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# Microvolume turbidimetry for rapid and sensitive determination of the acid labile sulfide fraction in waters after headspace single-drop microextraction with *in situ* generation of volatile hydrogen sulfide

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## ABSTRACT

In this work, we demonstrate the feasibility of applying headspace single-drop microextraction with in-drop precipitation for the quantitative determination of the acid labile sulfide fraction ( $\text{H}_2\text{S}$ ,  $\text{HS}^-$ , and  $\text{S}^{2-}$  (free sulfide), amorphous  $\text{FeS}$  and some metal sulfide complexes—clusters as  $\text{ZnS}$ ) in aqueous samples by microvolume turbidimetry. The methodology lies in the *in situ* hydrogen sulfide generation and subsequent sequestration into an alkaline microdrop containing  $\text{ZnO}_2^{2-}$  and exposed to the headspace above the stirred aqueous sample. The  $\text{ZnS}$  formed in the drop was then determined by microvolume turbidimetry. The optimum experimental conditions of the proposed method were:  $2\ \mu\text{L}$  of a microdrop containing  $750\ \text{mg L}^{-1}$   $\text{Zn(II)}$  in  $1\ \text{mol L}^{-1}$   $\text{NaOH}$  exposed to the headspace of a  $20\text{-mL}$  aqueous sample stirred at  $1600\ \text{rpm}$  during  $80\ \text{s}$  after derivatization with  $1\ \text{mL}$  of  $6\ \text{mol L}^{-1}$   $\text{HCl}$ . An enrichment factor of  $1710$  was achieved in only  $80\ \text{s}$ . The calibration graph was linear in the range of  $5\text{--}100\ \mu\text{g L}^{-1}$  with a detection limit of  $0.5\ \mu\text{g L}^{-1}$ . The repeatability, expressed as relative standard deviation, was  $5.8\%$  ( $N=9$ ). Finally, the proposed methodology was successfully applied to the determination of the acid labile sulfide fraction in different natural water samples.

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## 1. Introduction

Sulfide is an important parameter to be monitored in natural waters due to its high toxicity for aquatic organisms. In addition, it is gaining attention for understanding the redox processes in the aquatic environment owing to the important role that this species plays in the bioavailability of heavy metals [1]. Decomposition of organic matter and bacterial reduction of sulfate are the main sources of sulfides in anoxic natural aquatic environments [2]. Usually, concentrations below  $100\ \mu\text{g L}^{-1}$  are reached [3]. Sulfide concentration in oxic waters is very low and it has been recently attributed to kinetic stabilization through soft metal binding [4–6]. Therefore, very sensitive analytical methodologies for this determination are necessary.

Several analytical methods have been used for routine determination of sulfide, including titrimetric, electrochemical, spectrophotometric and chromatographic techniques. The iodometric method has been mostly used, however it is not sensitive enough for samples with concentrations below  $1\ \text{mg L}^{-1}$  [7]. More sensitive and selective is the methylene blue spectrophotometric method (formed by reaction of sulfide with *n,n*-dimethyl-*p*-

phenylenediamine in the presence of  $\text{Fe(III)}$ ) [8], which has been widely used for the determination of sulfide in the range of  $50\text{--}50,000\ \mu\text{g L}^{-1}$  [9]. The United States Environmental Protection Agency (USEPA) recommends the silver sulfide ion-selective electrode (concentrations over  $20\ \mu\text{g L}^{-1}$  of sulfide can be determined by potentiometry) [10]. Ion chromatographic/ion exchange systems have also been routinely applied to the determination of sulfide in waters [7].

Several strategies have been developed to enhance the sensitivity of the sulfide determination by preconcentration of the analyte, such as solid-phase extraction of methylene blue [11], pervaporation of the  $\text{H}_2\text{S}$  generated *in situ* with potentiometric detection [12], the use of flow-through stripping chronopotentiometry [13] or differential pulse cathodic stripping voltammetry (DPCSV) [14], which intrinsically involve a preconcentration step. Chromatographic methods using solid-phase extraction [15] or high performance liquid chromatography with electrospray ionization mass spectrometry (HPLC–ESI–MS) [16], both based on a previous methylene blue colour development, allowed the determination of sulfide at low concentrations in water samples. Nevertheless, the use of chromatographic methods for the determination of sulfide gives rise to a low sample throughput.

