# Determination of sulphide in liquid and solid samples by integrated pervaporation–potentiometric detection

B. Vallejo [a], P. Richter [b], I. Toral [c], C. Tapia [c], M.D. Luque de Castro [d,*]

[a] *Department of R&D, Gemasur, Polígono Las Quemadas, Parcela 271, E-14070 Córdoba, Spain*
[b] *National Environmental Center (CENMA), Av. Larraín 9975, La Reina, Santiago, Chile*
[c] *Department of Chemistry, Faculty of Sciences, University of Chile, P.O. Box 653, Santiago, Chile*
[d] *Department of Analytical Chemistry, Annex C-3, Campus of Rabanales, University of Córdoba, E-14071 Córdoba, Spain*

**Abstract**

A selective dynamic method for the determination of sulphide in liquid and solid samples based on the integration of hydrogen sulphide pervaporation and potentiometric monitoring of the sulphide in a laboratory-made module has been developed. The analyte was converted into hydrogen sulphide by reaction with an acidic donor stream and accepted into a dilute NaOH solution after pervaporation. The method proposed has a determination range between 0.1–30 $\mu g\,ml^{-1}$ and 0.3–50 $\mu g\,g^{-1}$ for liquid and solid samples, respectively, a precision (expressed as relative standard deviation) of 3.1 and 4.3%, respectively, and has been applied to a sulphide quality control standard containing a certified concentration of 10.10 $\mu g\,ml^{-1}$ with excellent results.

*Keywords:* Sulphide; Pervaporation; Selective electrode

## 1. Introduction

Membrane-based non-chromatographic continuous separation techniques can improve both the sensitivity of a method via preconcentration and selectivity through avoidance of either matrix effects or particular interferents [1]. However, these techniques suffer from two serious drawbacks, namely: potential clogging of membrane pores by suspended particles or components of a high molecular weight occasionally present in the sample, and deterioration of the membrane through contact with the sample. Both shortcomings can be overcome by using pervaporation (thus, called in order to emphasise that the analyte or its reaction product, known as the "permeate", undergoes a phase change from liquid to vapour before reaching the membrane). When compared with gas-diffusion for separation of volatile compounds, pervaporation presents as the most salient advantage the fact that the sample never enters into contact with the membrane, thus avoiding clogging or deterioration and making possible its use with complex environmental matrixes, such as solid and semisolid wastes, membrane corrosive liquids and slurries [2].

Analytical pervaporation can be defined as the integration of two different physical phenomena (evaporation and gas diffusion) in a single micromodule named pervaporator. The analytical pervaporator is, in principle, a separation module for removal volatile analytes or their volatile derivatives from the

* Corresponding author. Tel.: +34-957-218615; fax: +34-957-218615.
*E-mail address:* qa1lucam@uco.es (M.D. Luque de Castro).

sample matrix, but it can also be used for sample pre-treatment, e.g. for solid samples leaching, and derivatisation of the analytes can be done simultaneously in it [3–5]. The volatile analyte or its volatile derivative is transferred from the sample into the head space in the donor chamber of the pervaporator. Then, the specie in the gas phase passes through the membrane to reach the acceptor chamber, where it is dissolved and the detection process is carried out.

Miniaturisation is a subject of increasing development in analytical chemistry. At the laboratory scale, pervaporation is a microseparation technique as it involves the two general principles of miniaturisation: reduction of the equipment size and integration of different steps (evaporation and gas-diffusion). A higher level of miniaturisation is involved in approaches in which detection is integrated with pervaporation [6]. A major simplicity and miniaturisation of the experimental set up is thus obtained, and the human participation is also reduced so as to increase analytical quality and productivity.

Food analysis is the analytical field in which pervaporation has been most widely utilised, as shown in a review on this subject [7] particularly for the determination of volatile compounds in wine [8–11]. Analytical pervaporation has also been applied in the environmental studies such as the determination of fluoride in wastewater [12] involving the coupling of pervaporation with potentiometric detection in the same module; [13] sulphide in Kraft liquors, [14] cyanide in industrial samples, [15] phenol in water, [16] and pesticides in water and soil [17].

Sulphide is usually determined in solid and liquid wastes because when it is exposed to certain pH conditions toxic gas, vapour or fume can be generated in a quantity sufficient to present a danger to either human health or environment. The regulatory level for sulphide concentration in liquid wastes is 1 and $5\,\mu g\,ml^{-1}$ in Spain [18] and Chile [19], respectively. In the field of the solid wastes, the determination of releasable sulphide is an experimental test to assess the reactivity of a solid waste in order to determine its potential hazardous characteristics previous to determine its final deposition.

