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Bismuth Film Electrodes for Indirect Determination of Sulfide Ion in Water Samples at Trace Level by Anodic Stripping Voltammetry

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In this paper, the analytical applications of bismuth film electrodes (BiEFs) are summarized in recent years. Using BiEFs as working electrode, an indirect determination method for sulfide in water samples by anodic stripping voltammetry (ASV) is established, based on the determination of residual Cd^{2+} after reacting with S^{2-}. Under the optimal experimental conditions (0.1 mol L^{-1} pH 4.5 NaAc-HAc, $C_{Cd2+} = 3.6 \times 10^{-6}$ mol L^{-1}, deposition potential $E_d = -1.2$ V, and reaction time $t_R = 120$ s), the determination of S^{2-} can be achieved in the range of $(0.7–5.0) \times 10^{-6}$ mol L^{-1} with a detection limit (DL) of 2.1×10^{-7} mol L^{-1} and a relative standard deviation (RSD, n=10) of 3.6% for 1.7×10^{-6} mol L^{-1} S^{2-}. Compared with the previously proposed methods, this method can eliminate the interferences such as Br^-, SCN^-, PO_4^{3-}, CO_3^{2-}, NO_2^-, Al(III) and Fe(II) efficiently. In addition, the proposed method possesses the distinct advantages of cheap instrument and simple manipulation. It has been successfully applied to the determination of S^{2-} in different spiked water matrices (mineral water, lake water, synthetic wastewater and real wastewater) with recoveries ranging from 95 to 106%.

Keywords: Anodic stripping voltammetry; BiFEs; indirect determination; sulfide; water

1. INTRODUCTION

Sulfide, widely found in natural water and wastewater samples, is a very important pollution index due to its high toxicity for aquatic organisms and human beings [1,2]. It comes from a variety of sources, such as the activities of industry and agriculture [3], sediment pore water containing high levels of sulfide. The discharges of sulfide have vital influences on environment [4,5]. The toxicity of sulfide lies in that it can release hydrogen sulfide (H_2S)-a foul-smelling, corrosive, flammable, and deadly gas [3]. As a cellular poison, sulfide can deactivate aerobic respiration and result in death through asphyxiation [6]. Thus, the determination of sulfide is important particularly from environmental and biological point of view [2-5].

Several methods have been developed for the determination of S^{2-} based on the different analytical principles [7-15]. A review for the analytical strategy of sulfide has been published [16]. The electrochemical methods [17-30] possess distinct advantages of high sensitivity, rapidity, cheap instrumentation and a simple operation procedure. The determination methods of sulfide involve direct and indirect approaches, and the determination principles frequently used include cathodic stripping voltammetry (CSV) [17,18], the electro-catalytic oxidation of sulfide [19-23], electrochemically initiated reaction of sulfide with N,N-diphenyl-p-phenylenediamine [24] or N,N-dimethyl- phenylene-1,4-diamine [25,26], indirect determination of sulfide by measuring As(III) after reaction [27], inhibition biosensors [28,29] and cadmium ion selective electrode [30], *etc*.

At present, the most successfully used electrodes are mercury electrodes, which have many advantages such as high surface area/volume ratio, high sensitivity, good reproducibility and renewability [31]. However, with the enhanced awareness of environmental protection, the applications of mercury electrodes were reduced due to their high toxicities, and bismuth film electrodes (BiFEs) have become an attractive subject for electroanalytical research during the last decade as a substitute for mercury film electrodes in stripping voltammetry [32]. BiFEs maintain all the advantages of mercury-film electrode (MFE) and the toxicities of bismuth and its salts are negligible [33]. According to the determination objects, the developments of stripping analysis at BiFEs can be divided three kinds: heavy metal ions [34-50], inorganic anions [51] and organic pollutants [52-57], respectively. The most wide applications of BiFEs are the determination of heavy metal ions, such as As(III) [34]), Cd(II) [35-42], Cr(III) [43], Cr(VI) [43], Co(II) [44-46], Cu(II) [47], Ni(II) [45,46], Pb(II) [36-42,48], Sn [49], Tl (I) [50], Zn(II) [41,42], and so on. Wang [58] reviewed the development, behavior, scope and prospects of bismuth film electrodes for stripping analysis of trace metals before 2005. Economou [59] introduced BiFEs, including the substrate materials, the methods of forming the bismuth film and cleaning the electrodes, detection techniques, interferences and potential target analytes. Švancara et al. [60] reviewed the application of BiFEs for anodic stripping voltammetric analysis mixtures of heavy metals before 2006. However, the applications of BiEFs to the determination of inorganic anions are few, such as silicic acid [51]. In recent years, the BiFEs are also applied to the determination of organic compounds, such as paraquat [52], herbicides [53], methyl parathion [54], acetamiprid [55], imidacloprid [55], sulfadiazine [56], nitrobenzene [57] etc. Summaries of the determination applications for BiFEs in aqueous solution after 2005 are shown in Table 1.