Recently, other alternatives have been proposed. Multi-syringe flow injection analysis-based methods (MS–FIA) have been proposed for sulfide monitoring in combination with a miniaturized

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optical fiber spectrophotometer [17], with an optosensing system using disk-based solid-phase preconcentration [1] or with gas diffusion and chemiluminescence-based detection (MS-FIA-GDU-CL) [18]. Jin et al. [19] coupled flow injection on-line sorption in a knotted reactor with hydride generation atomic fluorescence spectrometry (FIA-KR-HG-AFS) for the indirect determination of sulfide, based on the HgS precipitation and chemical vapour generation of mercury. Hydrogen sulfide generation and its subsequent determination by inductively coupled plasma-mass spectrometry (VG-ICP-MS) [20] or inductively coupled plasma-atomic emission spectrometry (VG-ICP-AES) [9] has also been recently proposed. In general, good limit of detection and sample throughput were reported, however these strategies require sophisticated instrumentation for routine determinations.

Hydrogen sulfide generation by acidification of the aqueous sample is a common step in several of the methodologies mentioned above. This vapour generation can be exploited as a sample pretreatment since it allows a matrix separation, which gives rise to a decrease in the potential interferences. Moreover, its sequestration into a lower volume of alkaline media allows its preconcentration prior to the determination by the corresponding analytical technique.

In the last years, several microextraction techniques have been developed for sample preparation, owing to the advantages that they represent with respect to classic extraction approaches. The achievement of large enrichment factors with relatively low sample consumption as well as the use of negligible volumes of extractant phases, thereby diminishing waste generation, make these techniques powerful alternatives to liquid–liquid extraction [21]. Among the microextraction techniques, single-drop microextraction (SDME), based on a great reduction of the extractant phase-to-aqueous sample ratio, is being considered a mature technique, in spite of being introduced in 1997 [22]. Its headspace mode (HS-SDME), introduced by Theis et al. [23], is considered as the best possibility when the extraction of a volatile analyte must be performed, since a high degree of clean up can be achieved. Moreover, an aqueous drop could be used as extractant phase, unlike immersed SDME [24].

The use of microsample detectors in combination with microextraction techniques involves other step towards fulfilment of the analytical miniaturization. Spectrophotometric methods can be miniaturized and improved by direct coupling of microextraction techniques to microvolume spectrophotometers already disposable for routine analysis [25–27].

In this work, HS-SDME is employed in combination with a microvolume spectrophotometer for the acid labile sulfide fraction determination by turbidimetry. Determination of sulfide is accomplished by *in situ* H<sub>2</sub>S generation in the sample and subsequent extraction (by deprotonation and precipitation) in a Zn(II)-containing alkaline microdrop.

## 2. Experimental

### 2.1. Chemicals and samples

All reagents were of analytical reagent grade and solutions were prepared in ultrapure water. Due to the instability of sulfide, stock standard solution was prepared daily (100 mg L<sup>-1</sup> as S) and kept at 4 °C in the dark. This solution was prepared dissolving the required amount of Na<sub>2</sub>S·9H<sub>2</sub>O (Panreac, Barcelona, Spain) in 0.025 mol L<sup>-1</sup> NaOH (Prolabo, Paris, France) with deoxygenated ultrapure water. This solution was standardized by iodimetry daily (4500 S<sup>2-</sup> F. Iodometric Method) [28]. Potassium iodide and potassium iodate from Merck (Darmstadt, Germany), sodium tiosulfate 5-hydrate and sodium carbonate from Panreac, sulfuric acid from Prolabo and starch from Probus (Badalona, Spain) were used for standard-

ization. Working standard solutions of sulfide were prepared by suitable dilution of the stock standard solution in deoxygenated ultrapure water. Hydrochloric acid was purchased from Prolabo, ammonia and sodium chloride were obtained from Merck, zinc nitrate hexahydrate was obtained from Scharlau (Barcelona, Spain) and glycerine was obtained from Probus.

Different natural waters were analyzed in this work: river water, spring water, lake water and seawater. These samples were collected in the area of Vigo (Galicia, Spain). Samples were taken with a minimum of aeration. NaOH (pH > 9) and refrigeration at 4 °C were used for preserving the sample up to the laboratory. Then, analyses were started immediately.

