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Ion chromatographic determination of sulfide and cyanide in real matrices by using pulsed amperometric detection on a silver electrode

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Abstract

The determination of free sulfide and cyanide by pulsed amperometric detection (PAD) at a silver-working electrode was improved through a deep de-oxygenation (at least 10 min) of both standard and real solutions containing the two analytes and adopting a two-potential waveform able to eliminate Ag working electrode fouling. The waveform stepped around the oxidation of Ag in the presence of 0.1–0.4 M hydroxyl ion, from −0.1 to 0.1 V versus saturated calomel electrode (SCE). The eluent composition (0.4 M NaOH plus 7.5 mM oxalate solution) allowed a very good column efficiency and selectivity. The presence of a polysulfide species was hypothesized in sulfide solutions that had not been de-oxygenated and aged. The polysulfide eluted just before sulfide and was confirmed by a chemical test with SO_3^{2-} producing the elimination of the polysulfide peak. Detection limits, according to the Hubaux–Vos method, were 1.0 and 2.0 μg/l for S^{2-} and CN^-, respectively. We demonstrated good performance of the optimized method by repeatedly injecting standard solutions and by analyzing different real matrices. The method exhibited very good accuracy and repeatability (10 μg/l and a 500 μl injection loop, had a repeatability better than 3% for sulfide and 100 μg/l had a repeatability better than 1% for cyanide). The two-potential waveform ensured long-term stability of the electrode surface that required no manual polishing procedure for at least 1 month (20 analysis per day).

Keywords: Water analysis; Soil analysis; Pulsed amperometric detection; Sulfide; Cyanide

1. Introduction

The determination of sulfide and cyanide is becoming more and more important in different fields, such as industrial, environmental and biological ones. These species must be detected at very low concentration levels owing to their toxicity [1]. Their recovery from different real matrices is always cumbersome as they can undergo oxidation, and they can produce precipitates and metal complexes. Recovery tests based on spiking the sample with standards are therefore usually irreproducible. Argentometric or iodometric titrations, potentiometry [2,3] spectrophotometry [4,5], gas chromatography [6,7], amperometry [8–10], polarography [11], and voltammetry [12,13] have been proposed for determining cyanide and sulfide. However, titration is subject to interference from other ions while spectrophotometric and gas chromatographic methods are time consuming. Liquid chromatography combined with dc amperometry is easy to handle and shows excellent sensitivity. It has been widely used for the determination of various electroactive species at very low concentrations [14–16]. However, certain samples having contact with the electrode surface can foul the electrode surface and alter the surface characteristics of the electrode material [17]. These poisoned electrode surfaces should be cleaned periodically with a mechanical or electrochemical method for a more stable and repeatable analysis. The first amperometric analysis of free cyanide, which forms a soluble silver complex, with a silver electrode [18] was accomplished by Philar and co-workers [19,20] and followed by Koch [21]. Rocklin and Johnson also analyzed cyanide and sulfide ions with a silver-working electrode [22] applying a continuous 0.0 mV detection potential versus the Ag/AgCl reference electrode. They concluded that cyanide and sulfide did not poison the silver electrode in spite of the fact that sulfide deposits onto the silver electrode as Ag_2S. Unfortunately, when real matrices are analyzed,

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the electrode surface is easily degraded. For this reason the use of the pulsed amperometry seems appropriate as repeated multiple potentials for detection, cleaning and conditioning can decrease electrode fouling coming from the matrix and electrode processes [23,24]. The long-term stability and outstanding reproducibility of pulsed amperometric detection (PAD) have been made it one of the most widely used detection method for liquid chromatography systems [25]. In the particular case of sulfide and cyanide determination, Park et al. [26] published a quite interesting paper in which they proposed a pulse waveform optimization for a particular eluent composition, now abandoned as the ethylenediamine eluent caused column contamination.

In this work we show improved detection of both sulfide and cyanide and stable electrochemical response through the optimization of the eluent composition, a suitable sample degassing treatment and the use of a very simple pulsed potential waveform able to minimize the electrode surface poisoning due to sample matrices. We found evidence of a polysulfide species produced by sulfide oxidation in solution. We also suggest conditions for sampling and sample storage.

