Indirect determination of sulfide ions in water samples at trace level by anodic stripping voltammetry using mercury film electrode†

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A simple and sensitive indirect determination method for sulfide in water samples by anodic stripping voltammetry (ASV) using mercury-film electrode (MFE) has been developed, which is based on the determination of residual cadmium ion after reaction of Cd2+ with S2−. The linear range is adjustable depending on Cd2+ concentration, for example, the determination of S2− can be achieved in the range of 1.5–7.0 \times 10^{-6} \text{mol L}^{-1} by selecting 3.0 \times 10^{-6} \text{mol L}^{-1} Cd2+. The detection limit is 1.3 \times 10^{-8} \text{mol L}^{-1} under optimum conditions, and the relative standard deviation (RSD, n = 10) for 2.0 \times 10^{-6} \text{mol L}^{-1} S2− is 0.7%. Compared with other methods, this method has the following prominent advantages: with low detection limit, easy to operate and less interference. The proposed method has been successfully applied to the determination of S2− in synthetic wastewater, lake water, beverage, spring water and real wastewater samples.

Introduction

Sulfide is an anion found widely in both natural and waste waters, and it is one of the most important parameters to monitor in water due to its high toxicity for aquatic organisms. The toxicity of sulfide is attributed to the releasing of hydrogen sulfide (H2S). At a low concentration, H2S can produce personal distress, while at a higher concentration, it can result in loss of consciousness, permanent brain damage or even death through asphyxiation. In addition, hydrogen sulfide controls the bioavailability of heavy metals in anoxic environments. The sulfide concentrations are generally very low in real water samples, especially in sediment pore waters. Thus, it is very important to develop a highly sensitive and rapid method for sulfide determination.

Various methods have been developed for the determination of sulfide. They include spectrophotometric, fluorescence, chemiluminescence, inductively coupled plasma-atomic emission spectrometry (ICP-AES), atomic absorption spectrometry (AAS), flow injection analysis (FIA), ion chromatography, electrochemical methods and so on. However, the determination methods frequently used either have a relative high detection limit, low accuracy and precision, and poor selectivity or are time-consuming, cumbersome to operate, costly and need large-scale equipment. Classical spectrophotometric methods lack sensitivity. ICP-AES can be used for sulfide determination, but polyatomic oxygen ions greatly interfere with sulfur isotopes. Wardencki reviewed the problems encountered in the determination of sulfur compounds by gas chromatography. Methylene blue (MB) method plays a great role in the spectroscopic determination of sulfide, and the detection limit can be improved when combined with a smart multisyringe flow injection system. The nanomolar levels of sulfide can be measured when the MB generated was determined by a solid-phase extraction technique coupled with HPLC. Recently, our group presented a knotted reactor (KR) coupled with hydride generation atomic fluorescence spectrometry used for the indirect determination of sulfide, and the detection limit can be down to 1.6 \times 10^{-9} \text{mol L}^{-1}.

Compared with other methods, electrochemical methods possess some unique and distinct advantages: rapidity, cheap instrumentation, high sensitivity and a simple operation procedure. In particular, they have promising in situ applications, which is important for environmental monitoring. Generally, the determination of sulfide includes direct and indirect approaches. The direct determination methods involve cathodic stripping voltammetry (CSV) on mercury electrode, the electro-catalytic oxidation of sulfide on bare electrodes or modified electrodes, and so on. The indirect determination methods include several principles, such as electrochemically initiated reaction of sulfide with N,N-dimethylphenylene-1,4-diamine, and N,N-diphenyl-p-phenylenediamine, indirect determination of sulfide by measuring As(III) after reaction, and so on. Cadmium ion selective electrode can be used for sulfide determination, however, the sensitivity is low. Several inhibition biosensors and carbon nanotube (CNT) modified glassy carbon electrodes for sulfide determination have been developed. Now, it remains a challenge for trace/ultra-trace sulfide determination in a complex matrix. Thus, it is very important to develop a more rapid and sensitive determination method for sulfide. Currently, the successfully used electrodes are MFE, which has various advantages such as high surface area/volume ratio, resulting in a higher concentration of amalgam during the

†Electronic supplementary information (ESI) available: Table S1: The basic water quality parameters in various water samples. See DOI: 10.1039/b9ay00183b
deposition. In addition, MFE has a high mechanical resistance and remains stable under vigorous stirring or can be coupled with flow systems.\textsuperscript{51,52} In this paper, an indirect method for sulfide determination was developed based on the sensitive response of MFE to Cd\textsuperscript{2+}, this method has been successfully applied to the determination of sulfide in synthetic wastewater, lake water, beverage, spring water and real wastewater samples.