### 2.2. Apparatus

A Nanodrop® (Thermo Scientific, Wilmington, DE, USA) Model ND-1000 Spectrophotometer was used. A description in detail of the instrument, as well as a schematic illustration of the experimental setup can be seen in a previous work [27].

Headspace single-drop microextraction was performed with a commercially available 10-μL syringe containing a guided-PTFE plunger (Hamilton model 1701 RN, 10 AL) (Hamilton, Reno, NV, USA). Hydrogen sulfide generation was carried out in a 40-mL amber-vial with a silicone rubber septum.

### 2.3. HS-SDME procedure for sulfide determination

A 20-mL aliquot of water sample was placed in a vial, which in turn, was placed on a magnetic stirrer plate. After injecting 1 mL of 6 mol L<sup>-1</sup> HCl through the silicone rubber septum, 2 μL of a microdrop containing 750 mg L<sup>-1</sup> Zn(II) prepared in 1 mol L<sup>-1</sup> NaOH were exposed to the headspace of the sample stirred at 1600 rpm for 80 s. After extraction, the remaining drop is retracted back into the microsyringe and subsequently placed onto the pedestal of the Nanodrop® spectrophotometer in order to obtain the corresponding analytical signal. Turbidimetric measurements were carried out at 275 nm.

## 3. Results and discussion

*In situ* H<sub>2</sub>S generation followed by its sequestration onto a microdrop containing ZnO<sub>2</sub><sup>2-</sup> gives rise to in-drop precipitation of ZnS. Zn(II) was chosen as the most appropriate metal ion for the formation of insoluble metallic sulfide in the drop, since it forms a white, highly insoluble precipitate of ZnS, unlike the rest of metals capable of forming insoluble metallic sulfides (Cu, Pb, Hg, etc.), which give rise to coloured (mainly dark) precipitates incompatible with turbidimetric analysis [33]. The white colour and the low solubility of ZnS were, therefore, essential in the choice of this element. Moreover, Zn is considered to be a relatively non-toxic element. The decrease in the incident radiation intensity as a result of scattering by the drop solution containing colloidal particulate matter was measured (i.e., microvolume turbidimetry). This methodology provides five important advantages with respect to traditional turbidimetry: (a) absorbance, turbidity and fluorescence due to the present substances in the sample solution (interferences in turbidimetry) do not occur in the drop; (b) a shorter wavelength can be used, involving an enhancement of the sensitivity; (c) preconcentration of analyte occurs; (d) a drop itself can serve as an optical cell. The windowless nature of such a cell can be used to solve problems associated with optical windows, such as scattering and background fluorescence. For instance, when using conventional optical cells to monitor turbidity due to a precipitation reaction, a frequent problem is the adherence of deposits on all exposed surfaces, including the optical windows; (e) dilution is not needed in order to perform the turbidimetric measurement.

Precipitation is considered a very complex process due to the several interacting phenomena involved. Precipitates are formed through several steps, namely nucleation, crystal growth, and eventually aggregation and break-up [29], being the last two processes undesirable in turbidimetric analysis.

In general, metal sulfides behave as negatively charged hydrophobic colloids that have strong adsorptive properties towards sulfide ions. Then, the colloid is surrounded by the counter ion, forming a double electrical layer, so that aggregation of colloid particles is prevented as a result of the repulsion [30].

Precipitation of sulfide as ZnS has been used for preconcentration and indirect determination of the anion in waters [31,32]. Since the fraction of radiation scattered depends upon the number of particles, their size and shape, as well as the wavelength of the radiation [33], the effect of drop composition and wavelength were investigated.

### 3.1. Wavelength selection

In general, according to the Rayleigh law, diffraction of light is higher at short wavelengths. Then, an increase in sensitivity can be achieved when a short wavelength is used for turbidimetric determinations. Choosing the most appropriate wavelength is typically a difficult task in turbidimetric analysis, especially when absorbing or fluorescing species are present in the sample, or dispersion of light by suspended solids occurs. These interferences do not occur in the configuration proposed in this work because the precipitate is formed directly in the microdrop and then only the reagents employed in the drop could cause interferences. Fig. 1 shows the spectra obtained for a blank and for a solution of sulfide ( $25 \mu\text{g L}^{-1}$ ) after HS-SDME. The selection of the measurement wavelength was performed in order to achieve the maximum sensitivity and then 275 nm was selected for measurement on the basis of the above observations. The colloidal nature of this precipitate allows to explain the shape of the spectrum (i.e., between 250 and 300 nm a constant absorbance is observed) and this accounts for the good precision obtained, which is comparable to that of molecular absorption spectra.

