interference from sulfate and chloride, solutions containing 1 g/L sulfate prepared by Matrix C, 125, 250 and 500 mg/L chloride prepared by Matrix B were tested in quintuplicates with 30 mM KOH eluent.

2.4.3. Applicability to synthetic and real domestic wastewater

The accuracy and precision of the IC-PAD method for measuring sulfide in synthetic and real domestic wastewater were tested and compared with Hach Lange kit LCK-653 (Methylene blue method). Real domestic wastewater was taken from a sewer of the town of Bennekom, The Netherlands and synthetic wastewater from a lab-scale reactor investigating sulfate reduction were collected and were filtered with a 0.2 µm filter (CHROMAFIL® Xtra. Typ: PES 20/25, Marcherey-Nagel, Germany) in the anaerobic tent. The filtered real domestic wastewater and synthetic wastewater were spiked with sulfide to achieve the sulfide concentration of 0.18, 0.45 and 0.9 mg-S/L. The sulfide concentration in the spiked real domestic wastewater and synthetic wastewater samples was measured by IC-PAD method and Hach Lange kit LCK-653 ((Hach, Germany)). The performances of these two methods were evaluated based on RSD and recovery. The compositions of real domestic wastewater and synthetic wastewater were analyzed in terms of carbon sources, anions, and metal ions.

3. Results and discussion

3.1. Preservation performance of the proposed sample collection method

In order to avoid sulfide loss during sulfide-containing sample collection, the existing methods mainly relied on the use of SAOB. SAOB usually contains a reducing agent to minimize sulfide loss via sulfide oxidation. Ascorbic acid is a commonly used reducing agent in SAOB, and the concentration was usually between 1 and 17 g/L (Ebdon et al., 1997; García-Calzada et al., 1999; Keller-Lehmann et al., 2006; Kubaáň et al., 1992). This study found that the addition of ascorbic acid resulted in a high peak in chromatogram. The peak height of 1 g/L ascorbic acid (around 1400 nC) was about 3 times higher than 1 mg-S/L sulfide (around 470 nC) (See SI-Fig.S2). This could potentially decrease the service life of the disposable silver electrode.

In this study, a sulfide antioxidant buffer-free sample collection method was proposed, which was shown to minimize sulfide loss during sample collection. The use of 10 mM NaOH could mitigate the sulfide loss via sulfide emission during sample collection (See SI-Fig.S3). Moreover, the use of 10 mM NaOH had no significant interference on sulfide measurement by the IC-PAD method. The average peak area of background noise from Matrix B without sulfide (0.0033 nC-min) was lower than that of background noise from Matrix A without sulfide (0.0060 nC-min) (See SI-Fig.S4). Furthermore, the use of an anaerobic tent ($O_2 < 0.03$ mg/L and at atmospheric pressure) during sample collection minimized the sulfide loss through sulfide oxidation. No

significant new peaks (e.g., thiosulfate) appeared when comparing the chromatograms of samples prepared by the proposed sulfide-containing sample collection method and samples prepared in the anaerobic tent (See SI-Fig.S5).

The proposed sample collection method has no significant adverse effect on the accuracy and precision of IC-PAD method. The RSD of 10 $\mu g\text{-}S/L$ and 1 mg-S/L sulfide-containing samples (Matrix C) were 0.8% and 0.4%, respectively. The recovery of 10 $\mu g\text{-}S/L$ and 1 mg-S/L sulfide-containing samples (Matrix C) were 103.6% and 97.3%, respectively (Table S1).

3.2. Sulfide measurement by IC-PAD method

3.2.1. Sulfide species measured by IC-PAD method

The speciation of aqueous sulfide is strongly affected by pH changes and generally exists in three forms: $\rm H_2S$, $\rm HS^-$ and $\rm S^{2-}$ (Lewis, 2010). The dissociation constant between $\rm HS^-$ and $\rm S^{2-}$ should be between $\rm 10^{-17}$ (Meyer et al., 1983) and $\rm 10^{-19}$ (Myers, 1986), which implies that the equilibrium is difficult to achieve. May et al., 2018 also demonstrated that the aqueous sulfide cannot exist in the form of $\rm S^{2-}$ (May et al., 2018). Moreover, as the pH increases, the aqueous sulfide prefers to exist in the form of $\rm HS^-$ than $\rm H_2S$. When the pH is above 9, the aqueous sulfide is most probably only present as $\rm HS^-$ (Giuriati et al., 2004).