Experimental

Chemicals and instrumentation

An Autolab PGSTAT 302 (Metrohm China Ltd.) instrument was used for anodic stripping voltammetry (ASV). A three-electrode cell consisting of a bare glassy carbon disk working electrode (4 mm diameter) or a mercury-film glassy carbon working electrode, a saturated calomel reference electrode (SCE) and a platinum wire counter electrode was used for electro-chemical measurements. ICP-AES J-A1100 (Jarrell-Ash, America) was used for the determination of heavy metals and other elements in beverage and different spiked water matrices. An ultraviolet spectrophotometer UV-3600 (Shimadzu, Japan) was used for methylene blue (MB) method determination. The pH values were measured with a PHSJ-4A pH meter (Shanghai, China). All potentials are reported vs. the SCE. The GPES software (Metrohm China Ltd.) was used to control the instrument and to perform preliminary data processing.

All chemicals were at least of analytical grade and were purchased from Shanghai Chemicals Co., Ltd. (Shanghai, China) unless otherwise stated. All aqueous solutions were prepared in doubly quartz deionized water (DDW). The stock standard solution of inorganic mercury (1000 mg L\textsuperscript{-1}) was prepared with mercuric nitrate.\textsuperscript{53} The stock standard solution of cadmium ion (1000 mg L\textsuperscript{-1}) was prepared with cadmium chloride.\textsuperscript{53} The stock standard solution of sulfide (1000 mg L\textsuperscript{-1}) was prepared daily by dissolving the appropriate amount of crystal Na\textsubscript{2}S\cdot9H\textsubscript{2}O and diluting it to volume with DDW.\textsuperscript{54} For the MB method,\textsuperscript{55} 0.2\% (m/v) \(N_2N\)-dimethyl-\(p\)-phenylenediamine hydrochloride and 12.5\% (m/v) NH\textsubscript{4}Fe(SO\textsubscript{4})\textsubscript{2} were prepared by dissolving the proper quantity in 20\% (v/v) and 2.5\% (v/v) H\textsubscript{2}SO\textsubscript{4}, respectively.

Preparation of the MFE

Prior to use, the glassy carbon electrode was polished under clean conditions using a series of alumina slurried (1.0, 0.3 and 0.05 mm) in water, following this, they were rinsed twice with distilled water and sonicated in a water bath for 10 min. The MFE was prepared under the condition of \(-1.3\) V for 60 s in 0.1 mol L\textsuperscript{-1} hydrochloric acid containing 25 mg L\textsuperscript{-1} Hg\textsuperscript{2+} after deaerating this solution with a flow of nitrogen for 15 min.\textsuperscript{56} After this, the electrode was treated in 1 mol L\textsuperscript{-1} pH 4.5 sodium acetate by repetitive scanning in the potential range of \(-1.0\) and \(-0.5\) V for 90 cycles at a scan rate of 100 mV s\textsuperscript{-1}.