### 3.2. Study of microdrop composition

Study of the most appropriate drop composition is crucial to get a suitable particle size, as well as to sequester the volatile  $\text{H}_2\text{S}$  generated by sample acidification. A Zn(II)-containing alkaline microdrop should allow the deprotonation of  $\text{H}_2\text{S}$  ( $\text{pK}_1$  and  $\text{pK}_2$  are 6.88 and 14.15, respectively) [34] and subsequent precipitation of sulfide as ZnS. Then, pH of the microdrop was studied in the range 11–14. Since Zn is an amphoteric element that in moderate basic media firstly precipitates as  $\text{Zn}(\text{OH})_2$ , soluble ammonium complexes ( $\text{Zn}(\text{NH}_3)_4^{2+}$ ) were formed in drop in order to maintain the Zn in solution at pH values below the corresponding formation

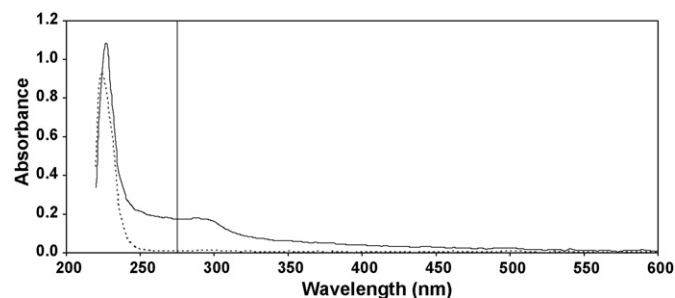


Fig. 1. Spectra obtained by HS-SDME- $\mu\text{Vol}$  turbidimetry of a  $25 \mu\text{g L}^{-1}$  sulfide solution (solid line) and a blank (dotted line).

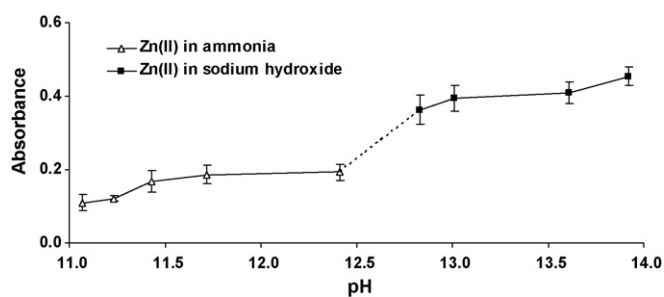


Fig. 2. Effect of pH of the drop on the extraction of the  $\text{H}_2\text{S}$  generated from sulfide.

of  $\text{ZnO}_2^{2-}$ . Results obtained for drops containing sodium hydroxide or ammonia are shown in Fig. 2. As it could be expected from  $\text{pK}_a$  values, pH 14, corresponding to  $1 \text{ mol L}^{-1}$  NaOH, provided the maximum analytical signal, since an efficient conversion of volatile  $\text{H}_2\text{S}$  into sulfide occurs in the drop, thereby allowing its precipitation. Therefore, this pH value was selected in further experiments.

Concentration of Zn(II) in the drop is an important variable influencing supersaturation, which plays an important role in controlling the particle size of the precipitate. In general, an increase in concentration of reagents gives rise to a decrease in particle size and, given the short wavelength selected, working in supersaturation conditions will improve the sensitivity. In the case of ZnS, supersaturation is produced when  $K_{\text{sp}} < [\text{Zn}^{2+}][\text{S}^{2-}]$ , where  $K_{\text{sp}}(\text{ZnS}) = 1.2 \times 10^{-23}$ . If we consider the preconcentration of sulfide produced onto the drop, small quantities of Zn(II) assure supersaturation conditions. Zn(II) concentration in the drop was then studied between 50 and  $1000 \text{ mg L}^{-1}$ . As can be seen in Fig. 3, the analytical signal increases by increasing the Zn(II) content in the microdrop up to  $500 \text{ mg L}^{-1}$ . From this value, no further improvements in absorbance were achieved. A very slight decrease in the analytical signal occurs at a Zn(II) concentration of  $1000 \text{ mg L}^{-1}$ , probably due to the growth and agglomeration of ZnS particles [29]. Thus, a Zn(II) concentration of  $750 \text{ mg L}^{-1}$  was chosen.

