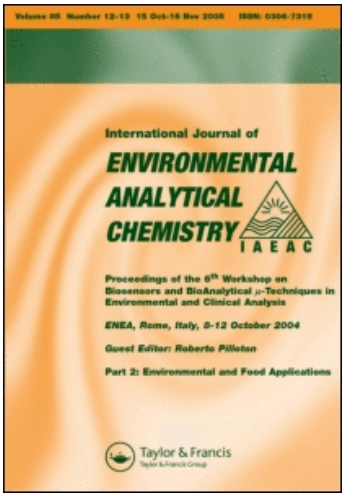

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New approach on the alkylthiol determination in water by *in situ* derivatization SPME followed by GC-ECD/NPD analysis

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Alkylthiols are very reactive and highly volatile compounds, and thus it is difficult to determine these in the water phase. In the present work, an *in situ* derivatization step prior to solid-phase microextraction (SPME) has been developed for their determination in water samples. The dinitrobenzylation reaction was selected because the high chemical stability of the corresponding thioethers formed provides a significant increase in the distribution coefficient between the SPME fibre and the aqueous phase, and a potential increase in the selectivity and sensitivity. Therefore, different derivatization reaction conditions (i.e. pH, temperature, reaction time and derivatizating reagent concentration) have been studied. Then, the main parameters affecting to the SPME process, that is coating selection, extraction time profile, extraction and desorption temperatures, have been optimized. Finally, a method based on a simple 2,4-dinitrophenylation reaction at pH 8–10, in 60 min at 75°C, coupled to direct SPME using PDMS-DVB fibres at 30°C for 45 min is proposed. The performance of the method provided a good linearity and precision data, and the detection limits were in the low ng L^{-1} level.

Keywords: *In situ* derivatization; Alkylthiols; SPME; 2,4-Dinitrophenylation; Dual GC-ECD/NPD

1. Introduction

Microbiological anaerobic degradation of organic matter in the aqueous environment leads to the formation of volatile compounds that can be released to the atmosphere, giving rise to unpleasant odours. Although many odorants may occur in water, the volatile sulphur compounds (VSCs) are one of the most relevant chemical classes [1].

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Natural emissions of alkylthiols are related mainly to the anaerobic degradation of sulphur-containing organic matter, such as sulpholipids or amino acids (i.e. methionine and cysteine). Moreover, industrial sources related to the petrochemical, tannery and pulp and paper production are the principal anthropogenic alkylthiol sources in the environment [2].

As they are very volatile compounds, headspace solid-phase microextraction (HS-SPME) coupled to gas chromatography (GC) is the most suitable technique for their determination at low concentrations in aqueous matrices. However, several factors make it difficult to analyse alkylthiols. In fact, they are extremely reactive compounds forming disulphides by oxidation at the GC injector port [2]. Their high reactivity as well as their volatility leads to irreversible losses during storage and analysis. To avoid these drawbacks, an *in situ* derivatization step previous to SPME and GC analysis appears to be the most convenient analytical approach. Derivatization increases both the analyte stability and the SPME water–fibre distribution coefficient as well as a reduction in the analyte volatility in comparison with the free forms (i.e. boiling points $<25^{\circ}C$ at n.c.). Therefore, an improvement in the GC separation, detection and quantification can be achieved by a suitable derivatization reaction.

A free –SH group can be protected as a thioether or a thioester, or oxidized to a symmetrical disulfide. In general, thioethers are formed by reaction of the thiol with a halide in basic solution and in ethanol as a solvent [3]. In fact, there are different organic compounds suitable to react with alkylthiols forming thioethers, but in almost all the cases, the reaction occurs in the organic phase. As target analytes are analysed in an aqueous matrix, a water-soluble derivatizating reagent is needed, so it can be spiked to the aqueous sample.