By using the proposed SAOB-free sample collection method, the pH of real domestic wastewater samples (influent of wastewater treatment plant of Bennekom, the Netherlands) with an initial pH of 5-9 could be increased to above pH 11 (See Table S2). The resulting high pH (>11) could convert all aqueous sulfide species (i.e., H_2S , HS^- and S^2^-) to the form of HS^- , which can then be measured by the IC-PAD method.

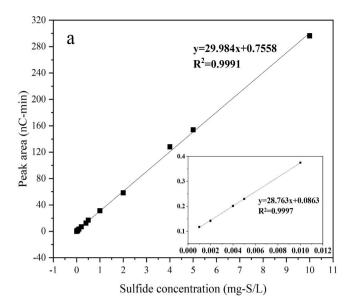
3.2.2. Waveform of IC-PAD method

The waveform of Disposable Silver (Ag) working electrode used in this study is (in time/potential vs Ag/AgCl reference electrode): 0 ms/-100 mV, 200 ms/-100 mV, 900 ms/-100 mV, 910 ms/-1000 mV, 930 ms/-300 mV, 1000 ms/-300 mV (Cheng et al., 2005). From 0 ms to 900 ms, an electrochemical potential of -100 mV is applied for the sulfide-facilitated oxidation of silver to free silver ions (Cheng et al., 2005). The generated current over time period from 200 ms to 900 ms is used as a signal for the sulfide quantification. At 910 ms, a stripping potential of -1000 mV is chosen for renewing the electrode surface by removing the precipitation of silver salts. From 930 ms to 1000 ms, an electrochemical potential of -300 mV is used to re-equilibrate the electrode surface (Cheng et al., 2005).

3.2.3. Analytical performance of IC-PAD method

The maximum linear range between peak area and sulfide concentration of IC-PAD method was from 0.001 to 10 mg-S/L sulfide in Matrix B. The linear regression coefficient ($\rm R^2$) of 0.001–10 mg-S/L sulfide was 0.9991 (Fig. 1a). When the sulfide concentration reached 20 mg-S/L and 100 mg-S/L, the $\rm R^2$ decreased to 0.9723 and 0.8445, respectively (Fig. 1b). The upper limit of linear range of IC-PAD method was 10 mg-S/L sulfide, which was higher than that of Methylene blue method (Keller-Lehmann et al., 2006). Moreover, this upper detection limit of IC-PAD method (10 mg-S/L sulfide) could fulfill the determination of aqueous sulfide in domestic wastewater. The sulfide concentration in the domestic wastewater was usually below 20 mg-S/L (Gutierrez et al., 2014; Jiang et al., 2010, 2013; Pikaar et al., 2012). A 10-fold dilution of the domestic wastewater sample by the proposed antioxidant buffer-free sample collection method could further lower the sulfide concentration to <2 mg-S/L.

IC-PAD method also showed good sensitivity (LOD), precision (RSD), and accuracy (recovery). LOD of IC-PAD method was 3 μ g-S/L sulfide which was significantly lower than the previous works of Font (Font et al., 1996) (capillary electrophoresis) and Spaziani (Spaziani et al., 1997) (methylene blue method with diode-laser-based fluorescence detection). The RSD of 10 μ g-S/L and 1 mg-S/L sulfide were 1.7% and



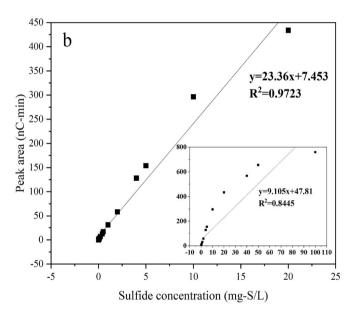


Fig. 1. The linearity between sulfide concentration and peak area. Fig. 1(a) was in the sulfide concentration range from 0.001 to 0.01 or 10 mg-S/L; Fig. 1(b) was in the sulfide concentration range from 0.001 to 20 or 100 mg-S/L.

