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Electrochemical detection of sulfide

Abstract: Because of its broad usage in industry and medical science, as well as the potential toxicity in the environment, the detection of sulfide, including hydrogen sulfide, metal sulfide and organic sulfide, has long attracted the attention of scientists working in diverse areas. Compared with other detection methods, electrochemical detection represents a highly sensitive, rapid, affordable, and simple technique. In this regard, the main objective of this report is to provide an up-to-date review of the electrochemical detection of sulfide. This review details different electrochemical approaches investigated between 2010 and 2012, together with the development of various electrodes. In addition to the commonly used techniques, such as, anodic stripping voltammetry (ASV), amperometry, cyclic voltammetry (CV), photoelectrochemical methods, and electrochemical detection methods coupled with other devices, have also been discussed, within the context of detection limit, linear detection range, and applicable conditions.

Keywords: amperometry; anodic stripping voltammetry; electrochemical detection; nanomaterials; sulfide.

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Introduction

The broad presence of sulfide in nature, including biological systems, has made the study of sulfide a great interest for chemists (Bineesh et al. 2012), biochemists (Gruhlke and Slusarenko 2012), environmentalists (Sheng et al. 2008, Joseph et al. 2012), mineralogists (Hettmann et al. 2012) and geochemists (Yin et al. 2008). There are two classes of sulfides, i.e., inorganic sulfides and organic sulfides. Many important metals are present in nature combined with sulfur as metal sulfides, such as: cadmium (Ehsan et al. 2012), cobalt (Muchez and Corbella 2012), copper (Zhao and Peng 2012), lead (Yuan et al. 2012b), molybdenum (Belin et al. 1998), nickel (Barnes et al. 2012), zinc (Yao et al. 2012), and iron (Rodriguez et al. 2012). For mineralogists and geochemists, determining the sulfides context is a key to understanding the formation mechanism and the geological processes by which certain ore deposits have formed (Krivolutskaya et al. 2012). For chemical engineers, the sulfide within oil and gas reserves can pose problems throughout the petroleum industry (Tang et al. 2009). The potential hazards faced by workers involved in the processing of sulfide contaminated feedstock has meant that there is a pressing need for the development of fast and sensitive detection technologies (Lawrence et al. 2000). Over the centuries, there has been widespread awareness of the toxicity of sulfide in its liberated hydrogen sulfide (H_2S) form (Evans 1967, Reiffenstein et al. 1992). Even at a low concentration, H_2S can lead to personal distress, while at a higher concentration it can result in loss of consciousness, permanent brain damage or even death due to the neurotoxic effect of the gas (Gunn and Wong 2001).

In the last 10 years, H_2S has also been identified as an important endogenous signaling molecule (Kimura 2002, Benavides et al. 2007), which has provided attractive opportunities for H_2S to be developed into an innovative class of drugs (Martelli et al. 2012, Wang 2012). Moreover, H_2S was discovered as an oxygen sensor in trout gill chemoreceptors, where the balance between constitutive production and oxidation, tightly couples tissue [H_2S] to Po_2 and may provide an exquisitely sensitive, yet simple, O_2 sensor in a variety of tissues (Olson et al. 2008). In addition to inorganic sulfide, organic sulfides, such as biological thiols, play crucial roles in biological systems for their biological activity (Yuan et al. 2012a). In addition, the abnormal levels of sulfide in the human body have been implicated in the etiology of several diseases (Seshadri et al. 2002, Ueland and Vollset 2004).

As a result, the detection of H_2S has gained significant importance within the analytical community, as a consequence of its toxicity, its biological/physiological roles, and its therapeutic potential (Faccenda et al. 2010).

Classical detection methods

In the last four decades, various techniques have been successfully developed to measure sulfide in a variety of media (Table 1), even down to nanomolar concentrations (Lawrence et al. 2000). Since the 1970s, for example, the titration