Dinitrophenylation of alkylthiols by reaction with 2,4-dinitrofluorobenzene (DNFB) is shown to yield stable GC amenable derivatives and displaying strong electron-capturing properties [4, 5]. This reagent has been widely used in structural and functional studies of peptides and proteins. Being a reactive aryl halide, it may react with several of the functional groups of proteins [6]. For instance, the sulphidryl group of cysteine can be selectively protected in the presence of the amino group by reaction with DNFB at basic pH [3]. Thiophenols and alkylthiols may react with other derivatizating reagents, such as 3,5-dinitrobenzoile chloride or 3-nitrophthalic anhydride to form thioesters. Mercury derivatives have also been employed, but they are less satisfactory than the above-mentioned derivatizating reagents [7].

Other problems related to alkylthiol determination are that the compounds are frequently present in wide concentration ranges (spanning several orders of magnitude). They occur in very complex aqueous matrices with high levels of other volatile organic compounds, which can lead to matrix effects that make quantification particularly challenging [2, 8, 9]. Because of all of these problems and in order to minimize them, working conditions such as pH, temperature and redox potential have to be carefully optimized.

Despite several papers dealing with their separation, the identification and determination of volatile sulphur compounds and alkylthiols in aqueous matrices are still problematic due to the high reactivity of the latter class of analytes leading to the formation of a variety of by-products along the analytical procedure [10]. Increasing importance is being attached to the selectivity in the choice of analytical procedures in order to enhance their sensitivity, since even low levels of these compounds can cause the above-mentioned problems. Several approaches are possible for the extraction

of alkylthiols, but almost all procedures involve a preconcentration step, in either water or air samples. Solid sorbent techniques and cryogenic trapping are the most widely applied methods for preconcentration of volatile compounds [11, 12]. In the present work, an *in situ* derivatization followed by an SPME method for the alkylthiol measurement in water is developed. Although SPME has been successfully applied for a wide range of organic compounds, there are very few papers dealing with the application of SPME to the analysis of volatile sulphide compounds in aqueous samples [1, 10].

The objectives of this study were to find a suitable derivatization reaction in the aqueous phase followed by an SPME preconcentration and dual GC-ECD/NPD determination. The derivatization reaction selected was the dinitrophenylation to obtain the corresponding thioether derivatives in the aqueous media [3–7]. Accordingly, the derivatization reaction conditions, such as pH, temperature, reaction time and derivatizating reagent concentration, were optimized. Direct SPME sampling has been used to preconcentrate analytes before they are thermally desorbed into the GC injector port. A detailed discussion of the SPME parameters (i.e. coating selection, extraction time and extraction as well as injector port temperatures) is provided along with linearity, precision, data accuracy and the associated matrix effects.

2. Experimental

2.1 *Reagents and materials*

The target compounds were all obtained from Sigma-Aldrich (Steinheim, Germany). Methylthiol (MeSH) was supplied in solid form as the methylsulfide sodium salt (MeSNa) (95%). The DNFB (99%) is also purchased as a solid, while ethylthiol (EtSH) (97%), 1-propylthiol (1-PrSH) (99%), 2-propylthiol (2-PrSH) (97%) and cyclopentylthiol (cycloPeSH) (98%) were supplied in the liquid form. NaOH was obtained from Carlo Erba (Milan, Italy). Alkylthiol individual standard solutions (2000–7000 mg L^{-1}) were prepared in MeOH Suprasolv, from Merck (Darmstadt, Germany). Individual (100 and 10 mg L^{-1}) and mixed standard solutions (from 100 mg L^{-1} to 50 μg L^{-1}) were obtained, diluting the individual solutions with MeOH. A 2,4-dinitrofluorobenzene stock solution (40 g L^{-1}) was prepared in toluene from Merck and then diluted 1:10, 1:100 in MeOH. Stock and working solutions were all stored at −20°C in the dark. The SPME holder and polydimethylsiloxane (PDMS 100 μm) and polydimethylsiloxane-divinylbenzene Stableflex^{TM} (PDMS-DVB 65 μm) fibres were obtained from Supelco (Bellefonte, USA). The fibres were conditioned as recommended by the manufacturer. After the conditioning process, a fibre blank was run to confirm that no other extraneous peaks co-eluted with the analytes.