2. Experimental

2.1. Reagents and standards

All chemicals used in this study were of analytical grade. Potassium cyanide, sodium sulfide nona-hydrate, sodium oxalate, and 50% (w/w) NaOH solution carbonate-free were analytical reagent grade NaOH by Baker (Deventer, The Netherlands). Working standard solution were prepared by serial dilution of stock standard solutions of analyte containing 1000 mg/l. All solutions were degassed with and kept under helium before use. NaOH solutions were made starting from a 50% (w/w) solution (carbonate free) suitably diluted with degassed water and then standardized with 1 M NORMEX HCl solution Carlo Erba (Milan, Italy).

Degassed, freshly prepared Na_2S solutions were potentiometrically standardized by argentometric titration at a silver electrode.

2.2. Instrumentation and procedures

Chromatographic analyses were performed on a metal-free high-pressure ion chromatograph, model DX-600 (Dionex, Sunnyvale, CA, USA) that included a gradient pump GP40, an AS50 autosampler and an ED40 electrochemical detector. Ag, stainless steel and Ag/AgCl, $KCl_{(sat)}$ electrodes were used as working, counter and reference, respectively. The 250 mm × 4 mm i.d. IonPac AS7 (Dionex) analytical column was used for the separation of cyanide and sulfide. The 50 mm × 4 mm i.d. IonPac AG7 guard column is placed prior to the IonPac AS7 to prevent potential fouling of the analytical column. Both columns were thermostated at 40 °C. Chromatographic and detection conditions are summarized in Table 1. All measurements were made isocratically and at room temperature. Synthetic samples were degassed for at least 10 min and eluent solutions were continuously degassed with helium.

Table 1
Chromatographic and detection conditions

Column	250 mm × 4 mm IonPac AS7 + AG7		
Eluent	7.5 mM sodium oxalate: 400 mM NaOH		
Flow rate	1.0 ml/min		
Injection volume	500 μl		
Detection	PAD		
PAD sequence	Time	Potential[a]	Integration
	0	−0.1	
	0.2	−0.1	Begin
	0.3	−0.1	End
	0.31	0.1	
	0.4	0.1	

[a] V vs. Ag/AgCl.

Water real samples were added at sampling site with oxygen-free 1 M NaOH so that the final hydroxide concentration was around 0.1 M, stored in plastic bottles and kept under nitrogen atmosphere. Soil real samples (1–5 g) were added at sampling site with 50 ml of oxygen-free 0.1 M NaOH solution, stored in plastic bottles and kept under nitrogen atmosphere. All samples must be analyzed within 48 h. Before analysis all samples were degassed for 10 min with Helium before injection. In all cases, sample was injected at least in triplicate. All the samples were filtered through 0.45 μm filter. A sample loop of 500 μl was used for all the determinations.

Data manipulation and the operation of all components in the system were controlled by Dionex Chromeleon 6.20 chromatography software.

3. Results and discussion

3.1. Preliminary considerations on the sulfide species

The solution pH determines the sulfide species present. The K_{a1} value is well established ($K_{a1} = 10^{-7}$), but the K_{a2} still remains uncertain, although its value should range between 10^{-17} [27] and 10^{-19} [28]. In this connection it must be noted that the dissociation constant results to be extremely low and the equilibrium quite difficult to be reached and studied. In all cases, the K_{a2} value implies that sulfide ion is actually never present in aqueous solutions and the only form present at pH greater than 9 is HS^-. The redox characteristics of the HS^- species allow the following reactions [29]:

$$HS^- + \tfrac{1}{2}O_2 = S + OH^- \quad (1)$$

$$xS + HS^- = S_xS^{2-} + H^+ \quad \text{(slow)} \quad (2)$$

$$S_xS^{2-} + xSO_3{}^{2-} + H_2O = HS^- + xS_2O_3{}^{2-} + OH^- \quad \text{(in neutral and alkaline solutions)} \quad (3)$$

$$S_xSH^- + H^+ = S_x + H_2S \quad (4)$$

$$4S_xS^{2-} + (3x-4)OH^- + 4H_2O = xS_2O_3{}^{2-} + (2x+4)HS^- \quad (5)$$

$$HS^- + CN^- = SCN^- + H^+ \quad (6)$$

Reactions (1) and (2) represent the production of polysulfide in solution [30] and they must be accounted for both in sampling and in the choice of the instrumental method, when a quantitative determination of sulfide is required, even when sulfides are present at low concentrations. Reaction (2) is favored in alkaline solution. Reaction (3) indicates a way to test the presence of polysulfide and reaction (4) represents a decomposition reaction. Reaction (5) is a relatively slow reaction always present in alkaline solutions of polysulfide [31]. Reaction (6) has to be taken into account when sulfides must be determined in solutions containing cyanide.