of sulfide with iodine has become a classical approach to sulfide determination (Khalifa et al. 1979). Unfortunately, the simplicity of this method comes with limitations in terms of sensitivity and selectivity when dealing with real world samples. Then, in the late 1800s, the methylene blue test was developed as the most common approach to the analysis of sulfide (Leggett et al. 1981, Rauh and Hammje 1983). This basic test, which involves the reaction of aqueous sulfide with N,N-dimethylphenyl-1,4-diamine in the presence of a small quantity of ferric ions, giving rise to a characteristic blue coloration, retains significant analytical value today in terms of simplicity, selectivity, and sensitivity (Lawrence et al. 2000). However, the methylene blue method has some limitations due to interferences from photosensitivity, cross-reactivity with nitrogen dioxide, aggregate formation (dimer, trimers or n-mers) leading to deviations from Beer's law, as well as pH artifacts that erroneously affect absorbance readings (Lai et al. 1984, Sidi et al. 1987, Kleemann 1990, Brown et al. 2011). After the 1990s, a number of investigation, such as, UV/visible absorption spectroscopy (Kuban et al. 1992), fluorescence (Spaziani et al. 1997, Eroglu et al. 2000), and HPLC (Tang and Santschi 2000) techniques, led to substantial improvements in sensitivity. For example, with the fluorescence method, the signal is linear over the range 0.75–15.0 mg l^{-1} of injected sulfide, with a limit of detection (LOD) of 0.08 mg l^{-1} injected sulfide when 9.0 M H_2SO_4 is used in the *N,N*-dimethyl-*p*- phenylenediamine (DMPD) carrier stream (Spaziani et al. 1997). Infrared spectroscopy has also been applied to the quasi-direct determination of sulfide (Isoniemi et al. 1999). Over the past decade, a variety of analytical methods for determining sulfides has been reported (Shan et al. 2010). Atomic spectroscopic techniques (Hoppstock and Lippert 1997) and chemiluminescent (Safavi and Karimi 2002) approaches have been investigated in the analysis of reduced sulfur species such as dimethyl sulfide. Spectrophotometric methods still played an important role in the detection of sulfide (Kosyakov et al. 2010, Kumeria et al. 2011). Ion-chromatographic techniques were also developed as a useful method to determine sulfides such as hydrosulfuric acids (Kolotilina and Dolgonosov 2005). In addition, Raman spectroscopy has also been used to measure sulfide. In the Raman studies, methemoglobin was bound to non-functionalized carbon nanotubes. The subsequent addition of H_2S resulted in significant changes to the Raman spectrum of the carbon nanotubes-hemoglobin complexes. These studies suggest that carbon nanotubes-hemoglobin complexes can potentially be utilized as biosensors to measure H_2S in blood (Wu et al. 2008, 2009). More recently, our group introduced a method based on the selective permeability of polydimethylsiloxane (PDMS) to detect free H_2S (Faccenda et al. 2012).

Electrochemical methods

Notably, the above classical methods require complex instrumentation and are time-consuming. The electrochemical methods, by contrast, offer distinct advantages of high sensitivity, rapidity, affordable instrumentation and relatively simpler procedures. As a result, there has been renewed interest in developing new electrochemical methods to determine sulfides, both in the inorganic and organic forms.

Anodic stripping voltammetry

In 2011, Huang and co-workers introduced an indirect determination method for sulfide in water samples by anodic stripping voltammetry (ASV) (Huang et al. 2012). A three-electrode system was used in their electrochemical experiment, utilizing a bismuth-film glassy carbon electrode as the working electrode, saturated calomel as the reference electrodes (SCE), and platinum wire as the counter electrode. There are two steps in the operation. In the first step, the working electrode was deposited for 120 s under a preconcentration potential of -1.2 V, while stirring in 25 ml of 0.1 M pH 4.5 NaAc-HAc (CH_3COONa-CH_3COOH), containing a certain amount of Cd^{2+}. Then, the linear sweep curve between -1.0 V and -0.5 V was performed in the same solution to get the modified working electrode. In the second step, a different amount of S^{2-} was added to the above solution for ASV.

The principle for sulfide determination by ASV is based on the interaction between Cd^{2+} and S^{2-} to form CdS precipitate, therefore, the concentration of sulfide can be determined by the peak current of Cd^{2+}. As can be seen from Figure 1, the peak current of Cd^{2+} decreased while more S^{2-} was added to the solution, and Δ^{2+}_{pCd} has a linear relationship with the concentration of sulfide. This proposed method can determine S^{2-} in the range of $(0.7–5.0)\times10^{-6}$ M (Figure 1) with an LOD of 2.1×10^{-7} M and a relative standard deviation of 3.6% for 1.7×10^{-6} M. The advantages of this method are affordable instruments and simple manipulation. It has been successfully applied to the determination of S^{2-} in different water matrices.