In turbidimetry, besides the use of reagents that allow the precipitation of the analyte, addition of a stabilizer such as glycerine can be important to stabilize the suspension and prevent the aggregation of particles. When this substance was used in the drop no significant differences in sensitivity and precision were obtained up to 0.2% (v/v), probably due to the stability of colloidal ZnS formed. Therefore, the use of glycerine was found unnecessary for the stabilization of the particles formed in the drop.

Hence, a drop containing  $750 \text{ mg L}^{-1}$  of Zn(II) in a solution of NaOH  $1 \text{ mol L}^{-1}$  was used throughout.

### 3.3. $\text{H}_2\text{S}$ generation and mass transfer

Acidification of the sample is necessary to efficiently generate the volatile form of the analyte, i.e.,  $\text{H}_2\text{S}$ . When a non-filtered

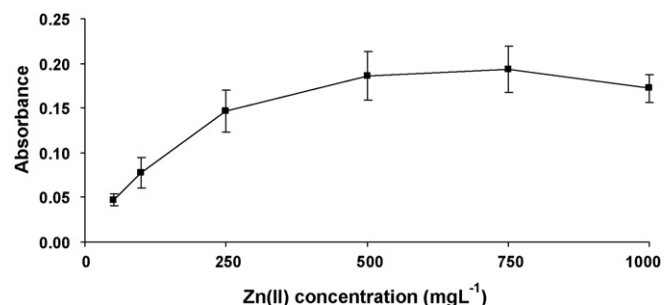


Fig. 3. Effect of Zn(II) concentration in the drop.

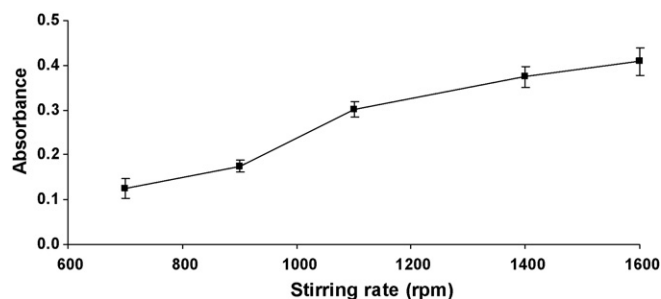


Fig. 4. Influence of the stirring rate on the analytical signal.

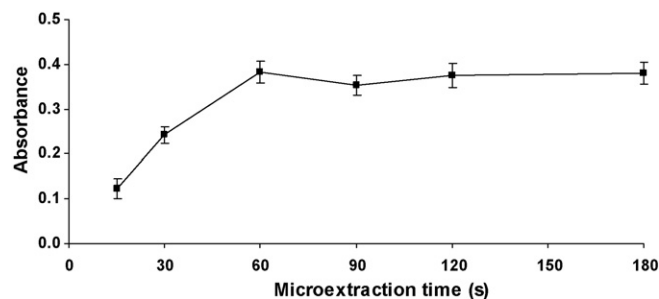


Fig. 5. Effect of the microextraction time on the analytical signal.

sample is used, the acid labile sulfide fraction is determined. This fraction includes the species  $\text{H}_2\text{S}$ ,  $\text{HS}^-$ , and  $\text{S}^{2-}$  (free sulfide), amorphous sulfide of iron and some metal sulfide complexes—clusters as zinc sulfide. Incomplete dissolution of Pb, Mn, Co, Ag, Cu and Hg sulfides is produced [6]. If samples are filtered, particulate metal sulfides are eliminated and then free sulfide and dissolved metal sulfide complexes are determined [35].

HCl was the acid used for *in situ*  $\text{H}_2\text{S}$  generation. The optimization of the HCl concentration has been performed taking into account the presence of NaOH in the aqueous solution, used to increase sulfide stability in standards and samples. HCl concentration added to the sample has been optimized between 0.1 and  $1 \text{ mol L}^{-1}$  HCl (final concentration). No influence of this variable was observed in the studied range, so total conversion of sulfide into  $\text{H}_2\text{S}$  is achieved. A  $0.3 \text{ mol L}^{-1}$  concentration of HCl has been finally selected in order to generate  $\text{H}_2\text{S}$  and dissolve the acid soluble sulfides prior to their determination.