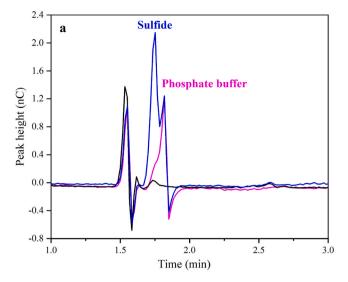
1.2%, respectively. The recovery of 10 $\mu g\text{-}S/L$ and 1 mg-S/L sulfide were 104.7% and 99.9%, respectively (Table S3).

3.3. Matrix effect on IC-PAD method

3.3.1. Interference of phosphate buffer and the potential solution

Phosphate buffer at a concentration of 5 mM could cause additional interference on sulfide measurement based on 62 mM eluent. According to Fig. 2a, the peak of phosphate buffer appeared at 1.65-1.85 min, while the peak of sulfide appeared at 1.65-1.88 min. Therefore, the peak of sulfide overlapped with the peak of phosphate buffer. The above results suggested that 62 mM eluent could not be used for the sulfide test when the sulfide-containing samples were composed of phosphate buffer.

The peak of sulfide was completely separated from the peak of the phosphate buffer by decreasing the eluent concentration from 62 mM to 30 mM. As shown in Fig. 2b, by using 30 mM eluent, the peak of phosphate buffer started at 2.77 min, and the peak of sulfide appeared at



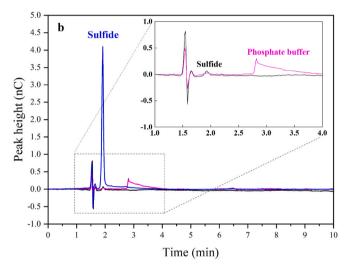


Fig. 2. Chromatograms with 62 mM KOH as eluent (a) and 30 mM KOH as eluent (b). Fig. 2(a): Matrix B without sulfide (black line), Matrix C without sulfide (pink line), 4 μ g-S/L sulfide in Matrix B (blue line); Fig. 2(b): Matrix B without sulfide (black line), Matrix C without sulfide (pink line), 10 μ g-S/L sulfide in Matrix B (blue line). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

1.80–2.02 min. The reason for peak separation might be due to the difference in the ionic charge of phosphate anion and sulfide anion. According to the linear solvent strength model, when the eluent contains the sole eluent anion, the retention time is mainly dependent on the eluent concentration and the ratio between the ionic charge of the anolyte anion and eluent anion (Madden and Haddad, 1999). Therefore, decreasing the eluent concentration shifts the retention time of phosphate and sulfide, thereby separating the peaks of phosphate and sulfide.

3.3.2. Interference of vitamins and minerals

Wolfe's vitamin mixture and Wolfe's modified mineral mixture could cause diminutive interference even with 30 mM eluent (see SI-Fig.S6). The retention time of the interference peak from Wolfe's vitamin mixture and Wolfe's modified mineral mixture without sulfide was between 1.80 and 2.02 min, which overlapped with the sulfide peak (see SI-Fig.S6). Wolfe's vitamins and modified mineral mixture (Matrix F) could lead to diminutive interference equivalent to 2.53 \pm 1.32 µg-S/L sulfide, which meant the deviation between actual and measured sulfide concentration was below 2.53 \pm 1.32 µg-S/L sulfide. Further test indicated that in Wolfe's vitamin mixture, biotin, thiamine HCl, vitamin B12

and thioctic acid have the major contribution to the interference observed in matrixes (Table 2). Since the common sulfide concentration in domestic water is between 2 and 15 mg-S/L (Gutierrez et al., 2014; Jiang et al., 2010, 2013; Pikaar et al., 2012), the interference by Wolfe's vitamin mixture and Wolfe's modified mineral mixture can be considered negligible.