Amperometric method

Amperometry is another attractive technique to obtain sensitive and fast-responsive results. Savizi et al. developed an amperometric inhibition biosensor for the determination of sulfide (Savizi et al. 2012). This biosensor was fabricated by immobilizing coprinus cinereus peroxidase

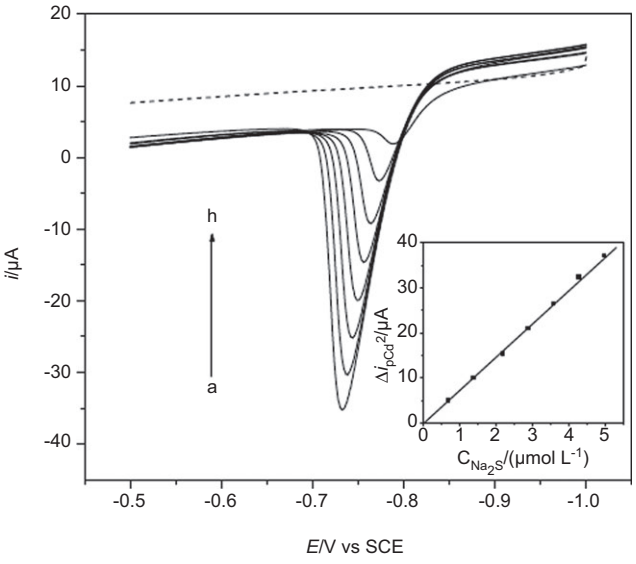

Figure 1 The anodic stripping voltammetry (ASV) response of Cd^{2+} changed with the addition of sulfide. 0.1 M pH 4.5 NaAc-HAc(---base line) buffer solution at 3.6×10^{-6} M; A–H: $C^{*}_{S^{2-}}$ =0, 0.7, 1.4, 2.2, 2.9, 3.6, 4.3, 5.0×10^{-6} M. Insert: plot of the relation between the peak current of Cd^{2+} and the concentration of sulfide added.

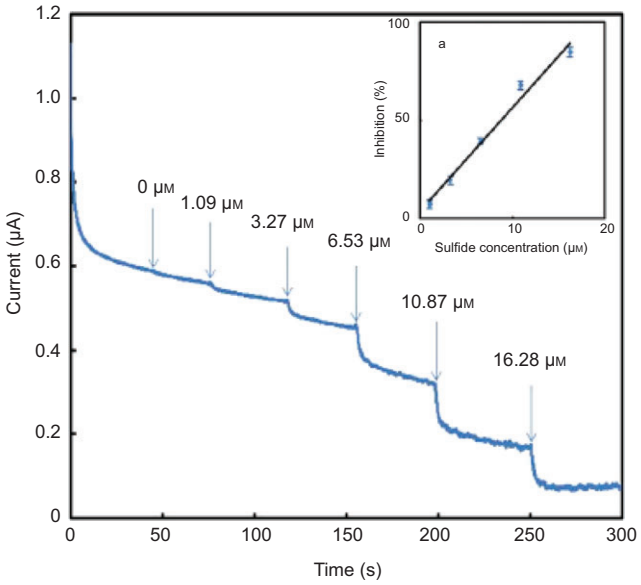

Figure 2 Amperometric response of coprinus cinereus peroxidase (CIP) biosensor for different concentrations of sulfide at -150 mV versus Ag/AgCl in 0.1 M phosphate buffer (pH 6.5) solution containing 0.6 mM H_2O_2 and 1.25 mM of hydroquinone. Inset (A): calibration curve for sulfide determination with CIP inhibition sensor.

(CIP) on the surface of a screen printed electrode (SPE). Chitosan/acrylamide was applied for the immobilization of peroxidase on the working electrode. The amperometric measurement was performed at an applied potential of -150 mV versus Ag/AgCl in the presence of hydroquinone as an electron mediator and a 0.1 M phosphate buffer solution of pH 6.5. Current inhibition with different concentrations of sulfide and a linear response of the elevation of sulfide concentration to the inhibition of current, are shown in Figure 2. The determination range of sulfide can be achieved between 1.09 μM and 16.3 μM, with a detection limit of 0.3 μM (Figure 2). This biosensor has also been successfully tested for the analysis of environmental water samples.