In this paper, an indirect method for sulfide determination at trace level was developed based on the sensitive response of BiFEs to Cd^{2+} and the high stability of CdS precipitate. It has been applied to the determination of S^{2-} in synthetic wastewater and real water samples, and satisfactory results were obtained.

Table 1. Summary of the determination applications for BiFEs in aqueous solution after 2005.

No.	Object	Linear range (mol L^{-1})	DL (mol L^{-1})	Ref.
	Heavy metal ions			
1	As(III)	1.3×10^{-10}–1.3×10^{-8}	9.3×10^{-12}	[34]
2	Cd(II)		2.2×10^{-5}	[35]
3	Cd(II)	$50.\times10^{-7}$–1.0×10^{-4}		[36]
4	Cd(II)	8.9×10^{-8}–8.9×10^{-7}	1.2×10^{-8}	[37]
5	Cd(II)		4.4×10^{-9}	[38]
6	Cd(II)	8.9×10^{-8}–8.9×10^{-7}	1.1×10^{-8}	[39]
7	Cd(II)	1.8×10^{-7}–9.0×10^{-6}	1.3×10^{-8}	[40]
8	Cd(II)	5.0×10^{-8}–3.5×10^{-7}	7.3×10^{-10}	[41]
9	Cd(II)		3.1×10^{-8}	[42]
10	Cr(III)		3.4×10^{-10}	[43]
11	Cr(VI)		4.1×10^{-10}	[43]
12	Co(II)	2.0×10^{-10}–2.0×10^{-8}	1.8×10^{-11}	[44]
13	Co(II)	3.3×10^{-9}–3.3×10^{-8}	1.2×10^{-9}	[45]
14	Co(II)	1.7×10^{-8}–3.4×10^{-7}		[46]
15	Cu(II)	3.1×10^{-8}–7.9×10^{-6}	2.2×10^{-8}	[47]
16	Ni(II)		1.5×10^{-9}	[45]
17	Ni(II)	1.7×10^{-8}–3.4×10^{-7}		[46]
18	Pb(II)	$50.\times10^{-7}$–1.0×10^{-4}		[36]
19	Pb(II)	4.8×10^{-8}–4.8×10^{-7}	3.3×10^{-8}	[37]
20	Pb(II)		2.0×10^{-9}	[38]
21	Pb(II)	4.8×10^{-8}–4.8×10^{-7}	4.3×10^{-9}	[39]
22	Pb(II)	9.7×10^{-8}–4.8×10^{-7}	1.1×10^{-8}	[40]
23	Pb(II)	2.0×10^{-8}–2.0×10^{-7}	7.9×10^{-10}	[41]
24	Pb(II)		2.4×10^{-9}	[42]
25	Pb(II)	6.3×10^{-9}–9.7×10^{-8}	3.9×10^{-9}	[48]
26	Sn	8.4×10^{-9}–8.4×10^{-7}	2.2×10^{-9}	[49]
27	Tl(I)		1.1×10^{-8}	[50]
28	Zn(II)	4.0×10^{-8}–6.0×10^{-7}	1.3×10^{-9}	[41]
29	Zn(II)		6.0×10^{-8}	[42]
	Inorganic anions			
30	Silicic acid	6.4×10^{-7}–4.0×10^{-4}	2.6×10^{-8}	[51]
	Organic compounds			
31	Paraquat	6.6×10^{-7}–4.8×10^{-5}	9.3×10^{-8}	[52]
32	Herbicides	1.0×10^{-5}–2.0×10^{-4}	6.0×10^{-6}	[53]
33	Methyl parathion	1.1×10^{-8}–3.8×10^{-7}	4.6×10^{-9}	[54]
34	Acetamiprid	1.3×10^{-5}–2.1×10^{-4}	4.0×10^{-6}	[55]
35	Imidacloprid	9.5×10^{-6}–2.0×10^{-4}	2.9×10^{-6}	[55]
36	Sulfadiazine	3.2×10^{-6}–9.7×10^{-5}	2.1×10^{-6}	[56]
37	Nitrobenzene	1.0×10^{-6}–1.0×10^{-4}	8.3×10^{-7}	[57]