In this work, a hybrid static-flow system is proposed for the rapid determination of sulphide in liquid and solid samples. Separation and potentiometric detection take place simultaneously in a pervaporation module in which a sulphide selective electrode has been placed. Because most of the available test methods for measuring reactivity of solid wastes suffer from a number of deficiencies [20,21] the main aim of this work was to develop a screening method for sulphide containing wastes, in order to cutting down the number of samples requiring time-consuming laboratory testing for US-EPA reactivity.

## 2. Experimental

### 2.1. Apparatus

One four-channel Gilson Minipuls-3 peristaltic pump, two Rheodyne 5041 injection valves and poly(tetrafluoroethylene) (PTFE) tubing of 0.8 mm i.d. were utilised to build the manifolds (Fig. 1a and b). The sulphide selective electrode (Metrohm, 6.0502.180, Switzerland) was fitted to the upper part of the pervaporation module faced to the acceptor side of the gas-diffusion membrane. A KCl reference electrode (Metrohm, 6.0233.100) was also used and located in a methacrylate flow-cell made in the laboratory. A PHM 64 potentiometer (Radiometer Copenhagen) was used for monitoring the potential.

A pervaporation cell designed in our laboratory [14] and PTFE membranes (47 mm diameter and 1.5 mm thickness) from Trace (Braunsweig, Germany) were also used for constructing the manifolds. A water-bath (Selecta, Barcelona, Spain), equipped with a thermostat, was used to preserve the temperature of the pervaporation cell. A magnetic stirrer was also used with solid samples.

### 2.2. Reagents and solutions

All reagents were of analytical grade and ultrapure water obtained from a Millipore Milli-Q system and used throughout. $Na_2S{\cdot}9H_2O$ (Merck, Darmstadt, Germany) was rinsed with ethanol and dried with filter paper. A $200\,\mu g\,ml^{-1}$ stock solution of sulphide was prepared by dissolving the appropriate amount of $Na_2S{\cdot}9H_2O$ in $0.01\,mol\,l^{-1}$ NaOH (Panreac, Barcelona, Spain), stored under refrigeration at

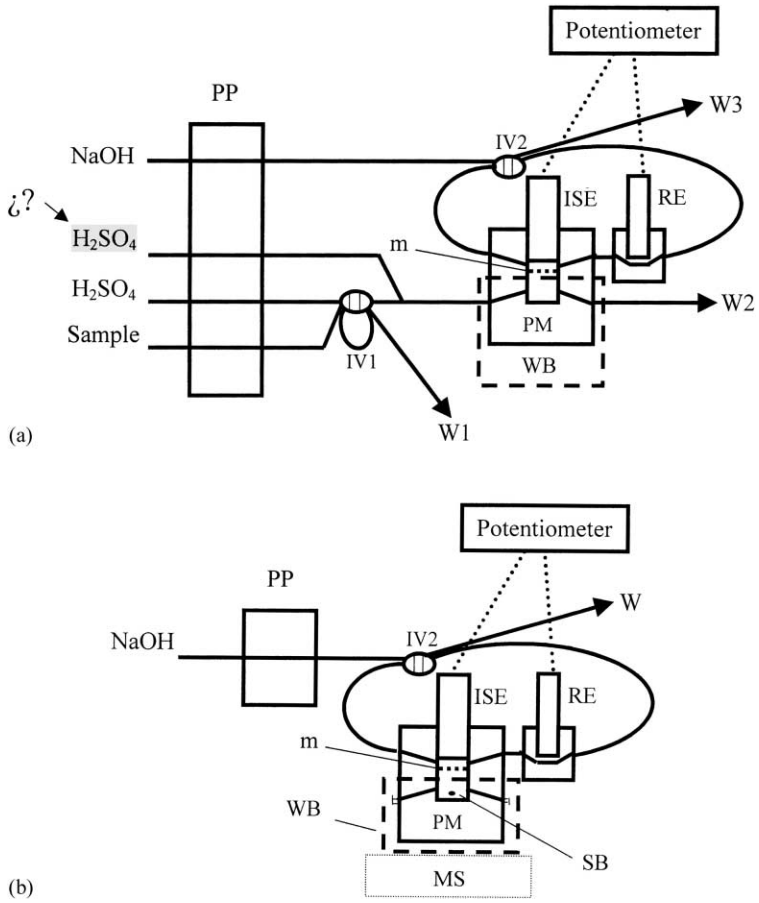


Fig. 1. Manifolds for the determination of sulphide. (a) In liquid samples and (b) in soil samples. PP: peristaltic pump; IV1 and IV2: injection valves; PM: pervaporation module; WB: water bath; m: membrane; ISE: ion-selective electrode; RE: reference electrode; W, W1, W2 and W3: waste; MS: magnetic stirrer; S: stirring bar.