3.3.3. Interference of carbon sources, sulfate and chloride

1 g/L glucose, formate, acetate, methanol, ethanol, lactate, propionate, butyrate or sulfate had no significant overlapping peaks that could cause interference on sulfide measurement (see SI-Table S6). However, the presence of chlorides interfered with the IC-PAD method for sulfide measurements. Chloride of 125, 250 and 500 mg/L could cause interferences equivalent to sulfide concentrations of 9, 17 and 31 μ g-S/L, respectively. Previous field studies indicated that the concentration of chloride in real domestic wastewater is usually below 500 mg/L (Pikaar et al., 2011, 2012). This means that the maximum interference of chloride in IC-PAD sulfide measurement in real domestic wastewater is mostly below 31 μ g-S/L sulfide. In comparison with real domestic wastewater sulfide concentrations of 2–15 mg-S/L (Gutierrez et al., 2014; Jiang et al., 2010, 2013; Pikaar et al., 2012), the interference from chloride can be considered insignificant.

Based on the aforementioned investigation of matrix effect, 30 mM KOH will be selected as the eluent for subsequent performance test of IC-PAD method when measuring aqueous sulfide in real domestic wastewater, which is effective in reducing the interference of phosphate buffer on sulfide measurement.

3.4. Measurement of aqueous sulfide in synthetic and real domestic wastewater by IC-PAD method

The IC-PAD method showed reliable performance when measuring aqueous sulfide in real domestic wastewater (Table 3). The recovery of 180, 450, 900 μ g-S/L sulfide in real domestic wastewater were 97%, 98.3% and 97.8%, respectively. The RSD of 180, 450, 900 μ g-S/L sulfide in real domestic wastewater were 1.2%, 0.1% and 0.5%, respectively.

Compared with real domestic wastewater, the sulfide measurement by IC-PAD in synthetic domestic wastewater showed a comparable precision; the RSD of 180, 450, 900 μ g-S/L sulfide in synthetic wastewater were 0.9%, 1.6% and 0.3%, respectively. However, the recovery

Table 2
Interference test of individual vitamin and mineral compound at 1 mg/L.

Vitamin	Equivalence to	Mineral	Equivalence to
compounds	sulfide	compounds	sulfide
	concentration (µg-		concentration (µg-
	S/L)		S/L)
Biotin	6	Na ₂ SeO ₃	Bdl
Folic acid	Bdl	NiCl ₂	Bdl
Pyridoxine hydrochloride	Bdl	Na ₂ WO ₄	Bdl
Thiamine HCl	4	Nitrilotriacetic acid	Bdl
Riboflavin	Bdl	MaSO ₄	Bdl
Nicotinic acid	Bdl	$MnSO_4$	Bdl
Calcium D- pantothenate	Bdl	NaCl	Bdl
Vitamin B12	4	FeSO ₄	Bdl
P-Aminobenzoic acid	Bdl	CoCl ₂	Bdl
Thioctic acid	4	CaCl ₂	Bdl
		ZnSO ₄	Bdl
		CuSO ₄	Bdl
		$AlK(SO_4)_2$	Bdl
		H_3BO_3	Bdl
		Na_2MoO_4	Bdl

Note: Bdl means below detection limit, the chromatogram of each compound was in SI-Tables S4 and S5.

of sulfide measurement by IC-PAD method was relatively low, which was 93.3% for 180 $\mu g\text{-}S/L$ sulfide, 89.6% for 450 $\mu g\text{-}S/L$ sulfide and 82.8% for 900 $\mu g\text{-}S/L$ sulfide (Table 3). The reason might be that the synthetic wastewater contains a higher concentration of metal ions, including Fe, Mn, and Zn (Table S7). The concentration of Fe, Mn and Zn in synthetic wastewater was 178, 1499 and 231 $\mu g/L$, respectively, while in real domestic wastewater was 36.2, 33.1 and 15 $\mu g/L$, respectively (Table S7). These metal ions in synthetic wastewater, mainly originating from the addition of mineral mixture, might react with sulfide and form poorly soluble products (Giuriati et al., 2004). Further investigation revealed that the addition of Wolfe's modified mineral mixture resulted in a reduction in the sulfide peak area. The average peak area of 1 mg-S/L sulfide in Matrix C was 28.7 \pm 0.7 nC-min, while the average peak area of 1 mg-S/L sulfide in Matrix containing 1 mL/L mineral mixture was only 11.4 \pm 0.4 nC-min (See SI-Table S8).