2. EXPERIMENTAL

2.1. Chemicals and instrumentation

Anodic stripping voltammetry (ASV) was performed on an Autolab PGSTAT 302 (Metrohm China Ltd.) instrument. Three–electrode system was used for the electrochemical experiment, containing a bismuth-film glassy carbon electrode (3 mm diameter for bare glassy carbon electrode), a saturated calomel reference electrode (SCE) and a platinum wire counter electrode, respectively. The UV-3600 Ultraviolet Spectrophotometer (Shimadzu, Japan) was used for methylene blue (MB) method determination. ICP-AES (J-A1100, Jarrell-Ash, America) was used for the determination of heavy metals and other elements in different water matrices. The pH values were measured with a PHSJ-4A pH meter (Shanghai, China).

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. The stock standard solution of Bi^{3+} (1000 mg L^{-1}) and Cd^{2+} (1000 mg L^{-1}) were prepared as the literature reports [61]. The stock standard solution of sulfide (1000 mg L^{-1}) was prepared daily by dissolving the appropriate amount of crystal $Na_2S{\cdot}9H_2O$ and diluting it to volume with water [61]. 0.1 mol L^{-1} and 1 mol L^{-1} pH 4.5 acetate was prepared with certain amount of CH_3COOH and CH_3COONa. For the MB method [7], 0.2% (m/v) N,N-dimethyl-p-phenylene-diaminehydrochloride and 12.5% (m/v) $NH_4Fe(SO_4)_2$ were prepared by dissolving the proper quantity of corresponding chemicals in 20% (v/v) and 2.5% (v/v) H_2SO_4, respectively.

2.2. Preparation of the BiFEs

The glassy carbon electrode was polished to a mirror finish using a BAS-polishing kit with 1.0, 0.3 and 0.05 μm alumina slurry, then rinsed with water and sonicated in a water bath for 10 min. The BiFE was prepared under the condition of –0.8 V for 240 s in 0.1 mol L^{-1} pH 4.5 NaAc-HAc containing 100 mg L^{-1} Bi^{3+} [32]. After deposition, the electrode was treated in 1 mol L^{-1} pH 4.5 NaAc-HAc by repetitive scanning in the potential range of –1.0 and –0.5 V for 90 cycles and then 0.1 mol L^{-1} pH 4.5 NaAc-HAc in the same potential range until a stable background was obtained at a scan rate of 100 mV s^{-1}.

2.3. Sample preparation

The synthetic wastewater samples [61] were prepared to contain (mg L^{-1} in parentheses) phenol (500), CH_3COONa (500), NaCl (500), KC1 (500), $CaCl_2$ (500), KSCN (500), Na_2CO_3 (500), and $(NH_4)_2SO_4$ (150), in the presence of sulfide with the concentration of 3.0, 6.0 and 12 × 10^{-6} mol L^{-1}, respectively. Mineral waters were purchased from market. Lake water samples were collected locally.

Wastewater samples were collected from sewage treatment plant. After sampling, lake water and wastewater samples were filtered through a 0.45 μm membrane immediately and determined at once [7]. For MB methods, after adding water samples, 0.2% (m/v) N,N-dimethyl-p-phenylenedi-aminehydrochloride and 0.5 mL 12.5% (m/v) $NH_4Fe(SO_4)_2$ were added to a volumetric flask of 50 mL, diluted to 50 mL, then the solution shaken and balanced for 10 min, followed by measuring at 665 nm by UV-3600 ultraviolet spectrophotometer. All experiments were performed at room temperature (25 ± 1 ºC)

2.4. Procedure

There are two steps for the operation: (I) Cd^{2+} response without S^{2-}. 25 mL of 0.1 mol L^{-1} pH 4.5 NaAc-HAc containing certain amount of Cd^{2+} was added into an electrolyte cell and the linear sweep curve was recorded between –1.0 and –0.5 V after deposition 120 s under the preconcentration potential of –1.2 V under stirring condition; (II) S^{2-} determination. Then a certain amount of S^{2-} was added into above solution, and the linear sweep curve was recorded again under the same conditions.