4°C and standardised by titration daily [19]. Standards of different concentrations were prepared by appropriate dilution of the stock solution in 0.01 mol $l^{-1}$ NaOH. The solution used as the donor stream was 0.4 mol $l^{-1}$ $H_2SO_4$ (Panreac) for liquid samples and a 1 mol $l^{-1}$ $H_2SO_4$ solution was injected for solid samples. Sodium hydroxide solution (0.1 mol $l^{-1}$) was used as the acceptor stream. Standard solutions of 1000 μg $ml^{-1}$ $SO_3^{2-}$ and 3000 μg $ml^{-1}$ $S_2O_3^{2-}$ (both from Merck) were prepared by dissolving their sodium salts in a 0.01 mol $l^{-1}$ NaOH solution for the study of interferences. Reference material (AccuStandard Inc., New Haven, USA) was used for validation of the method.

### 2.3. Manifolds and procedures

The hydrodynamic approaches constructed for liquid and solid samples are shown in Fig. 1a and b, respectively.

#### 2.3.1. Procedure for liquid samples

The sample or standard solution was injected through IV1 into a 0.4 mol $l^{-1}$ $H_2SO_4$ stream to form hydrogen sulphide. This volatile derivative was lead to the lower part of the pervaporation cell, which was thermostated at 50°C. There, the $H_2S$ evaporated, diffused through the hydrophobic membrane and was accepted into a 0.1 mol $l^{-1}$ NaOH solution.

Table 1
Optimisation of variables

| Variable | Sample state | Range studied | Optimum value |
|---|---|---|---|
| Donor stream ($mol\,l^{-1}$) | Liquid | 0.1–1.5 | 0.4 |
| | Solid | 0.1–1.5 | 1 |
| Acceptor stream ($mol\,l^{-1}$) | Liquid and solid | – | 0.1 |
| Temperature (°C) | Liquid and solid | 30–70 | 50 |
| Injection volume (ml) | Liquid | 300–2000 | 1000 |
| | Solid | – | 100 |
| Donor flow rate ($ml\,min^{-1}$) | Liquid | 0.6–2.0 | 0.8 |
| Acceptor flow rate ($ml\,min^{-1}$) | Liquid and solid | 0.6–2.0 | 0.8 |

The acceptor stream (0.1 $mol\,l^{-1}$ NaOH) was halted for 4 min, by turning IV2 to the filling position, and the increase of the potential due to the accumulation of sulphide in the upper part of the pervaporator was monitored by the sulphide selective electrode whose active surface was faced to the acceptor side of the membrane.

*2.3.2. Procedures for solid samples*

Air-dried clay soil was sieved to a size smaller than 1 mm and 0.07 g of it was accurately weighed in the lower chamber, then spiked with 100 μl sulphide solution and a small stirring bar was introduced in the chamber. The pervaporation cell was closed, after positioning the membrane and the upper chamber. The acceptor stream was then circulated through the upper part of the pervaporator in order to establish the baseline of the detector. Subsequently, 0.2 ml of 1 $mol\,l^{-1}$ $H_2SO_4$ was injected by syringe provided with a hypodermic needle into the lower chamber through a septum located in its inlet while the outlet was closed by a screw, thus avoiding possible leaks with loss of the analyte. The lower part of the pervaporation cell was thermostated at 50°C and located in a magnetic stirrer. The $H_2S$ formed in the lower chamber evaporated and diffused through the membrane and was accepted by the static 0.1 $mol\,l^{-1}$ NaOH solution. The signal corresponding to the sulphide hydrogen added to the sample was recorded as described for the liquid samples.

## 3. Results and discussion

A detailed study of variables affecting the system was performed using the univariate method. A solution of 1 $\mu g\,ml^{-1}$ sulphide prepared from the standard solution of 200 $\mu g\,ml^{-1}$ by appropriate dilution with a 0.01 $mol\,l^{-1}$ NaOH solution was used as sample in the optimisation study. All the variables studied and their optimum values found are listed in Table 1.