3.2. Chromatography of HS^-

The chromatographic conditions to elute the HS^- ion are alkaline (pH close to 13) with oxalate to complex metal ions that are usually present in sulfide-containing samples [22,32]. Cyanides and sulfides form complexes and/or precipitates with many transition metals therefore large amounts of complexing agents are required to avoid loss of analyte.

Fig. 1 shows two chromatograms of a 100 μg/l sulfide standard solution prepared with degassed (a) and un-degassed (b) eluent. The retention time of the HS^- species is approximately 6 min and it elutes as a single peak. The two peak areas differ by more than 71%, demonstrating that reaction (1) is significant in these samples, and that a thorough purging with He is necessary both for standard preparation and for real solution sampling and storage prior to analysis. The decrease of the base-line in the peak tail is due to electrochemical recovery of the electrode surface after the Ag_2S precipitation. In other words, the Ag_2S precipitate is likely eliminated by the potential cycling producing an overall negative current. A degassed standard solution kept closed for increasing lengths of time is the subject of the chromatograms shown in Fig. 2a–d. This aged solution was not kept under controlled atmosphere on purpose thus allowing oxygen to slowly and spontaneously penetrate.

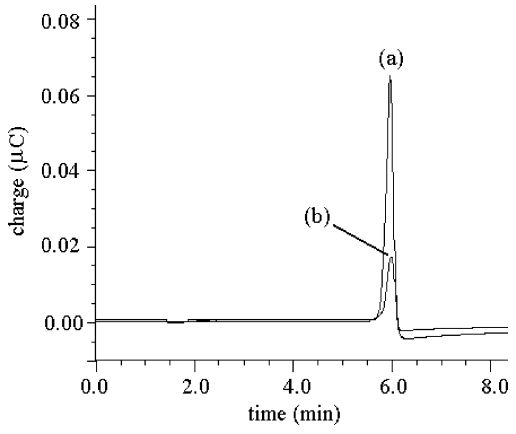

Fig. 1. Chromatogram relative to an injection of a 100 μg/l HS^- standard solution in 0.1 M NaOH previously (a) degassed and (b) un-degassed. Chromatographic conditions as in Table 1.

As in Fig. 1 the peak relative to the freshly prepared solution of HS^- elutes close to 6 min Fig. 2a. After 1 week a second peak appears (Fig. 2b) and a third one after 2 weeks (Fig. 2c and d) as pointed out by the presence of peaks 1 and 2. The two extra peaks elute at shorter retention times than sulfide. In Fig. 2b the overall signal decreased by 70% and peak 1 appears more intense than HS^-. In Fig. 2c the signal of the peak 1 decreased and peak 2 appears in between peak 1 and HS^-. Peak 2 seems to evolve and fade as shown in Fig. 2d. It must be noted that: (1) the electrode performance was periodically checked by using a freshly prepared degassed standard; (2) the same standard was sampled at different time interval to monitor the multiple peak formation.

We attributed the extra peaks to the slow oxidation of HS^- to some S_xS^{2-} form that is slowly formed through reactions (1) and (2) and in slow equilibrium one another according to the general reaction [33]:

$$HS^- + OH^- + xS_{x-1}S^{2-} = (x-1)S_xS^{2-} + H_2O \quad (7)$$

where $x = 1$–4. It is, in fact, well known that polysulfides can be directly formed into a Na_2S basic solution if oxygen is present [30]. Despite the fact that $x = 3$ would correspond to the most concentrated species [33] the low sulfide concentration in the standard suggests the formation of species with a lower number of sulfur atoms (i.e. $x = 1$ or 2). The total peak areas decreased with time as further oxidation reactions produce thiosulfate, sulfite, etc. that are not detected by electrochemical detection. This was verified by injecting Na_2SO_3, $Na_2S_2O_3$, Na_2SO_4 solutions. Therefore, the mass balance could not be verified. The experimental qualitative demonstration of the presence of the polysulfide species was obtained by treating an aged 1 mg/l sulfide solution with Na_2SO_3 and heating at 50 °C for 1 h to allow reaction (3) to occur. Fig. 3a shows the chromatogram of a sulfide solution that was aged for 25 days, before the sulfite treatment. The single peak before the HS^- seems to indicate a single polysulfide species. After sulfite treatment that peak disappeared almost completely (Fig. 3b). A very low level amount is pointed out by the small negative peak coincident with the polysulfide elution according to the discussion made above that is, the trace amount of silver polysulfide deposited on the electrode surface, analogously to HS^-, produces a base-line dip.

In general, a quantitative evaluation of the molar conversion from polysulfide to HS^- is cumbersome due to the

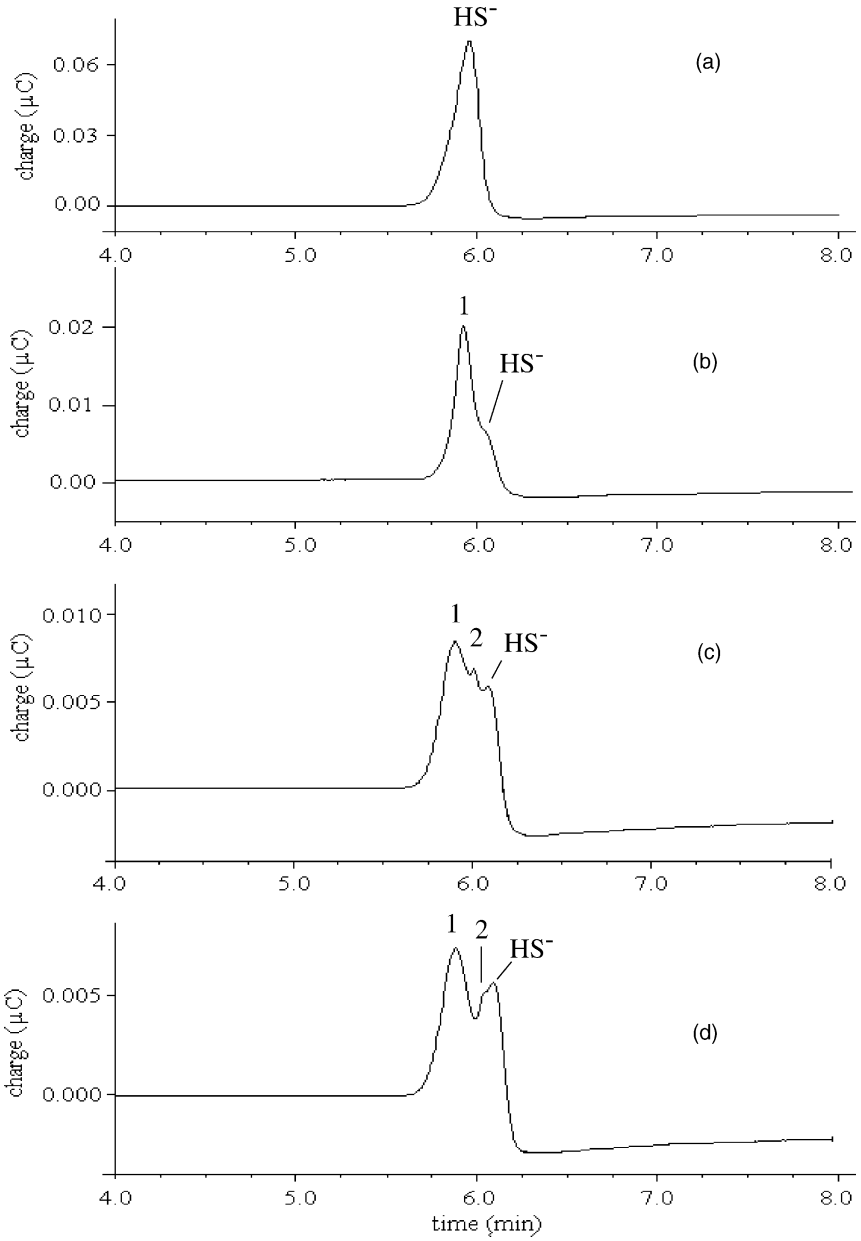

Fig. 2. Multiple peaks chromatograms: (a) freshly prepared solution (100 μg/l); (b) after 1 week; (c) after 13 days; (d) after 14 days. Chromatographic conditions as in Table 1.