3. RESULTS AND DISCUSSION

The principle for sulfide determination by ASV is based on the selective reaction between Cd^{2+} and S^{2-} to form CdS precipitate, and the residual Cd^{2+} can be determinated by ASV using the sensitive response of BiFE to Cd^{2+}. The ASV formula eq (1) on MFE was then used to represent the Cd^{2+} current $i_{\mathrm{pCd}^{2+}}$ on BiFE [62]. The peak current of Cd^{2+} ($i_{\mathrm{pCd}^{2+}}$) without S^{2-} can be shown using eq (1). After adding S^{2-}, the peak current of residual Cd^{2+} ($i'_{\mathrm{pCd}^{2+}}$) can be expressed by eq (2). Then the concentration of S^{2-} can be calculated through the difference ($⊿ i_{\mathrm{pCd}^{2+}}$) between eq (1) and eq (2), as shown in eqs (3) and (4).

$$i_{\mathrm{pCd}^{2+}} = \frac{4F^2 vlA}{2.73RT} C^*{}_{\mathrm{Cd}^{2+}} \qquad (1)$$

$$i'_{\mathrm{pCd}^{2+}} = \frac{4F^2 vlA}{2.73RT} (C^*{}_{\mathrm{Cd}^{2+}} - \gamma C^*{}_{\mathrm{S}^{2-}}) \qquad (2)$$

$$\Delta i_{\mathrm{pCd}^{2+}} = i_{\mathrm{pCd}^{2+}} - i'_{\mathrm{pCd}^{2+}} = \frac{4F^2 lA}{2.73RT} \gamma C^*{}_{\mathrm{S}^{2-}} \qquad (3)$$

Let $K = \frac{4F^2 vlA}{2.73RT}$, $⊿ i_{\mathrm{pCd}^{2+}}$ can be expressed by eq (4):

$$\Delta i_{\mathrm{pCd}^{2+}} = \gamma K C^{*}_{\mathrm{S}^{2-}} \qquad (4)$$

$C_{\mathrm{Cd2+}}$ represents the concentration of Cd^{2+}; $C^{*}_{\mathrm{S}^{2-}}$ represents the concentration of S^{2-} added, F is Faraday constant; v indicates scan rate; l is the thickness of membrane on electrode surface; A is the electrode area; R represents gas constant and T indicates the temperature, respectively. In real water samples, if other ion species do not interfere, these equations will be valid, and they are the fundamental principle for indirect determination of S^{2-} by BiFEs.

In 0.1 mol L^{-1} pH 4.5 NaAc-HAc, the stoichiometric ratio for the actual reaction between S^{2-} and Cd^{2+} is less than 1 because S^{2-} is not the only form in the above solution (Total sulfide is the sum of $\mathrm{H_2S}$, HS^{-} and S^{2-}), and the amount of S^{2-} reacted with Cd^{2+} is partial of total sulfide. Also, under such a pH 4.5 condition, the reaction could not progress entirely due to the reaction kinetics, which also cause only a part of sulfide participated in the form of CdS precipitation. Thus, a reaction coefficient γ should be introduced into the equations, namely $C'_{\mathrm{Cd}^{2+}}$ is equal to $\gamma C^{*}_{\mathrm{S}^{2-}}$, indicating that the added S^{2-} does not all react with Cd^{2+}. Also, under such a pH condition, the reaction could not progress entirely due to the reaction kinetic reasons, which also cause only a part of sulfide participated in the form of CdS precipitation. Thus, a reaction coefficient γ should be introduced into the equations, namely $C'_{\mathrm{Cd}^{2+}}$ is equal to $\gamma C^{*}_{\mathrm{S}^{2-}}$, indicating that the added S^{2-} does not all react with Cd^{2+}. Under certain conditions, the value of γ is constant, and $\Delta i_{\mathrm{pCd}^{2+}}$ is linear relationship with $C^{*}_{\mathrm{S}^{2-}}$, which is consistent with the experimental results (Fig.1).