2.2 *Sample handling*

Samples for method development were prepared by adding 6.5 mL of Milli Q water into a 7-mL vial, and the pH was adjusted with small volumes of a NaOH solution. A stir bar was added before vials were sealed with a PTFE septum and then spiked with known amounts of the working standard solution of the analytes, as well as an excess amount of the derivatizating reagent, by injection through the septum. Vials were

immersed in a thermostated water bath, and samples were magnetically stirred at 1100 rpm. The pH, temperature, reaction time and excess of derivatizating reagent concentration were studied in order to achieve the best reaction conditions. Samples were extracted with hexane (2×1 mL), and then these extracts were dried with anhydrous sodium sulphate and reduced in volume to 0.5 mL with a gentle stream of N_2.

Once the derivatization reaction was optimized, the main parameters that affect the SPME process (i.e. coating selection, extraction time profile, extraction temperature and desorption temperature) were optimized using a GC coupled to a dual detector of ECD and NPD. The fibre was exposed in the direct mode to the aqueous sample, after the derivatization reaction had taken place, by inserting the syringe through the septum and then immediately into the GC injector so that the chromatographic analysis could be carried out. The desorption time was set at 2 min.

2.3 *Instrumental analysis*

GC analysis was carried out with a Carlo Erba, Mega 5300 dual GC-ECD/NPD detection by splitting the column effluent into 1:1. The GC column used was a DB1701 (14% cyanopropylmethyl, 86% polydimethylsiloxane, $30\,m \times 0.25\,mm \times 0.25\,\mu m$, J&W Scientific, Folsom, USA). Samples were injected in the splitless mode for 2 min and 0.80 min in the SPME and solvent modes, respectively. Injector temperature was set at 250°C; the oven temperature was programmed at 50°C for 2 min, then at 15°C min^{-1} rate up to 150°C, then increased by 2°C min^{-1} until 200°C, and finally at 15°C min^{-1} until 280°C, were it was held for 5 min (total analysis time, 44 min). The ECD temperature was set at 280°C, and helium was employed as carrier gas at 1 mL min^{-1}.

3. Results and discussion

3.1 *Reaction optimization*

Derivatization reactions can convert polar analytes into their less polar analogues, therefore increasing their coating/water or coating/gas distribution coefficients leading to an improvement in the SPME efficiency and method sensitivity [13]. In the method developed, an *in situ* derivatization step was included so that analyte losses by volatility and reactivity could be minimized. The first experiments were conducted to evaluate the DNFB feasibility as a derivatizating reagent of alkylthiols, and also to test the ability of SPME to extract their derivatives from water samples. Two *in situ* derivatization-SPME procedures were tested: *in solution* and *in fibre derivatization* [13]. In the first approach, an excess amount of derivatizating reagent was spiked to a water sample in a sealed reaction vial. Following the derivatization reaction, the SPME fibre was introduced into the sample to extract the reaction derivatives. DNFB showed successful results when in-solution derivatization was tested. In the *in-fibre derivatization*, the polymeric coating of the SPME device acts as an organic medium where the reaction takes place. The fibre is exposed to the headspace of a vial containing the derivatizating reagent where the derivatization reagent is preconcentrated and then exposed to the sample vial. After the extraction time was reached, the fibre was transferred to the GC injector port. However, no successful results using DNFB for alkylthiol using in-fibre derivatization were obtained.

Once the *in situ* derivatization procedure was established, different reaction variables (i.e. pH, temperature, reaction time and derivatizating reagent concentration) were studied. The shorter the alkylthiol alkyl chain, the less favourable the derivatization reaction becomes. As MeSH and EtSH are the most volatile of all the target compounds, the reaction parameters are conditioned by their behaviour, and therefore, in the first part of this work, only the extraction of these two analytes was optimized.