Even though this method has the advantage of a quicker response time against sulfide, the disadvantage is the poor selectivity. Fe^{3+} and Cd^{2+} have significant interference with the detection of sulfide and the error caused by CN^{-} is up to 43.25%.

Chang et al. have reported that they have used hydrodynamic chronoamperometry to detect sulfide at a highly stable $Fe(CN)_6^{3-}$ -immobilized polymeric ionic liquid-modified electrode (designated as FeCN-PIL-SPCE) (Chang et al. 2013). Under a detection potential of 0.0 V in pH 7 PBS buffer solution, a linear calibration in the range of 1 μM to 3 mM, with a limit detection (S/N=3) of 12.9 nM was obtained (Figure 3A). As shown in Figure 3B, the relative standard deviations are all less than 5% for various concentrations of sulfide, which demonstrates that the FeCN-PIL-SPCE electrode is stable and reproducible toward the detection of sulfide.

The proposed system shows good selectivity in real sample analysis. A practical test of the above system included the determination of sulfide content in hot spring water and ground water.

Cyclic voltammetry

Cyclic voltammetry (CV) is another useful and widely applied method in the field of electrochemical detection of sulfide (Giovanelli et al. 2003). Qi and co-workers showed the rapid detection of sulfide on reduced graphene sheets (RGS) modified GC electrodes by CV in 2011 (Qi et al. 2011). The morphology and electrochemical properties of the RGS were characterized by atomic force microscopy (AFM) and CV. The AFM results indicate that the fascinating electrical properties may be due to the fact that the nanosized sheets, which are single-layer sheets, contained a large amount of open graphitic edge planes (Paredes et al. 2009, Wang et al. 2010). The CV detection at RGCs/GC electrodes with 0.5 mM sulfide at various scan rates indicated the adsorption-controlled kinetics of this system. The stability of the RGSs/GC electrodes was studied by repeating the determination of 0.5 mM sulfide at set intervals for 22 h with a scan rate of 0.1 V s^{-1}, in a potential range of -0.6–0.8 V in