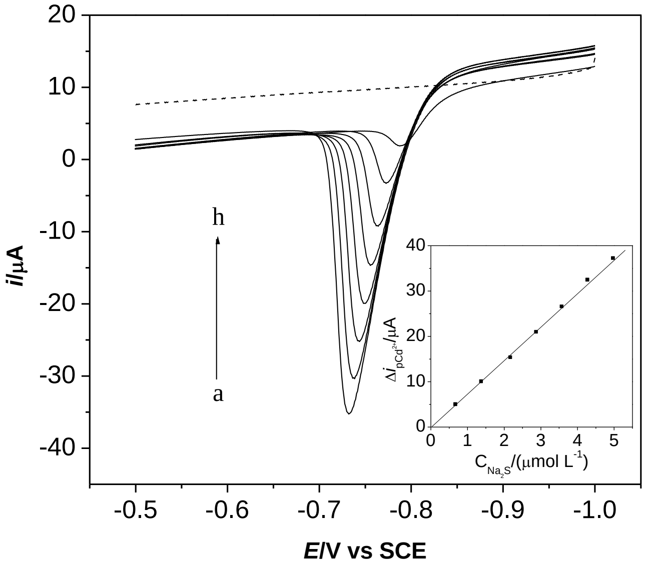

Figure 1. The ASV responses of Cd^{2+} changed with the addition of sulfide. 0.1 mol L^{-1} pH 4.5 NaAc-HAc (-----base line) buffer solution at 3.6 × 10^{-6} mol L^{-1} Cd^{2+}; a → h: $C^{*}_{\mathrm{S}^{2-}}$ = 0, 0.7, 1.4, 2.2, 2.9, 3.6, 4.3, 5.0 × 10^{-6} mol L^{-1} S^{2-}. $E_{\mathrm{d}} = -1.2$ V; $t_{\mathrm{R}} = 120$ s; $v = 100$ mV s^{-1}. Inset: plot of the relationship between the peak current of Cd^{2+} and the concentration of sulfide added.

3.2. Optimization of experimental parameters, relative standard deviation and detection limit

The main parameters including Cd^{2+} concentration C_{Cd2+}, buffer pH, reaction time t_R, and deposition potential E_d were investigated. Fig.2 indicates the optimal conditions are: $C_{Cd^{2+}} = 3.6 \times 10^{-6}$ mol L^{-1}, pH = 4.5, $E_d = -1.2$ V and $t_R = 120$. Under the optimum conditions, the relative standard deviation (RSD) (n = 10) for 1.7×10^{-6} mol L^{-1} S^{2-} is 3.6% (at 3.6×10^{-6} mol L^{-1} Cd^{2+}), which indicates that the BiFEs show good reproducibility. The detection limit (3σ) of this method for S^{2-} is 2.1×10^{-7} mol L^{-1} calculated as 3σ blank [63]. The linear range is 0.7×10^{-6}–5.0×10^{-6} mol L^{-1} S^{2-}.