heating procedure that generally increases oxidation kinetics. Taking into account the dilution due to sulfite addition (1 volume sample plus 3 volumes of sulfite), polysulfides disappeared and the HS^- peak decreased to 12% of its original value. The HS^- concentration in chromatogram Fig. 3a, obtained from a calibration graph, was 130 μg/l, indicating a large loss of analyte during aging. If the unknown peak is a polysulfide species, it should disappear when the pH is adjusted to 6, due to reaction (4). This is what we observed.

Schwarzenbach and Fisher [34] computed the acidic dissociation constants of polysulfides and reported pK_{a2} values of 9.7, 7.5, 6.3 and 5.7 for the H_2S_2, H_2S_3, H_2S_4, H_2S_5 species, respectively, showing the tendency of H_2S_2 to be negatively mono-charged in alkaline solution. Since the accuracy of the given p*K* values is unknown, it is reasonable to hypothesize the presence of the single charged species, HS_2^-, in spite of the strongly alkaline eluent proposed in this paper justifying the observed retention time. Work is still in progress for understanding this aspect.

3.3. Pulsed amperometric detection (PAD)

One of the major problems in the electrochemical detection of sulfides is electrode fouling [22]. In this context we tried to improve the peak area repeatability, while keeping a sufficiently low detection limit, by using a pulsed potential

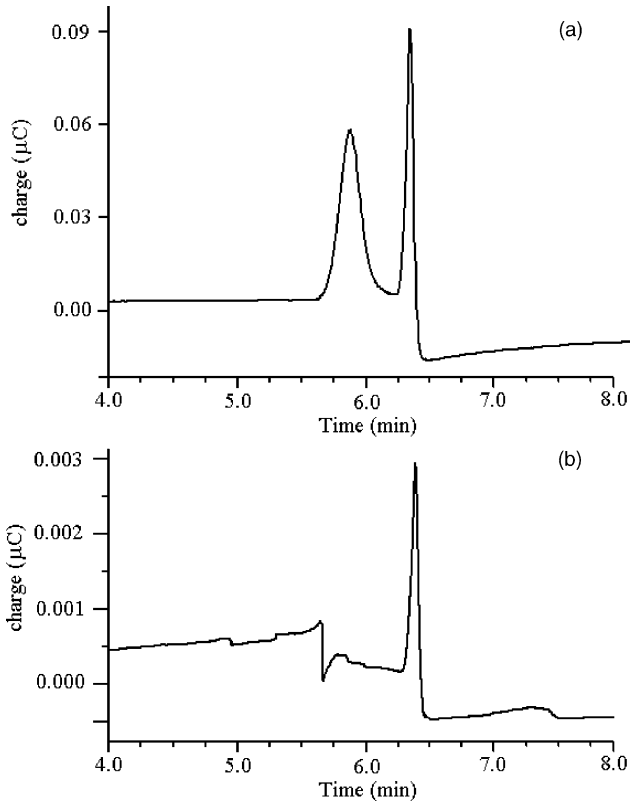

Fig. 3. Disappearance of the polysulfide peak: (a) aged HS^- solution initially 1 mg/l; (b) solution (a) after addition of 0.01 g Na_2SO_3/100 ml NaOH 0.1 M. Chromatographic conditions as in Table 1.