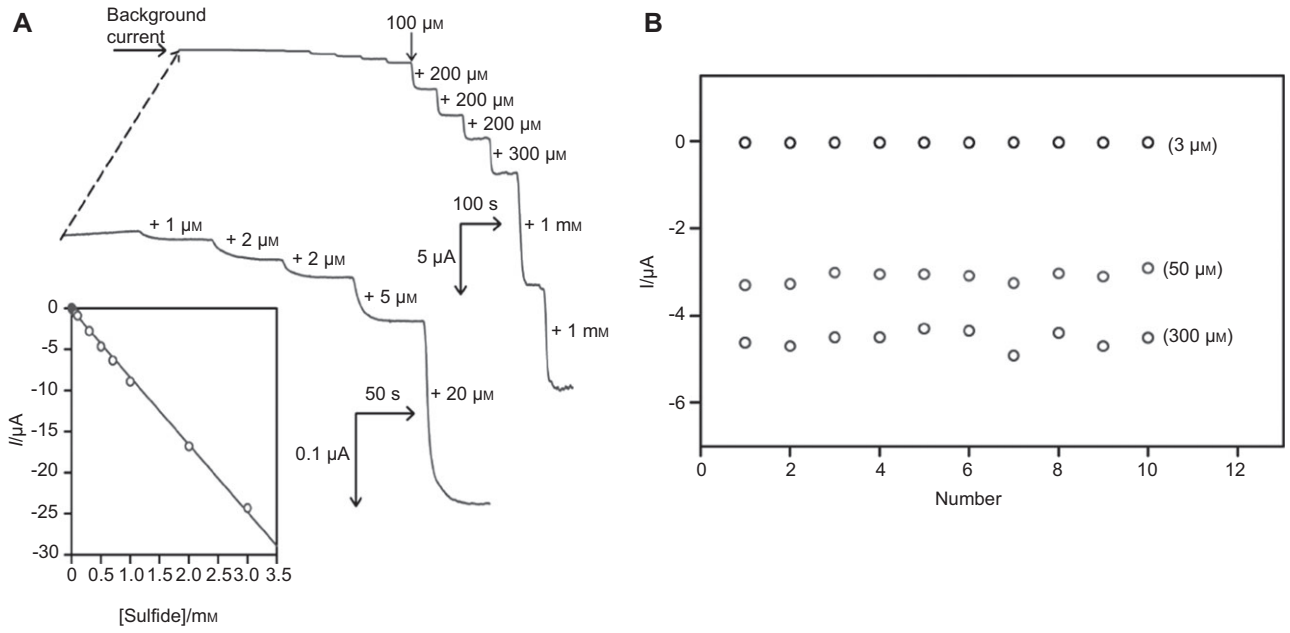

Figure 3 (A) Chronoamperometric response of sulfide at the FeCN-PIL-SPCE in pH 7, 0.1 M PBS at a detection potential of 0.0 V versus Ag/AgCl. The insert graph is the calibration curve with a linear concentration range of 1 μM to 3 mM; and (B) the results at the FeCN-PIL-SPCE for 10 continuous additions of 3 μM, 50 μM and 300 μM sulfide, respectively.

0.2 M PBS buffer solution (pH 7.4). The results showed good reproducibility for the detection of sulfide.

It can be seen from Figure 4A that the oxidation peak current increases with the increase of sulfide concentration. Figure 4B shows that the detection limit was 4.2×10^{-3} mM with a linear correlation coefficient of 0.999 and the detection range was between 5×10^{-3} and 7.4 mM. The analytical application was assessed for the direct determination of sulfide in water samples. The recovery of sulfide was in the range of 97.62% to 106.90%, indicating that the sensor is sufficient for practical application.

Another study utilizing the CV method to detect sulfide was reported by Paim and Stradiotto (2010). They modified a glassy carbon electrode with cobalt pentacyanonitrosylferrate (CoPCNF) film. The redox couple of the CoPCNF film presented an electrocatalytic response to

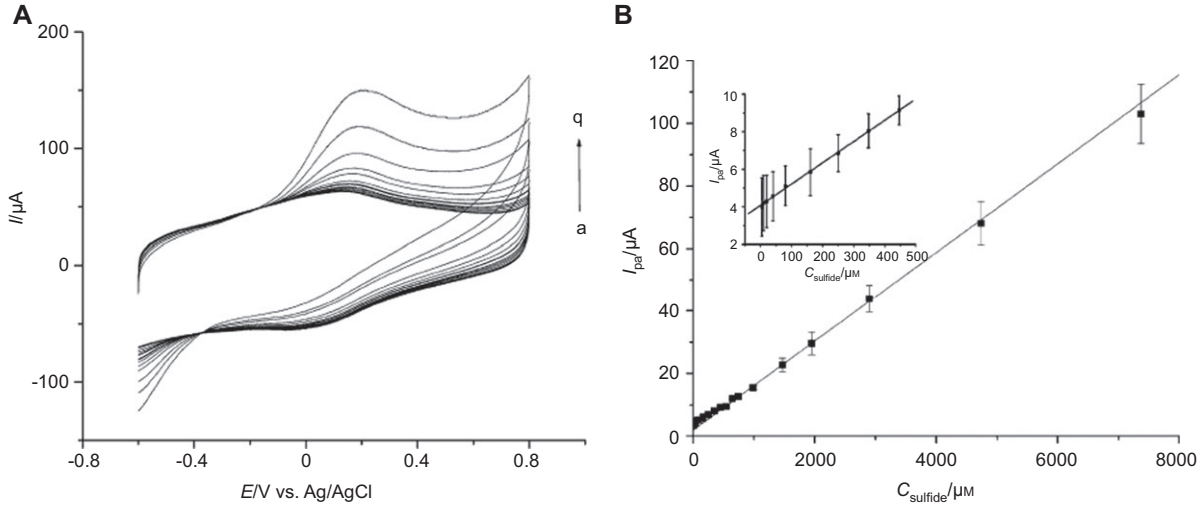

Figure 4 (A) Cyclic voltammograms of reduced graphene sheets (RGSs)/glassy carbon (GC) electrode in 0.2 M PBS (pH 7.4) containing different concentrations of sulfide of (a) 5×10^{-3}, (b) 1.0×10^{-2}, (c) 2.0×10^{-2}, (d) 4.0×10^{-2}, (e) 8.0×10^{-2}, (f) 0.16, (g) 0.25, (h) 0.35, (i) 0.45, (j) 0.54, (k) 0.74, (l) 0.98, (m) 1.47, (n) 1.95, (o) 2.9, (p) 4.7, and (q) 7.4 mM; and (B) the changes of I_{pa} versus concentrations of sulfide ranging from 5×10^{-3} to 7.4 mM. Inset: Plot of changes of I_{pa} versus concentration of sulfide ranging from 5×10^{-3} to 0.45 mM.