Sample pretreatment

The synthetic wastewater samples\textsuperscript{54} were prepared to contain (mg L\textsuperscript{-1} in parentheses) phenol (500), CH\textsubscript{3}COONa (500), NaCl (500), KC\textsubscript{1} (500), CaCl\textsubscript{2} (500), KSCN (500), Na\textsubscript{2}CO\textsubscript{3} (500), and (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} (150), in addition to sulfide with the concentration of 1.0, 2.0 and \(5.0 \times 10^{-4}\) mol L\textsuperscript{-1}. The beverage and spring water samples were purchased from the market. Lake water samples were collected locally. Wastewater sample was collected from a sewage treatment plant. After sampling, lake waters and wastewater samples were filtered through a 0.45 \(\mu\)m membrane immediately and determined at once.\textsuperscript{9} The basic water quality parameters are shown in Table S1 (Supporting Information).\textsuperscript{†} For MB method determination,\textsuperscript{56} to a 50 mL flask containing water samples, 1 mL 0.2\% (m/v) \(N_2N\)-dimethyl-\(p\)-phenylenediamine hydrochloride and 0.5 mL 12.5\% (m/v) NH\textsubscript{4}Fe(SO\textsubscript{4})\textsubscript{2} were added, shaken, equilibrated for 10 min, then diluted to 50 mL, and measured at 665 nm by a UV-Vis method.

Results and discussion

The basic principle for indirect determination of sulfide by ASV

The basic principle for sulfide determination by ASV is based on the selective precipitation reaction between Cd\textsuperscript{2+} and S\textsubsuperscript{2-} to form CdS. Cd\textsuperscript{2+} can be determined by ASV using the sensitive response of MFE to Cd\textsuperscript{2+}. Therefore, S\textsubsuperscript{2-} concentration can be calculated by determining the Cd\textsuperscript{2+}. The theoretical formula is derived as follows:

The ASV formula\textsuperscript{57} is shown as eqn (1):

$$i_p = knD_{ox}^{3/2} \eta^{-1/6} AvtC_{ox}$$  \hspace{1cm} (1)

In which \(n\) is number of electrons, \(D_{ox}\) is diffusion coefficient, \(\omega\) is stirring speed, \(\eta\) is viscosity of solution, \(A\) is electrode area, \(v\) is scan rate, \(t\) is deposition time and \(C_{ox}\) is initial concentration.

Step I: Cd\textsuperscript{2+} response with absence of S\textsubsuperscript{2-}. 25 mL 0.1 mol L\textsuperscript{-1} pH 4.0 NaAc-HAc containing certain amount of Cd\textsuperscript{2+} were added into a electrolyte cell, and the linear sweep curve was recorded after deposition 120 s under the condition of \(-1.3\) V of preconditioning potential. Then a certain amount of Cd\textsuperscript{2+} was added into the cell and repeated the above procedure, and a linear sweep curve was recorded. Then a certain amount of S\textsubsuperscript{2-} was added into the cell, and the corresponding linear sweep curve was recorded again after reacting for 2 min under stirring conditions. The concentration of S\textsubsuperscript{2-} was calculated through the peak current difference of Cd\textsuperscript{2+} in the absence and presence of S\textsubsuperscript{2-}. The data treatment was performed with Excel 2003 and Origin 6.0 software.
the unique form (There are three forms including S\textsuperscript{2–}, HS\textsuperscript{−} and H\textsubscript{2}S) in solution at pH 4.0, thus, the linear relationship with experimental results, as shown in Fig. 1. 

The ASV responses of Cd\textsuperscript{2+} reaction system changed with the Cd\textsuperscript{2+} content (There are three forms including S\textsuperscript{2–}, HS\textsuperscript{−} and H\textsubscript{2}S) in solution at pH 4.0, thus, the linear relationship with experimental results, as shown in Fig. 1. 

The main parameters affecting the system containing the pH of buffer and reaction time \(t\). The experiments results showed that 120 s was the most proper value for \(t\). 

\[
\Delta_{Ip,Cd^{2+}} = \gamma KC^{*}_{S2–}
\]

The linear range for sulfide determination can be extended according to different determination requirements by selecting different concentrations of Cd\textsuperscript{2+}, and the corresponding results are shown in Table 1.