waveform. Our main goal was to find a waveform allowing to efficiently maintain the Ag electrode surface and therefore to increase the electrode life-time limiting the poisoning due to the precipitation on the electrode. In this kind of analysis, this condition is, in our opinion, even more important than the maximum sensitivity condition as it guarantees the repeatability of the measurements. Fig. 4 shows the background current (continuous line) obtained with a cyclic voltammetry on Ag working electrode using the eluent described in the previous sections. The background curve indicates that with this eluent the potential window is cathodically limited by hydrogen evolution close to −1.3 V versus saturated calomel electrode (SCE) and anodically limited by Ag dissolution (as AgOH) at about 0.1 V versus SCE. This last limit is supported by the AgOH solubility product, $K_s = 2 \times 10^{-8}$ [35]. The theoretical formal potential can be computed from the Nernst equation as furnishing the value of 0.35 V versus normal hydrogen electrode (NHE) which is 0.11 V versus SCE as it is shown in the voltammogram. The oxalate present does not produce any Ag oxidation wave under these experimental conditions. When sulfide is added to the solution an Ag oxidation wave starting at −0.80 V appears as expected and the corresponding reduction wave is well evident around −0.89 V. The usual potential adopted for the sulfide detection after IC separation is 0.0 V [22] which is chosen because it is the highest potential allowed before Ag oxidation in a highly alkaline medium. This lowers the background current when the eluent flows in the chromatographic system. Nevertheless, the Ag_2S deposited on the electrode surface accumulates and decreases electrode performance. All attempts to pulse the electrode

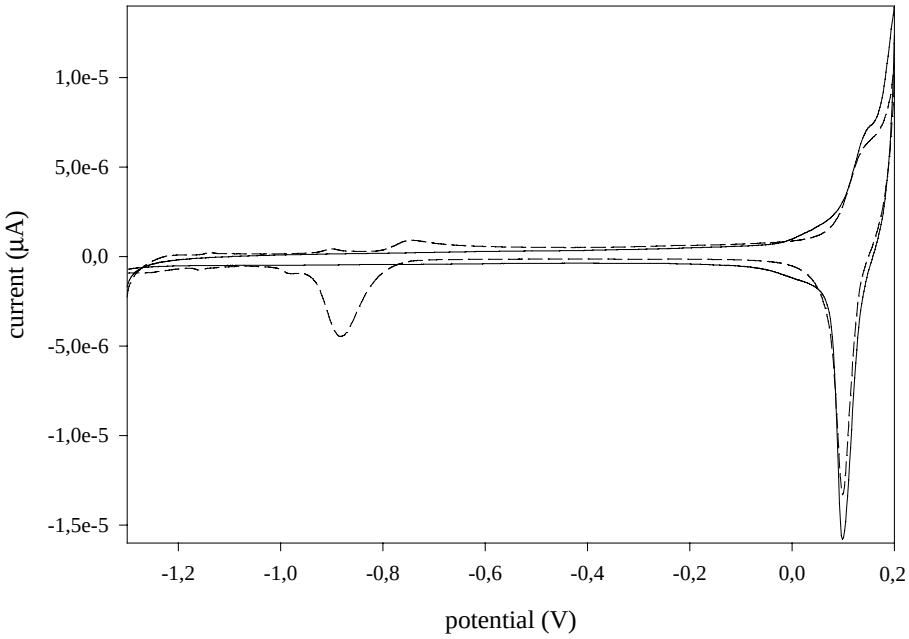

Fig. 4. Cyclic voltammetry of 10^{-4} M sulfide in eluent solution: (—) background; (- - -) 1 mg/l sulfide added. Experimental conditions: working electrode, Ag; reference SCE; counter scan rate, 100 mV/s; electrolyte, NaOH 0.4 M and $Na_2O \times 7.5$ mM; starting potential, −1.3 V vs. SCE.

potential beyond −0.85 V failed, producing very high and noisy background currents and, at the same time, they did not prevent electrode fouling. We tested the electrode responses with pulses in the ranges −0.1 to −1.0 and −0.5 to −1.0 V and sampling current both at anodic and cathodic potentials.

After these failures we worked at potentials around the AgOH system. Our investigation yielded a successful oxidative cleaning step in the potential range at which the AgOH species is formed. The hydroxide formation removed the Ag_2S precipitate present on the surface. The very simple potential waveform reported in Table 1 allowed a very stable baseline and a long-term electrode stability. Freshly prepared 100 μg/l S^{2-} solutions exhibited a repeatability better than 3% during 30 days without any electrode clean-up (20 analysis per day). Moreover, electrode recession due to erosion by oxidation pulse was not observed indicating that the chosen durations of each potential allowed the physical elimination of the Ag_2S precipitate by producing AgOH that was immediately reduced back to Ag. On the basis of our experience, the electrode recession can be seen quite easily also by eye examination as the physical polishing fails showing a dark electrode surface. The use of an optical microscope allows to see a shadow produced by the insulator edge when recession is present.