Owing to the three-phase nature of HS-SDME, an efficient mass transfer of  $\text{H}_2\text{S}$  to the headspace must be reached. Agitation of the sample improves mass transfer in the aqueous solution and increases convection in the headspace, thus reducing the time needed to achieve a thermodynamic equilibrium. Magnetic stirring was used, and the effect of the stirring rate was studied in the range 700–1600 rpm. The results are shown in Fig. 4 and, as can be seen, a drastic increase in the analytical signal with increasing stirring rate was produced. Therefore, a stirring speed of 1600 rpm was used for subsequent experiments.

The effect of sample volume on the extraction of  $\text{H}_2\text{S}$  was examined from 5 to 20 mL. An increase in the analytical signal was observed using large sample volumes, due to the decreased headspace volume, which gives rise to an increased  $\text{H}_2\text{S}$  concentration in the headspace, potentially captured by the Zn(II)-containing alkaline microdrop. In addition, a small headspace minimizes the possible oxidation of the sulfur content in the sample. Therefore, a 20-mL aqueous solution has been selected as the most appropriate sample volume.

Addition of salt to the aqueous sample is typically performed in HS-SDME to decrease the solubility of analytes in the sample, hence favouring the mass transfer to the headspace. In the present work, no influence of the addition of salt was seen in the studied range (0–30% (m/v) of NaCl). Therefore, extractions were performed with no addition of NaCl to the sample, since an efficient mass transfer of the  $\text{H}_2\text{S}$  generated *in situ* to the headspace is achieved.

#### 3.4. Microextraction time

Sampling time is one of the most important parameters to be optimized when HS-SDME is performed. This statement is especially true for in-drop precipitation, since aggregation of the ZnS particles can be produced in the drop at large microextraction times. Then, the effect of microextraction time was studied in the range 15–180 s. Fig. 5 shows the results of this study. As can be seen,

the analytical signal increased with sampling time up to 60 s, and then it levels off. Equilibrium between the three phases is therefore reached in a short time. Thus, an 80-s microextraction time was used for subsequent extractions. The use of such a short microextraction time provides two advantages: (a) it prevents the possible aggregation of ZnS particles in the drop, and (b) the sample throughput is improved.

#### 3.5. Analytical characteristics of the proposed methodology

Under the optimal conditions, linear range, limit of detection, repeatability and enrichment factor were obtained. A typical equation for the calibration curve was:  $\text{Abs} = 0.0069 [\text{S}^{2-}] + 0.0020$ , where the sulfide concentration was expressed in  $\mu\text{g L}^{-1}$ . The regression coefficient was  $r = 0.9993$ . The calibration function was linear between 5 and  $100 \mu\text{g L}^{-1}$  of sulfide. The detection (LOD) and quantification limits (LOQ), calculated as  $3\sigma/m$  and  $10\sigma/m$  ( $\sigma$  being the standard deviation of 10 blank measurements and  $m$  the slope of the calibration line), were 0.5 and  $1.5 \mu\text{g L}^{-1}$ , respectively. The enrichment factor, defined as the ratio between the final analyte concentration in the acceptor phase ( $C_a$ ) and initial sample concentration within the sample ( $C_o$ ), was calculated to be 1710.

Repeatability, established from nine consecutive replicates of a  $25 \mu\text{g L}^{-1}$  sulfide solution and expressed as relative standard deviation, was 5.8%. In general, turbidimetric determinations are characterized by their poor precision at the levels of concentration at which this technique is employed (typically beyond  $1 \text{ mg L}^{-1}$ ), especially for batch procedures. This fact is due to the high dependence on the particle size uniformity. Taking into account the large number of experimental variables involved in the process, it could be thought that the repeatability of the proposed method would be worsened with respect to other methodologies that employ HS-SDME. Nevertheless, this assumption is not observed in the present work, where the repeatability was on the order of a previous work involving the combination of HS-SDME with microvolume UV–vis spectrophotometry [27].

A comparison of the analytical characteristics of the proposed method with other recent related methodologies for the determination of sulfide is shown in Table 1. As can be seen, only a few methodologies, such as FI-KR-HG-AFS, HPLC-ESI-MS, and DPCSV, provide LODs lower than that of this work. Moreover, our analysis time is shorter as compared to most of the methodologies developed for sulfide determination, being comparable with automated methodologies such as MS-FIA. As a result, the combination of HS-SDME with microvolume turbidimetry allows the determination of low concentrations of sulfide with a high sample throughput.