Optimization of experimental parameters

The main parameters affecting the system containing the pH of the buffer and reaction time \(t\) were investigated. (a) The pH of the buffer: the acidity of the solution was controlled by adjusting the pH of buffer solution. \(58,59\) The experiments results showed that

Table 1 The characteristics of linear regression equations

<table>
<thead>
<tr>
<th>Cd\textsuperscript{2+} content ((\mu)M)</th>
<th>Regression equation ((C_{S2–}/\mu\text{M}))</th>
<th>Linear range ((\mu)M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.08</td>
<td>(\Delta_{Ip,Cd^{2+}} = 6.47C_{S2–} - 0.05)</td>
<td>0.02–0.22</td>
</tr>
<tr>
<td>0.3</td>
<td>(\Delta_{Ip,Cd^{2+}} = 0.615C_{S2–} - 0.013)</td>
<td>0.3–0.7</td>
</tr>
<tr>
<td>0.8</td>
<td>(\Delta_{Ip,Cd^{2+}} = 2.36C_{S2–} + 0.014)</td>
<td>0.7–1.5</td>
</tr>
<tr>
<td>3.0</td>
<td>(\Delta_{Ip,Cd^{2+}} = 9.77C_{S2–} - 9.32)</td>
<td>1.5–7.0</td>
</tr>
</tbody>
</table>

Practical application

In natural water samples, the concentrations of heavy metals are very low. \(58,59\) Thus, this proposed method can be used for the determination of sulfide in environmental water samples.
determination of S\textsuperscript{2−} in natural water samples. In real water samples containing low levels of heavy metals, this method can be used for the determination of free S\textsuperscript{2−} because heavy metals can react with S\textsuperscript{2−} to form MS precipitate. However, if the concentrations of heavy metals in real water samples are too high, this method will be not suitable. The proposed method has been applied to the determination of S\textsuperscript{2−} in synthetic wastewater, lake water, beverage, spring water and real wastewater samples. (Table S1 in Supporting Information gives the basic water quality parameters.)† Compared with the classical MB method, the results listed in Table 2 demonstrate the validity of the developed method. The analytical results in Table 2 showed that sulfide contents in these water samples were very low.

**Conclusions**

A rapid, sensitive and simple electrochemical method for the indirect determination of trace amount of sulfide was developed. Table 3 is a comparison of this method with other methods reported in recent five years. Compared with other methods, this proposed method has the following prominent advantages: (1) Sensitive, the detection limit of this method for S\textsuperscript{2−} can be reduced to 1.3 \times 10^{-8} \text{ mol L}^{-1}. From Table 3 we can see that only the limit of detection (LOD) of Ref. 12 and 30 is lower than that of this method, but Ref. 30 needs to be combined with flow system. This proposed method is simple and does not require a flow system; (2) Less interference, it does not suffer from

<table>
<thead>
<tr>
<th>Sample</th>
<th>Added (\text{\mu M})</th>
<th>Found (\text{\mu M})</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic waste water 1</td>
<td>1.00</td>
<td>0.93 ± 0.03</td>
<td>93</td>
</tr>
<tr>
<td>Synthetic waste water 2</td>
<td>2.00</td>
<td>2.00 ± 0.01</td>
<td>100</td>
</tr>
<tr>
<td>Synthetic waste water 3</td>
<td>5.00</td>
<td>5.10 ± 0.04</td>
<td>102</td>
</tr>
<tr>
<td>Lake water 1</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Lake water 2</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Lake water 3</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Maidong beverage</td>
<td>0</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>1.00</td>
<td>1.03 ± 0.02</td>
<td>103</td>
<td></td>
</tr>
<tr>
<td>2.00</td>
<td>2.00 ± 0.04</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Nongfu spring water</td>
<td>0</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>1.00</td>
<td>0.99 ± 0.04</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>2.00</td>
<td>2.03 ± 0.05</td>
<td>102</td>
<td></td>
</tr>
<tr>
<td>Wastewater</td>
<td>0</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>1.00</td>
<td>1.04 ± 0.02</td>
<td>104</td>
<td></td>
</tr>
<tr>
<td>2.00</td>
<td>2.02 ± 0.02</td>
<td>101</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) ND means not detected. The sulfide concentrations for lake waters, beverage, nongfu spring water and wastewater samples are also ND by MB method.