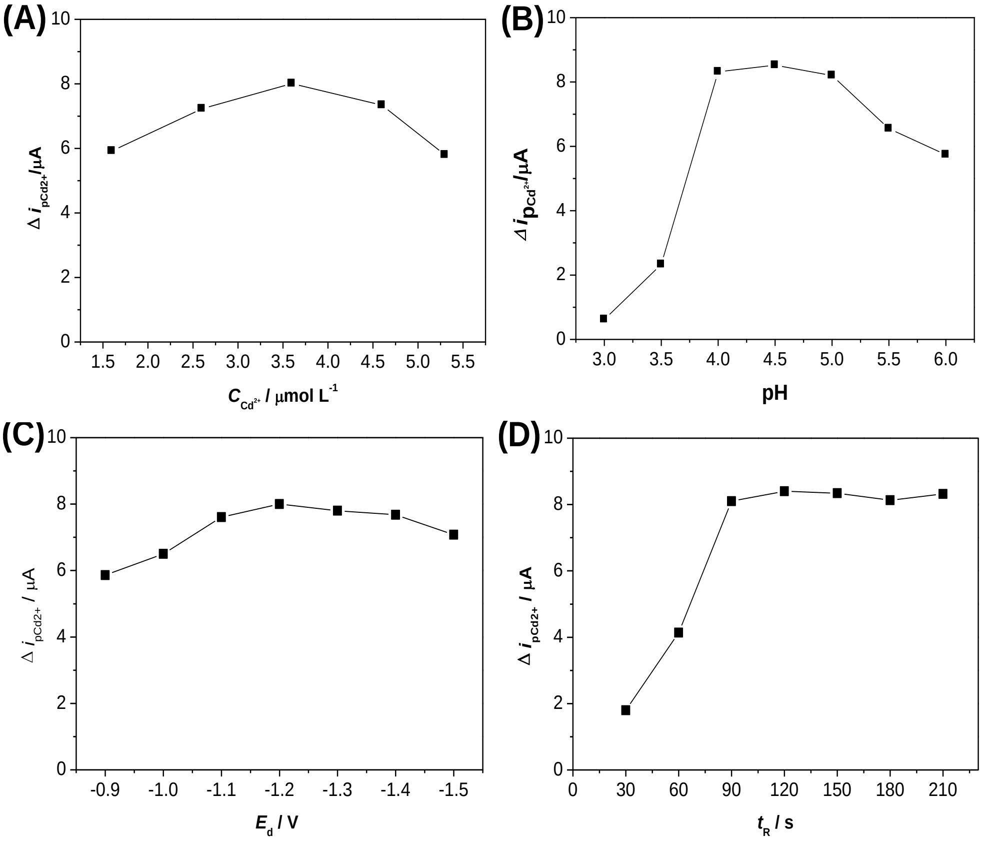

Figure 2. Effects of important parameters on Δi_{pCd2+} at 1.0×10^{-6} mol L^{-1} S^{2-}. (A) C_{Cd2+}; (B) pH; (C) E_d; (D) t_R. Other conditions are shown in Fig. 1.

3.3. Practical analysis of S^{2-} in various water samples

The possible interference from environmental matrix components on the determination of S^{2-} was studied. 2.0×10^{-6} mol L^{-1} S^{2-} (at 3.6×10^{-6} mol L^{-1} Cd^{2+}) both in the presence of various ions and in their absence was detected. The tolerance ratios ($C_{ion}/C_{sulfide}$) are shown in Table 2 as the interferent concentrations affecting the analyte signal by ± 10%.

Table 2. Investigation of potential interferences in the determination of sulfide at 2.0×10^{-6} mol L^{-1} concentration and comparison with literature reports (interferent/sulfide ratio).

SO_4^{2-}	$S_2O_3^{2-}$	SO_3^{2-}	I^-	Br^-	F^-	Cl^-	NO_3^-	SCN^-	CO_3^{2-}	PO_4^{3-}	NO_2^-	CN^-	Ref.
2000	15	2000	50	200	2000	2000	2000	1200	5000	5000	2000		This work
200	133	133	33	33	33		200	33			133	5	[6]
250	250	1000	1000	500	500	5000	5000	2500	5000	3000	500		[7]
1428	1428	Interfered	1428	1428	1428	1428	1428	1428	1428	1428		1428	[63]
100		10	200	100	100		100	10	100	100			[64]
400	400					400	400	400		400	400	50	[65]
Zn(II)	Ca(II)	Mg(II)	K(I)	Na(I)	Al(III)	Cu(II)	Ni(II)	Pb(II)	Ag(I)	Fe(III)	Fe(II)		
4	2000	2000	2000	5000	3000	<0.05	<0.05	0.5	1	90	150		This work
	200	200	200	200		200	200	200	33	200	200		[6]
500	250	500	2500	5000	500	500	500		75	500	250		[7]
	1428	1428	1428	1428	143	14	143	1.4	1.4	286	286		[63]
10	100	100	100	100	10	10	10			10			[64]
50	400	400	400	400		0.8	400		10	10			[65]

Table 3. The basic water quality parameters of spiked water matrices by ICP-AES (mg L^{-1})*.