sulfide in aqueous solution and the analytical curve was linear in the concentration range of 7.5×10^{-5} to 7.7×10^{-4} M, with a detection limit of 4.6×10^{-5} M for sulfide ions in 0.5 M KNO_3 solution. Compared with other electrochemical systems, a wide linear range was observed here. Furthermore, the CV method can provide much more information than other electrochemical methods. For example, the anodic current might change linearly with the square root of the scan rate, indicating diffusion-controlled kinetics (Hu and Wang 2012). The transfer electron number, the redox potential and the surface coverage (Gooding et al. 2003) can also obtained from the CV spectrum. However, the sensitivity and the detection limit of 4.6×10^{-5} M were not as good as other methods mentioned above.

Photoelectrochemical method

A facile and effective photoelectrochemical method was developed for *in situ* determination of aqueous H_2S based on the deposition of CdS nanoclusters onto TiO_2 nanotubes by Li et al. (2012) Their article demonstrated that the photocurrent produced by bare TiO_2 is negligible compared with that from CdS/TiO_2 films. Moreover, the photocurrent increased with increasing amounts of CdS nanoclusters which were deposited onto TiO_2 nanotubes exposed to $CdSO_4$ solution and increased concentrations of Na_2S. A good linearity of the logarithm of photocurrent intensity with the logarithm concentration of Na_2S which added in the process for depositing CdS nanoparticles on TiO_2 nanotubes $CdSO_4$ solution. This work exhibited a broad linear range for H_2S detection from 1×10^{-8} to 1×10^{-3} M. The detection limit was 0.31 nM (~9.92 ppt), lower than for other methods. The most obvious advantages of this approach are high sensitivity, broad linear range, and a low detection limit. In addition, because of the good selectivity, this method can be applied to detect sulfide in complex samples.

Electrochemical detection methods coupled with other devices

Recently, an increasing number of groups have attempted to couple electrochemical detection methods to other devices for the direct, routine, sensitive and simultaneous measurement of aminothiols, disulfides, and thioethers in either plasma or tissue homogenates (Hiraku et al. 2002, Cataldi and Nardiello 2005, Bailey et al. 2010, Chand et al. 2013).

As was mentioned before, the amperometric detection (AD) technique is a highly sensitive electrochemical method to detect sulfide. However, capillary electrophoresis (CE) analysis combined with the AD technique can achieve unparalleled sensitivity up to attomole levels. Particularly, recent advances in microfabrication techniques make the development of on-chip CE devices coupled with electrochemical detection methods quicker. Recently, Chand and co-workers published an article dealing with separation, aliquot and detection of amino thiols on a microchip capillary electrophoresis with electrochemical detection in a microchannel (Chand et al. 2013). The advantages of the modified microchannel are that it can collect the separated thiols in different reservoirs for further analysis and also ignore the need of electrode regeneration, which are totally different from those of conventional capillary electrophoresis. In Chand's work, the gold electrodes, which were fabricated on glass wafers, were used to separate and detect thiols, while microchannels were laid in PDMS. The microchannel had an inverted double Y-shaped structure which was required to easily store the separated analytes in different reservoirs. They also fabricated a potentiostat array to simultaneously detect analytes in different channels. The CE-AD microchip in Chand's work was fabricated by standard photolithographic procedures (Jang et al. 2011). The chip was built on a single soda lime glass substrate with microchannel engraved in PDMS. There were three sets of a three-electrode system (working electrode, reference electrode and counter electrode) in the CE-AD microchip and these were used for electrochemical detection; in addition, electrodes for applying separation electric fields were fabricated on the soda lime glass wafer using the vacuum thermal evaporation method (Aousgi and Kanzari 2013). After completion, the PDMS mold carrying the microchannel was linked to the glass substrate containing Au microelectrodes by UV-ozone treatment. The configuration of the CE-AD microchip is shown in Figure 5.