### 3.1. Chemical variables

The *concentration of $H_2SO_4$* in the donor stream required for converting sulphide ion into $H_2S$ was varied in the range from 0.1 to 1.5 $mol\,l^{-1}$. For the full protonation of all sulphide ions in the samples 0.4 $mol\,l^{-1}$ $H_2SO_4$ was selected as appropriate because it provided the highest signal, which was stable for concentrations of $H_2SO_4$ higher than 0.4 $mol\,l^{-1}$. In the case of solid samples, 0.2 ml of $H_2SO_4$ 1 $mol\,l^{-1}$ was added to the spiked soil in order to achieve the total volatilisation of the sulphide ions as $H_2S$.

A solution 0.1 $mol\,l^{-1}$ sodium hydroxide was used as acceptor solution with the purpose of having an acceptor stream sufficiently basic for converting into sulphide ion all the transferred $H_2S$.

An increase in *temperature* had a positive effect on both the rate of volatile compound formation and the separation process as a consequence of a higher evaporation. The temperature of the water-bath into which lower chamber of the pervaporator was plunged was studied between 30 and 70°C. The signals increased with increased temperature up to 50°C and levelled off at higher temperatures. Therefore, a temperature of 50°C was sufficient for optimal development of the pervaporation process. The increase of temperature had a negative effect on the membrane life.

Table 2
Features of the method

| Sample state | Linear range | Equation[a] | $r^2$ | LOD[b] | LOQ[c] | RSD[d] (%) |
|---|---|---|---|---|---|---|
| Liquid | 0.1–30 $\mu g\,ml^{-1}$ | $Y = 51.25X + 16.53$ | 0.995 | 0.03 $\mu g\,ml^{-1}$ | 0.1 $\mu g\,ml^{-1}$ | 3.1 |
| Solid | 0.3–50 $\mu g\,g^{-1}$ | $Y = 38.41X + 8.16$ | 0.991 | 0.09 $\mu g\,g^{-1}$ | 0.3 $\mu g\,g^{-1}$ | 4.3 |

[a] $Y$ = potential in mV; $X$ = logarithm of sulphide concentration in $\mu g\,ml^{-1}$ and $\mu g\,g^{-1}$ for liquid and solid samples, respectively.
[b] As three times $S_{blank}$.
[c] As 10 times $S_{blank}$.
[d] At 3 $\mu g\,ml^{-1}$ sulphide ($n = 6$).

### 3.2. Flow injection variables

The *injection volume of the sample* in the case of liquid samples had a marked influence on the analytical signal as it increased by increasing the injection volume of the sample from 300–2000 μl. Injection volumes higher than 1000 μl resulted in wide time-consuming peaks. A volume of 1000 μl was selected as a compromise between sensitivity and sampling frequency. In the case of solid samples 100 μl of sulphide solution was chosen as appropriate for adding to the soil in order to favour a good mixing between the soil and sulphide solution by stirring until total homogeneisation. These samples were not previously prepared because of the high volatility of the analyte.

As established in a previous study on pervaporation[6] the best performance of the pervaporation module is obtained when both the donor and acceptor streams circulate at the same *flow rates*. The effect of variation of the donor and the acceptor stream flow rates was studied at identical values of both in the range from 0.6 to 2.0 ml $min^{-1}$. As expected, better sensitivity was achieved at low flow rate. Taking into account that the sampling frequency decreases on lowering the flow rate, a flow rate of 0.8 ml $min^{-1}$ in both channels ensured both acceptable sensitivity and sample throughput to the liquid samples and the same flow rate was used for the acceptor stream in the case of the soil samples.

### 3.3. Pervaporation variables

The time necessary to obtain a stable potential was studied halting the flow of the acceptor stream in the acceptor chamber by placing it in the loop of an auxiliary injection valve (IV2 in Fig. 1). In the filling position of this valve, the flow through the system was continuous, except in the loop of the valve, where the upper chamber of the pervaporation cell was located; the flow through this loop was restored by switching the valve to the injection position. A 4 min stopped-flow time was enough for obtaining the analytical signal.

### 3.4. Features of the method

Calibration curves were obtained using both liquid and solid samples by triplicate injection of different concentrations of sulphide. The results obtained in terms of equations, linear ranges, correlation coefficients, detection and quantification limits, and precision (studied as repeatability and expressed as relative standard deviation) are listed in Table 2.