#### 3.6. Analysis of spiked/fortified water samples

Although sulfide is most commonly found in groundwaters, which are characterized by relatively low concentrations of dis-



**Table 1**

Analytical figures of merit of the HS-SDME optimized method for acid labile sulfide fraction determination in water samples and comparison with other techniques.

Analytical technique	LOD ( $\mu\text{g L}^{-1}$ )	Repeatability (RSD %)	Working range ( $\mu\text{g L}^{-1}$ )	Analysis time (min)	Ref.
MS-FIA with spectrophotometric detection	90	1.38	200–2000	1.3	[17]
MS-FIA-optosensing system using disk-based solid-phase preconcentration	2.9	0.7	20–200	7.5	[1]
MS-FIA-GDU-CL	3	2.4	20–2000	3	[18]
VG-ICP-MS	2	0.4	1–500		[20]
VG-ICP-AES	6	1	5–25,000		[9]
Flow-through stripping chronopotentiometry	1.6	2.6	5–400		[13]
DPCSV	0.05	2.5	Up to 50	<10	[14]
FI-KR-HG-AFS	0.05	3.3	0.1–2.5	3	[19]
HPLC-ESI-MS	0.05	6.3	0.1–500		[16]
HS-SDME-microvolume turbidimetry	0.5	5.8	5–100	1.3	This work

**Table 2**

Analytical results for the determination of acid labile sulfide fraction in natural waters.

Sample	Found sulfide ( $\mu\text{g L}^{-1}$ )	Added sulfide ( $\mu\text{g L}^{-1}$ )	Recovery (%)
River water 1	<LOQ <sup>a</sup>	25	101 $\pm$ 4
River water 2	2.8 $\pm$ 0.5	25	98 $\pm$ 7
Spring water 1	<LOQ	25	99 $\pm$ 6
Spring water 2	3.4 $\pm$ 0.13	25	105 $\pm$ 7
Lake water 1	<LOQ	25	101 $\pm$ 6
Lake water 2 <sup>b</sup>	–	25	106 $\pm$ 5
Seawater 1	<LOQ	25	103 $\pm$ 9
Seawater 2	<LOQ	25	97 $\pm$ 7

<sup>a</sup> LOQ = 1.5  $\mu\text{g L}^{-1}$ .<sup>b</sup> Corresponding to NWRI-TM 27-2, trace element fortified Lake Ontario water.

solved oxygen, we have mainly analyzed surface waters samples due to the low LODs achieved. The proposed method was applied to the determination of trace levels of the acid labile sulfide fraction in different natural water samples. The obtained results are shown in Table 2. As can be seen, low contents of the acid labile sulfide fraction were found in river water 2 and spring water 2 samples, while concentrations in the rest of samples were found under the LOQ of the proposed method. A surface oxic seawater, where typical sulfide levels are below 2 nmol L<sup>-1</sup> ( $\sim 0.06 \mu\text{g L}^{-1}$ ) [36], was analyzed in order to evaluate matrix effects.

Recovery studies were also carried out in order to evaluate matrix effects. Since natural waters can contain elements that form insoluble sulfides such as CuS, thereby giving rise to low recoveries, the recovery study was made by addition of EDTA to water samples where low recoveries were found. Analytical results are shown in Table 2. In general, good results were obtained in all cases, with recoveries between 97 and 106%.

Interferences from non-volatile compounds are avoided due to the phase separation produced by using HS-SDME. H<sub>2</sub>S generation, together with the precipitation of sulfide by an alkaline drop of Zn(II) exposed to the headspace, makes the proposed methodology practically specific for the acid labile sulfide fraction.

#### 4. Conclusions

HS-SDME with in-drop precipitation has been coupled to micro-volume turbidimetry for the determination of sulfide in natural water samples. The methodology proposed in this work is simple and effective, providing a high enrichment factor in a very short time. The volume of extractant phase needed to carry out the microextraction process is exactly the same required (i.e., 1–2  $\mu\text{L}$ ) for the turbidity measurement, so dilution of the enriched microdrop before turbidimetric analysis is avoided. This work may constitute a starting point for the development of new miniaturized turbidimetric methodologies, and represents an interesting example of the broad possibilities that the combination of microex-

traction techniques with a microvolume spectrophotometer offers for routine analysis.

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