Electrochemical measurements included CV and chronoamperometry (i-t curve). The CV analysis of cysteine (Cys) and homocysteine (Hcys) was the prerequisite in order to find the detection voltage to be applied in the CE-AD procedure, as well as the peak current range that the chemicals would generate. The CV experiments were employed separately in a 0.1 M NaOH solution with 100 μM Cys and Hcys, respectively. A stable voltammogram demonstrated no sign of thiols depositing on the electrode surface. From the CV curves, Cys and Hcys produced defined oxidation peaks in the anodic scan at 0.42 V and 0.48 V, respectively. Hence, a detection voltage of 0.5 V was applied to detect the sample in straight microchannel. Then, a small volume of a 2 μl mixture

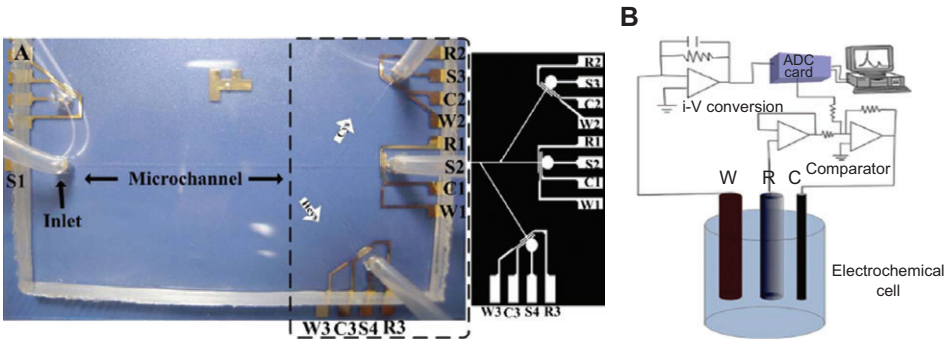

Figure 5 (A) Image of capillary electrophoresis-amperometric detection (CE-AD) microchip showing microchannel engraved in polydimethylsiloxane (PDMS) mold, sample reservoirs, silicon tubes carrying sample and NaOH solution into the microchannel, gold microelectrodes (W1-3=working; C1-3=counter; R1-3=reference; S1-4=separation electrodes); and (B) schematics for electronic circuit and the operation of the in-house built dual potentiostat.

containing 5 μM Cys and Hcys each were injected into the reservoir and subsequently analyzed on the microfluidic chip at 0.5 V. The resulting electropherogram showed that the migration times of Cys and Hcys were 280 s and 345 s, respectively. Thus, the effectiveness of using such a device in the separation of Cys and HCys was proven. For the simultaneous detection of both Cys and Hcys, 2 μl of an equiproportionate mixture of Cys and HCys was injected into a fresh device filled with 1.5% (w/v) agarose gel and an initial separation voltage between the inlet and outlet reservoir of the straight channel was applied. The electric field was switched in the direction of the outlet of the branched channels after 230 s. Thereafter, the detection voltage was set to 0.42 V and 0.48V for Cys and Hcys, respectively, which was obtained from CV figures. In order to accurately calibrate the system for quantitative analysis, the calibration plots which were obtained for each analyte over a concentration range of 0.1–5 μM, represented a typical sigmoidal correlation between peak current and concentration. A linear response was obtained for a range from 0.5 μM to 3 μM and the calculated LOD for the sensor was 0.05 μM (S/N=3). Compared with other conventional CE or flow injection based detection procedures, the advantages of this method were the lower separation voltage (Pasas et al. 2002), the lower LOD (Wang et al. 2005) and the higher peak resolution (Chen et al. 2004). This CE-AD device has been successfully tested for the detection of amino thiols in real blood samples, without the need of any sample pretreatments.

In addition, HPLC coupled to electrochemical detection is another sensitive approach that was recently developed for the direct measurement of thiols, disulfides and thioethers (Bailey et al. 2010). Bailey et al. introduced two different methods, using reversed-phase HPLC with the

Table 1 Different methods used in different periods.