The sampling frequency was 8 and 5 $h^{-1}$ for the liquid and solid samples, respectively. This parameter was calculated for solid samples by considering the time elapsed between the preparation of the separation module and the obtainment of the analytical signal from the analyte.

### 3.5. Study of interferences

The effect of other ions on the determination of the sulphide by the proposed method was studied. Standard solutions 1000 and 3000 $\mu g\,ml^{-1}$ of $SO_3^{2-}$ and $S_2O_3^{2-}$, respectively, were prepared as established under experimental, and added to the sample (the volume appropriate of interferent was spiked with 3 $\mu g\,ml^{-1}$ of sulphide and the signal obtained was compared to that provided by the same concentration of sulphide without foreign species). $SO_3^{2-}$ and $S_2O_3^{2-}$ interfered when their concentrations were equal or higher than 300 and 2500 $\mu g\,ml^{-1}$ for solid and liquid samples, respectively.

Table 3
Validation of the method for the liquid samples (a quality standard for sulphide)

| Dilution[a] | Certified value ($\mu g\,ml^{-1}$) | Found value ($\mu g\,ml^{-1}$) ($n = 3$) |
|---|---|---|
| 1:10 | 10.10 ± 0.12 | 9.75 ± 0.41 |
| 1:20 | 10.10 ± 0.12 | 9.59 ± 0.56 |

[a] Dilutions of the 10.10 $\mu g\,ml^{-1}$ sulphide quality standard solution.

### 3.6. Validation of the method

A quality control standard for sulphide containing a certified concentration of 10.10 $\mu g\,ml^{-1}$ was used to validate the proposed method. Two dilutions (1:10, 1:20) were prepared in 0.01 $mol\,l^{-1}$ NaOH. Both solutions were injected in triplicate directly using the method for liquid samples and the results obtained are shown in Table 3. In the case of solid samples, 0.07 g of soil was spiked with 100 µl of 1:10 dilution (1.44 µg sulphide per gram of soil). The sulphide concentration was determined following the proposed method for solid samples and the measurement was repeated three times. The concentration found was 1.33 ± 0.16 µg sulphide per gram of soil. An excellent agreement between the certified value and the experimental value obtained with proposed methods can be observed both in liquid and solid samples.

## 4. Conclusions

A method with continuous and hybrid continuous–discontinuous format for the determination of sulphide in liquid and solid samples, respectively, is proposed, involving the integration of separation with potentiometric detection in both cases.

There is no contact of the sample with the membrane and therefore no clogging of the pores of the membrane. The method could be applied to samples containing high concentrations of interfering species because it allows the determination of sulphide in the presence of up to 2500 $\mu g\,ml^{-1}$ of thiosulphate and 300 $\mu g\,ml^{-1}$ of sulphite while these analytes interfere in the standard methylene blue method at concentrations above 10 $\mu g\,ml^{-1}$. Therefore, the pervaporation is specially useful when the detection system is sensitive to these interferences from the matrix.

Taking into account the toxicity of sulphide, the method here proposed could be very useful for monitoring this analyte in environmental matrixes, such as liquid and solid residues. The legislation [18,19] for liquid residues establishes upper limits around 1 $\mu g\,ml^{-1}$ for sulphide. By the proposed method this species can be determined in complex matrixes with both good selectivity and sensitivity, at concentrations much lower than 1 $\mu g\,ml^{-1}$.

On the other hand, the proposed approach also enables the determination of the target analyte in solid residues by circumventing the interferences from these matrixes. When a solid residue contains more than 500 $mg\,kg^{-1}$ of releasable sulphide it is considered as reactive residue, and toxic, as a consequence. The experimental test for determining this character is relatively slow and it is a not a quantitative test under the working established conditions. In this context, the proposed method can also be applied as a screening method to perform a fast discrimination between toxic and not toxic residues in order to apply the official method only to the former if the sulphide in the sample corresponds to the releasable species regulated by EPA.

As compared with other methods appeared in the literature, this here reported offers as unique advantage its applicability to solid samples. Most of the methods proposed so far involve the design and construction of ion selective electrodes checked in synthetic samples [22–24] or special natural samples [25]. Gas-phase molecular absorption spectrometry has also been used for the determination of sulphide [26,27]. Only a method, published in 1986, has been reported for the determination of this analyte in solid samples such as soil and sediments [28]. In this method, the release of sulphide from the solid requires 16 h.

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