	Binglu mineral water	Quechao mineral water	Nongfu spring water	Wastewater 1 (Alkali tank)	Wastewater 2 (Aerated filter outlet)	Lake water 1	Lake water 2	Lake water 3	Waterworks water	DL
K	3.89	0.20	1.13	1.44	4.66	3.01	2.77	3.51	2.25	0.06
Ca	ND	4.37	14.0	2.04	433	35.2	35.5	31.6	37.6	0.002
Na	1.54	7.68	5.45	2028	1430	15.7	15.2	15.2	14.7	0.005
Mg	3.41	2.10	1.91	ND	29.8	8.61	8.68	8.21	8.77	0.02
Al	ND	ND	ND	1.00	ND	0.08	0.05	0.02	0.15	0.01
Si	0.02	1.39	2.04	20.94	5.38	3.29	3.29	4.01	3.81	0.002
B						0.07		0.07	0.09	0.001
Cu	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.002
Zn	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.002
Pb	ND	ND	ND	ND	ND	ND	ND	0.11	ND	0.02
Cd	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.002
Ni	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.003
Cr	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.002
As	ND	ND	ND	ND	ND					0.02
P	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.02
Co	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.001
Ba	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.001
Fe	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.002
Ti	ND	ND	ND	ND	ND					0.003
Mn	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.005
V	ND	ND	ND	ND	ND					0.001
Mo	ND	ND	ND	ND	ND					0.003

* ICP-AES data are provided by Analytical Center of Nanjing University. DL means the ICP-AES detection limit for different elements.

Compared with other methods [6,64,65], this method can eliminate the interferences such as Br^-, SCN^-, PO_4^{3-}, CO_3^{2-}, NO_2^-, Al^{3+} and Fe^{2+} efficiently.

Table 4. Electrochemical determination of sulfide in real samples and spiked water matrices (n=3)*.

No.	**Samples***	**Added (μmol L^{-1})**	**Found (μmol L^{-1})**	**Recovery (%)**
1	Binglu mineral water	0	ND	
		1.00	0.99 ± 0.02	99
		1.50	1.50 ± 0.04	100
2	Nongfu spring water	0	ND	
		1.00	1.02 ± 0.05	102
		1.50	1.49 ± 0.03	99
3	Quechao mineral water	0	ND	
		1.00	1.04 ± 0.04	104
		1.50	1.48 ± 0.03	99
4*	Synthetic wastewater	0	ND	
		3.00	3.10 ± 0.10	103
		6.00	6.30 ± 0.10	105
		12.0	12.0 ± 0.20	100
5*	Wastewater 1 (Alkali tank)	0	2.50 ± 0.20	
		1.00	3.55 ± 0.01	105
		1.50	3.93 ± 0.03	95
6	Wastewater 2 (Aerated filter outlet)	0	ND	
		1.00	1.04 ± 0.03	104
		1.50	1.51 ± 0.07	101
7	Lake water 1	0	ND	
		1.00	1.01 ± 0.08	101
		1.50	1.54 ± 0.08	103
8	Lake water 2	0	ND	
		1.00	1.06 ± 0.03	106
		1.50	1.50 ± 0.07	100
9	Lake water 3	0	ND	
		1.00	1.00 ± 0.02	100
		1.50	1.48 ± 0.01	99
10	Waterworks water	0	ND	
		1.00	1.01 ± 0.05	101
		1.50	1.49 ± 0.05	99

* ND means not detected.

* For samples 1, 2, 3, 4, 6, 7, 8, 9, 10, the sulfide concentrations for MB method are ND.

* For sample 4, the concentrations are ND, 3.10 ± 0.10, 6.30 ± 0.10 and 12.0 ± 0.20 mol L^{-1} by MB method, respectively, and the electrochemical measurement was performed by diluting 10 times. For sample 5, the concentration of sulfide is 2.50 ± 0.20 mol L^{-1} by MB method, and it was diluted 100 times by both electrochemical and MB method.

The most serious interferences are obviously caused by heavy metal ions which are able to form metal precipitates. However, in natural waters, the levels of heavy metals are very low [66,67]. For real waters containing low concentrations of heavy metals, since heavy metals can react with S^{2-} to form MS precipitate, and they can not coexist in real water samples.

Table 5. Comparison of the proposed method with other methods[*].