Time range	Methods	Advantages	Disadvantages
1970s	Titration with iodine (Faccenda et al. 2010)	Simplicity	Significant limitations
1980s	Methylene blue test (Khalifa et al. 1979)	Simplicity	Interferences from light and nitrogen dioxide
		Selectivity	
		Sensitivity	
1990s	UV (Kuban et al. 1992), fluorescence (Spaziani et al. 1997, Eroglu et al. 2000), HPLC (Tang and Santschi 2000)	Selectivity	Time consuming
		Sensitivity	Large scale instruments
2000s–now	Atomic spectroscopic (Hoppstock and Lippert 1997), Chemiluminescent (Safavi and Karimi 2002),	Sensitivity	Time consuming
	Ion-chromatographic (Kolotilina and Dolgonosov 2005)	Selectivity	Large scale instruments

Table 2 Different analytical characteristics by different electrochemical methods.

Electrochemical method	WE	LOD	Detection range	Real application
Anodic stripping voltammetry	BiEFs (Huang et al. 2012)	0.21 μM	0.7 μM–5.0 μM	Sulfide in water
Amperometric method	CIP biosensor (Savizi et al. 2012)	0.3 μM	1.09 μM–16.3 μM	Sulfide in water
	FeCN-PIL-SPCE (Chang et al. 2013)	12.9 nM	1 μM–3 mM	Sulfide in water
Cyclic voltammetry	RGSs/GC (Qi et al. 2011)	4.2 μM	5×10^{-3} mM–7.4 mM	Sulfide in water
	CoPCNF/GC (Paim and Stradiotto 2010)	46 μM	75–770 μM	
Photoelectrochemical method	CdS/TiO_2 (Li et al. 2012)	0.31 nM	1×10^{-8} μM–1×10^{-3} M	Aqueous H_2S in water
CE-AD	Gold (Chand et al. 2013)	0.05 μM	0.5 μM–3 μM	Aminothiols in real blood
HPLC-ECD	BDD (Bailey et al. 2010)	0.66 nM		Aminothiols, disulfides and thioethers in plasma or tissue

BiEFs, bismuth-film glassy carbon electrode; CE-AD, capillary electrophoresis combined with amperometric detection; HPLC-ECD, high performance liquid chromatography with electrochemical detection; LOD, limit of detection; WE, working electrode.

electrochemical detection on a boron-doped diamond (BDD) working electrode for the direct, routine, sensitive and simultaneous measurement of a number of aminothiols, disulfides, and thioethers, in either plasma or tissue (Bailey et al. 2010). Firstly, the hydrodynamic voltammograms for aminothiols, thioethers, and disulfides were obtained to illustrate that the optimal applied potential for the detection of these compounds on BDD electrodes was approximately +1500 mV (vs. the palladium reference electrode). Then, the analysis of various concentrations of aminothiols using HPLC with a BDD electrode produced a linear response curve, which showed that the LOD was about 0.66 nM (on column). The analysis of a typical plasma sample using the plasma chromatography method showed that the plasma levels of glutathione (GSH) and glutathione disulfide (GSSG) were 4.5 nM and 0.59 nM, respectively. The analysis of GSH and GSSG in rat brain and liver samples were also presented as 0.204 μM, 9.04 nM, 3.659 μM and 35.68 nM, respectively.

Summary

Many of the electrochemical methods discussed here to detect sulfide, including inorganic and organic sulfide, with different working electrodes, showed different analytical characteristics (Table 2). It can be seen from the table that CV had the highest LOD (4.2 μM), yet it also had a very broad detection range. In other words, CV can be used to detect a high concentration of sulfide. By contrast, the photoelectrochemical method is uniquely capable of detecting sulfide when the concentration is extremely low, as the LOD is 0.31 nM and the detection range is from 1×10^{-8} to 1×10^{-3} M. The amperometric method is another sensitive method to detect sulfide in water. The LOD was only 12 nm with the FeCN-PIL-SPCE working electrode. In addition, electrochemical techniques coupled with other devices such as capillary electrophoresis or HPLC, developed into more promising methods to test organic sulfide in real blood and other bodily fluids and tissues.

In conclusion, there is a sufficiently large range of electrochemical techniques developed recently for sulfide detection. Compared with non-electrochemical techniques, the electrochemical techniques reported here are clearly superior with respect to sensitivity, selectivity, portability of the instrumentation and the relative ease of use. In the future, the development of new electrochemical technology, such as using new types of Q-dots or the other nanoparticles based electrochemical detection methods, or the application of new modified sensors, will make electrochemical detection of sulfide even more specific and efficient.

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