**Table 3** Comparison of this method with other methods

<table>
<thead>
<tr>
<th>No.</th>
<th>Principle or method</th>
<th>Sample</th>
<th>Linear range (\text{\mu mol L}^{-1})</th>
<th>LOD (\text{\mu mol L}^{-1})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Indirect determination of S\textsuperscript{2−} by detecting residual Cd\textsuperscript{2+} after reaction of Cd\textsuperscript{2+} with S\textsuperscript{2−} on MFE</td>
<td>Environmental water samples</td>
<td>0.02–0.22</td>
<td>0.013</td>
<td>This work</td>
</tr>
<tr>
<td>2</td>
<td>Stripping chronopotentiometry on macroporous MFE</td>
<td>Waste water</td>
<td>0.16–12.5</td>
<td>0.016</td>
<td>21</td>
</tr>
<tr>
<td>3</td>
<td>An electrocatalytic oxidation of sulfide by ferrocene carboxylate</td>
<td>River water</td>
<td>200–1000</td>
<td>2</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>Electrochemical oxidation of sulfide on Ni powder modified sol−gel CCE</td>
<td>Environmental, biological and industrial samples</td>
<td>10–1000</td>
<td>1.19</td>
<td>29</td>
</tr>
<tr>
<td>5</td>
<td>The electrocatalytic oxidation of sulfide with [Fe(CN)\textsubscript{6}]\textsuperscript{3−} on modified SPE by flow injection analysis</td>
<td>Cigarette smoke, hot spring water</td>
<td>0.1–1000</td>
<td>0.0089</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>Direct electrochemical oxidation of sodium sulfide</td>
<td>River water</td>
<td>5–60</td>
<td>4.9</td>
<td>31</td>
</tr>
<tr>
<td>7</td>
<td>The electrocatalytic reaction of sulfide with ferrocyanide</td>
<td>Aqueous solution</td>
<td>0.04</td>
<td>0.04</td>
<td>32</td>
</tr>
<tr>
<td>8</td>
<td>Electrocatalytic reaction of sulfide with ferrocene sulfonates</td>
<td>Aqueous solution</td>
<td>20–1000</td>
<td>14</td>
<td>33</td>
</tr>
<tr>
<td>9</td>
<td>Electrochemical oxidation of sulfide on nikelate modified SPE</td>
<td>Cigarette smoke</td>
<td>10–1000</td>
<td>0.06</td>
<td>34</td>
</tr>
<tr>
<td>10</td>
<td>Exploring alkylated ferrocene sulfonates as electrocatalysts for sulfide</td>
<td>Aqueous solution</td>
<td>0–14</td>
<td>0.4</td>
<td>35</td>
</tr>
<tr>
<td>11</td>
<td>Indirect determination of sulfide by measuring As(III) on Au nanoparticles modified SPE</td>
<td>Acid rain and hot spring water</td>
<td>0.04–700</td>
<td>0.04</td>
<td>41</td>
</tr>
<tr>
<td>12</td>
<td>The inhibitory effect of sulfide on horseradish peroxidase</td>
<td>Waste water</td>
<td>0.1–3.85</td>
<td>0.05</td>
<td>44</td>
</tr>
<tr>
<td>13</td>
<td>Electrogenenerated superoxide ion react with sulfide ion using ECL on CNTs-modified electrode</td>
<td>Environmental water samples</td>
<td>0.0006–0.01</td>
<td>0.0002</td>
<td>12</td>
</tr>
<tr>
<td>14</td>
<td>Bi-film gold disk electrode by CSV</td>
<td>Seawater</td>
<td>1</td>
<td>1</td>
<td>60</td>
</tr>
</tbody>
</table>

\(^a\) GCE: glassy carbon electrode; CCE: carbon ceramic electrode; HMDE: hanging mercury drop electrode; SPE: screen-printed electrode; MWCNTs: multi-wall carbon nanotubes; ECL: electrogeminated chemiluminescence.
interference by the common cations and anions in water samples. Generally, ECL is easy to suffer from interference; (3) Easy to operate, the MFE is easy to prepare and has good reproducibility. Coupled with FIA-KR technique, the LOD can be reduced and we anticipate the development of some simple and portable electrochemical sensors for detecting sulfide in environmental water samples.

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