No.	Principle or method	Samples	Linear range (mol L^{-1})	DL (mol L^{-1})	Ref.
		Spectrometric methods			
1	FIA-KR-HG-AFS	Natural water, wastewater	3.1×10^{-9}–7.8×10^{-8}	1.6×10^{-9}	[7]
2	VG–ICP–QMS	Natural water, sediment	6.3×10^{-8}–1.6×10^{-5}	6.3×10^{-8}	[8]
3	VG-ICP-AES	Water	1.6×10^{-7}–1.6×10^{-4}	6.3×10^{-8}	[9]
4	ICP-AES	Environmental water samples	1.6×10^{-7}–7.8×10^{-4}	1.6×10^{-7} 1.9×10^{-7}	[10]
5	Kinetic spectrophotometry	Tap water, wastewater, river water	6.3×10^{-7}–1.3×10^{-5}		[11]
		Chromatographic methods			
6	Ion chromatography	Aqueous solution	3.1×10^{-8}–3.1×10^{-3}	3.1×10^{-8}	[12]
7	Methylene blue derivatization then LC–MS analysis of sulfide	Surface and sediment pore water	3.1×10^{-9}–1.5×10^{-5}	1.5×10^{-9}	[13]
		Flow injection methods			
8	Optical fiber sensor for automatic sulfide determination in waters by multisyringe flow injection analysis	Environmental water samples	6.3×10^{-7}–6.3×10^{-6}	9.1×10^{-8}	[4]
9	Multi-syringe flow injection analysis with chemiluminescence detection	Environmental samples	6.3×10^{-7}–6.3×10^{-5}	9.4×10^{-8}	[14]
10	Based on the reaction of sulfide with three aromatic amines	Industrial wastewater	1.6×10^{-6}–9.4×10^{-5}	5.9×10^{-7} 1.6×10^{-6}	[15]
		Electrochemical methods			
11	Indirect determination of S^{2-} by detection residual Cd^{2+} after reaction of Cd^{2+} with S^{2-} on BiFE	Environmental water samples, mineral water, wine	7.0×10^{-7}–5.0×10^{-6}	2.1×10^{-7}	This work
12	Electrocatalytic oxidation of sulfide on nickel powder modified ceramic electrode	Environmental, biological and industrial samples	1.0×10^{-5}–1.0×10^{-3}	1.2×10^{-6}	[68]
13	Indirect determination of S^{2-} on mercury film electrodes		1.5×10^{-6}–7.0×10^{-6}	1.3×10^{-8}	[69]

[*] FIA-KR-HG-AFS: Flow injection on-line sorption in a knotted reactor coupled with hydride generation atomic fluorescence spectrometry; VG-ICP-AES: Vapor generator coupled to an inductively coupled plasma quadrupole mass spectrometer; ICP-AES: Inductively coupled plasma-atomic emission spectroscopy; VG-ICP-QMS: Vapor generator coupled to an inductively coupled plasma quadrupole mass spectromete.

Thus this method can be used for the determination of free S^{2-}. If the concentrations of heavy metals in real water samples are too high, this method will be not suitable.

The applicability of the method was evaluated through the determination of S^{2-} in various water matrices (mineral water, lake water, synthetic wastewater and real wastewater). Samples were immediately analyzed after collection to prevent oxidation of the S^{2-} (Table 3 gives the basic water quality parameters.). The analytical results are shown in Table 4, indicating that sulfide contents in some water samples are very low. The concentration of S^{2-} in alkali tank water is about 2.5×10^{-4} mol L^{-1}, and the results verified well with MB method. While in aerated filter outlet, the level of S^{2-} is very low, and not detected. The recoveries of the samples varied from 95 to 106% for sulfide, indicating the proposed method is reliable.

4. CONCLUSIONS

A rapid, sensitive and simple electrochemical method using BiFEs for S^{2-} determination has been established, which extends the determination applications of BiFEs for anion.

Table 5 is a comparison of this method with other methods reported in recent years. The detection limit of this method is 2.1×10^{-7} mol L^{-1}. For most water samples, this method can meet requirement. Compared with other methods, this approach is less sensitive than some spectrometric methods, but the most prominent advantages are less interference, simplicity, rapidity and less expense.

In addition, it is mercury free and unnecessary to eliminate oxygen. This proposed method has promising applications for batches water samples determination for S^{2-}, which is important for environmental monitoring.

Coupled with various recently developed composites Bi-film electrodes, the detection limit can be reduced and anticipated to develop more simple and portable electrochemical devices for S^{2-} on-line monitoring in environmental waters [70-92].

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