3.4. Cyanide separation and detection

Cyanide is often determined together with sulfide. Fortunately both the separation and detection conditions that were optimized for sulfide improve cyanide detection too. In particular, the 0.4 M NaOH concentration sharpens the cyanide peak and the repeatability is improved by the electrode clean-up due to the pulse sequence. The chromatographic peak of the cyanide ion, usually very unsymmetrical and late-eluting, elutes as a symmetrical peak with the 0.4 M NaOH eluent. It must be pointed out that, the presence of oxalate is necessary only to remove metal interferences whilst it is the NaOH concentration increase to determine the result. In fact, the same oxalate concentration with a lower NaOH concentration (0.1 M) makes the peak shape much worst.

The pulse sequence keeps the repeatability of the peak area close to 1% for 100 μg/l CN^- injections. The presence of CN^- in alkaline solutions containing sulfides compels us to consider reaction (6) and the cyanide oxidation due to dissolved oxygen (reaction (8)).

$$CN^- + \tfrac{1}{2}O_2 = CNO^- \quad (8)$$

Reaction (6) is actually quite unlikely, in our experimental conditions, as concentrations of both sulfides and cyanides are very low. We did not observe any evidence of reaction (8) as the chromatographic peak of a cyanide standard remains constant for days.

Environmental and industrial matrices usually contain chloride ions. A typical sulfide/cyanide separation in the presence of chloride is shown in Fig. 5b. Injections of chloride standard solution allowed us to ascribe the negative peak to the Cl^- ion (Fig. 5a). The negative signal is due to the chosen pulsed waveform, that is from 0.1 to −0.1 V (integrating potential) just versus $Ag/AgCl/Cl_{(sat)}{}^-$. It is clear that 0.1 V are enough to oxidize Ag even in the presence of low Cl^- concentrations and that −0.1 V (current sampling potential chosen in this work) is enough to reduce the AgCl precipitate back to Ag so producing a cathodic current.

3.5. Application to real matrices

The reported method was widely applied for the simultaneous determination of both analytes in soils, ground and waste waters, sludge, solid and liquid wastes. The most difficult problem for the accurate determination of both analytes is their recovery from these real matrices as they can undergo precipitation, complexation, and above all oxidation reactions. Official methods often require recovery tests based on spiking the real sample with known amounts of standard solutions [36,37]. The majority of real samples containing sulfides obtained from different sources exhibited the sulfide multiple peak (e.g. Fig. 2c) indicating incorrect sampling and storage. Spiked water real samples exhibited the highest recoveries (see Table 2) while more complex matrices such as soils and sludge, did not allowed a similar recovery. In all samples there was a higher yield if they were degassed

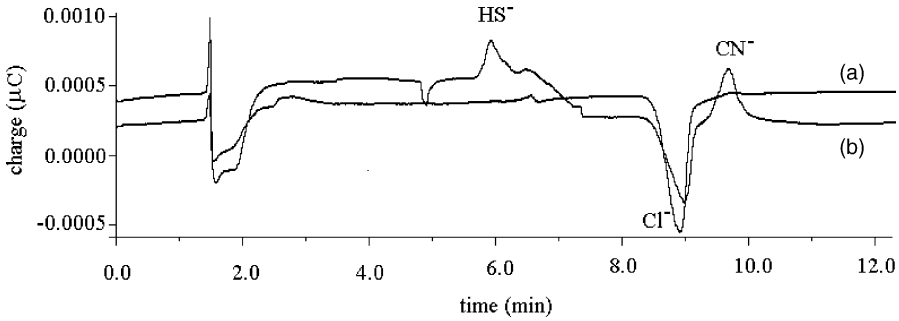

Fig. 5. Cl^- interference on the CN^- peak: (a) 10 mg/l Cl^- solution; (b) real solution containing 0.003 mg/l HS^- and 0.005 mg/l CN^- and Cl^- (not quantified). Chromatographic conditions as in Table 1.