Using oxalic acid (a metal-chelating agent) could mitigate the sulfide loss caused by the reaction with metal ions and did not cause additional interferences to sulfide measurement. After adding oxalic acid, the recovery of sulfide in synthetic wastewater was improved compared with that without adding oxalic acid. In the presence of 0.5 mM oxalic acid, the recovery of 180, 450 and 900 $\mu g\text{-S/L}$ sulfide in synthetic wastewater was 96.5%, 93.2% and 91.0%, respectively (Table S9). However, the presence of 0.5 mM oxalic acid could not completely reduce the sulfide loss caused by the reaction with metal ions. Increasing oxalic acid concentration to 1 mM could not further reduce the sulfide loss. The average peak area of 1 mg-S/L sulfide in matrix containing 1 mM oxalic acid was slightly lower than in matrix containing 0.5 mM oxalic acid (Table S8). Therefore, alternative metal-chelating agents could be explored in future studies to better reduce the sulfide loss caused by the reaction with metal ions during sample collection.

With the same sulfide-containing sample collection method and operational conditions, the IC-PAD method showed improved precision and accuracy compared to Hach Lange kit LCK-653 (data not shown). Collectively, the IC-PAD method could accurately measure aqueous sulfide in real domestic wastewater with high precision for commonly investigated domestic and synthetic wastewater.

3.5. General recommendation for future studies

The IC-PAD method combines the advantages of ion chromatography (IC) for separation of sulfide from most potentially interfering ions and electrochemical detectors (pulsed amperometric detection) for sensitive sulfide detection. The sulfide measurement range of IC-PAD method of 0.003–10 mg-S/L coupled with the dilution by proposed sulfide antioxidant-free sample collection method could meet the needs of sulfide measurements in most domestic wastewater. In this study, the IC-PAD method showed good sensitivity and precision for the sulfide measurement in real domestic wastewater with a chloride concentration of 68 mg/L (see section 3.4). The results of matrix effect studies suggested that the application of IC-PAD method is not limited to domestic wastewater; sulfide in wastewater with low chloride content could also

Table 3Precision and accuracy of IC-PAD method in the measurement of aqueous sulfide in synthetic and real domestic wastewater.

Type of wastewater	Spiked sulfide concentration (μ g-S/L)	Recovery (%)	RSD (%)
Synthetic wastewater	180 450 900	93.3 89.6 82.8	0.9 1.6 0.3
Real domestic wastewater	180 450 900	97.0 98.3 97.8	1.2 0.1 0.5

Note: the recovery was the average in triplicate, RSD was determined based on three different injections.

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be analyzed by the investigated IC-PAD method. Due to the different compositions of different types of wastewaters, further matrix effect studies are required to determine the feasibility of IC-PAD for sulfide measurement in a specific low-chloride wastewater. In addition to the IC-PAD measurement method, the proposed sulfide antioxidant-free sample collection method further reduces the chemical input compared to conventional sample collection method that rely on SAOB.

4. Conclusion

In this study, an aqueous sulfide quantification process, namely sulfide antioxidant buffer-free sulfide-containing sample collection method coupled with IC-PAD sulfide measurement method, was proposed and investigated. The proposed SAOB-free sample collection method minimizes the sulfide loss during sampling. At the same time, this SAOB-free sample collection method (1) does not cause additional interference on IC-PAD method; (2) avoids potential decrease of the service life of disposable silver electrode in IC-PAD method; (3) reduces the chemical input during sampling. The IC-PAD method (1) shows high sensitivity in measuring aqueous sulfide with the LOD of 3 μg -S/L; (2) has a wide linear detection range up to 10 mg-S/L; (3) has a high selectivity of sulfide detection with insignificant interference from the wastewater sample matrix. In practical application, the IC-PAD method shows reliable accuracy (recovery >97%) and precision (RSD <1.2%) when measuring aqueous sulfide in real domestic wastewater.

Credit author statement

Yue Sun: Conceptualization, Methodology, Validation, Writing - Original Draft; Jill Soedarso: Methodology, Writing - Review & Editing; Jiamin Wang: Methodology, Validation, Writing - Original Draft; Pieter Gremmen: Conceptualization, Methodology, Validation, Resources, Writing - Review & Editing, Project administration; Huub Rijnaarts: Conceptualization, Writing - Review & Editing, Funding acquisition; Wei-Shan Chen: Conceptualization, Writing - Review & Editing, Supervision, Project administration, Funding acquisition.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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