Table 2
Recovery yield for sulfide and cyanide in a sample of surface water in the optimized conditions

	Mean[a] (μg/l)	S.D. (μg/l)	Recovery (%)
100 μg/l spiked S^{2-}	93	3	93 ± 3
20 μg/l spiked S^{2-}	13	1	65 ± 1
100 μg/l spiked CN^-	107	3	107 ± 3
20 μg/l spiked CN^-	22	2	110 ± 2

[a] Mean and standard deviation of 10 different spiked solutions.

prior to spiking. Recovery tests on blank solutions exhibited 100% recovery even after a prolonged use of the electrode (also after many real matrices injections). The same precautions were taken for cyanide.

Transition metal containing solutions produced an unwanted effect. In fact, not only they avoided the determination of cyanide and sulfide owing to their precipitation/complexation, but can also prevent the successive detection of sulfide and especially of cyanide. This occurs because the AS7 anion exchange column has residual cationic exchange sites that can accumulate transition metal ions. A periodic column clean-up with a concentrated oxalate solution (1 M) can elute the retained cations from the AS7 phase and preserve the column performance.

All these findings imply that statistical considerations based on the recovery of the analyte cannot be made and that the most suitable way to quantify free sulfide and cyanide is through the simple external calibration plot. Calibration plots were linear up to 100 μg/l for both analytes and the detection limits, determined with low concentrations calibration plots by means of the Hubaux–Vos method [38], resulted 1.0 and 2.0 μg/l for sulfide and cyanide, respectively.

Typical regression parameters for the two analytes are reported in Table 3. These results, given as concentration versus concentration, point out a very good linearity of the calibration graphs even if the cyanide curve tended to bend slightly upward. This behavior, not yet interpreted, might explain the recovery greater than 100% reported in Table 2. Recovery lower than 100% for sulfide indicated its greater attitude (with respect to cyanide) to be oxidized by trace of oxygen.

Repeatability data are reported in Table 4 for two concentration levels for both analytes. In particular, relative standard deviations better than 3.1% were always found even at lower concentrations. The better relative standard deviation of more dilute solutions for both cyanide and sulfide can be explained by the improved electrochemical conditions.

For all the findings reported above, HS^- and CN^- amounts heavily depend on sampling and storage procedures and therefore the proposed method is most applicable to the determination of free cyanide and sulfide present at the time of analysis.

Table 3
Regression parameters obtained from calibration plots ranging between 5 and 100 μg/l for both analytes

	Sulfide[a]	Cyanide[a]
Slope	1.000	1.02
Intercept	5×10^{-6}	-1×10^{-3}
R^2	1.000	0.996
Slope error	3×10^{-3}	2×10^{-2}
Intercept error	1×10^{-4}	9×10^{-4}
Regression error	4×10^{-4}	2×10^{-3}

[a] Five concentrations three repetitions each.

Table 4
Repeatability on standard solutions of sulfide and cyanide at two concentration levels

	Mean[a] (μg/l)	S.D. (μg/l)	R.S.D. (%)
Sulfide: 5.00 μg/l	5.03	0.05	0.96
Sulfide: 10.00 μg/l	10.53	0.02	2.25
Cyanide: 5.00 μg/l	5.11	0.07	1.44
Cyanide: 10.00 μg/l	11.31	0.03	3.13

[a] Means and standard deviations of 10 different injections.

4. Conclusions

The determination of free sulfide and cyanides at trace level with ion chromatography and amperometric detection was improved by the careful de-oxygenation of the solutions containing the two analytes and by adopting a suitable potential waveform to eliminate the electrode fouling and improve the baseline stability. Sulfide ion appears more sensitive to oxygen than cyanide and this was demonstrated by the appearance of a polysulfide species eluting at a slightly lower retention times than sulfide. Transition metal presence should be tested for a good determination of both analytes. Good results on real matrices were obtained and detection limits of 2.0 and 1.0 μg/l for cyanide and sulfide were found, respectively. Further studies are in progress in order to improve the limit of detection by using a microbore system and to confirm the polysulfide peak by mass spectrometric detection.

Acknowledgements

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