3.1.1. Influence of pH and temperature. Experiments at pH 7, 8, 10 and 12 were performed to evaluate the pH effect in the derivatization reaction of alkylthiols in a pure aqueous sample. NaOH aqueous solution was used to achieve the pH values at the different levels. Figure 1 shows that pH does not affect to the analyte response. At alkaline pH, derivatization yield was similar or slightly higher than at neutral pH, so a pH between 8 and 10 was selected. Reaction was performed at different temperatures 30, 50 and 75°C, and the best responses were achieved working at the highest temperature. Therefore, 75°C was selected as the most appropriate reaction temperature.

3.1.2. Reaction time. The reaction time profile for the two alkylthiols is shown in figure 2. The reaction was performed at 15, 30, 60, 120, 180, 240 and 300 min. As can be seen, reaction times longer than 60 min did not lead to increased responses. Thus, 60 min was selected to complete the derivatizating reaction for all the analytes.

3.1.3. Influence of DNFB concentration. The reaction yields with DNFB were investigated using reagent concentrations from two to five times equivalent to the total molarity of the alkylthiols in the sample vial. Results shown in figure 3 indicated that it was not necessary to use a large derivatizating reagent excess because with a 2 : 1 molar ratio, the yield of the reaction products was the highest. Experiments have also indicated that reagent concentrations higher than twice the total alkylthiol concentration did not produce a higher derivativatization yield. Thus, a 2 : 1 ratio was selected in subsequent experiments.

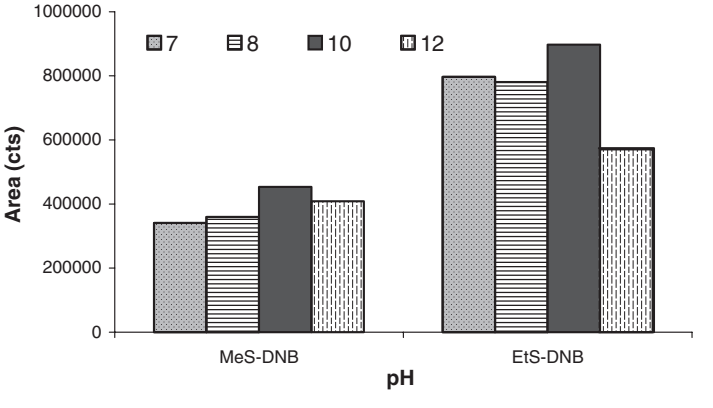

Figure 1. Influence of pH 7–12 in the derivatization reaction of methyl (MeSH) and ethyl (EtSH) thiols in aqueous samples as DNB derivatives.

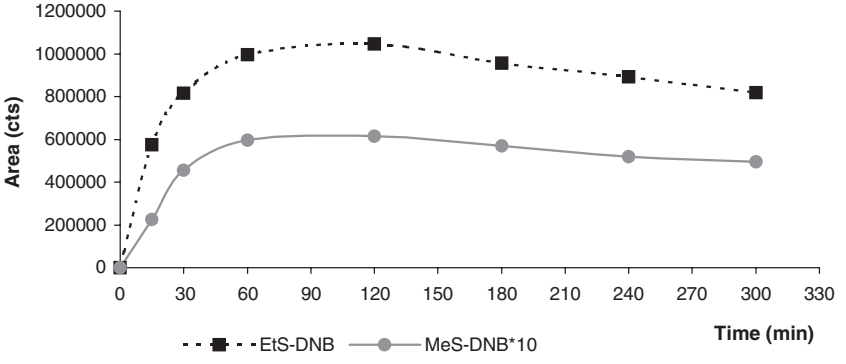

Figure 2. DNB derivatization reaction time of methyl (MeSH) and ethyl (EtSH) thiols in aqueous samples (The methyl thiol derivative response was multiplied by a factor of 10, in order to include both analytes with a similar scale in a single figure).

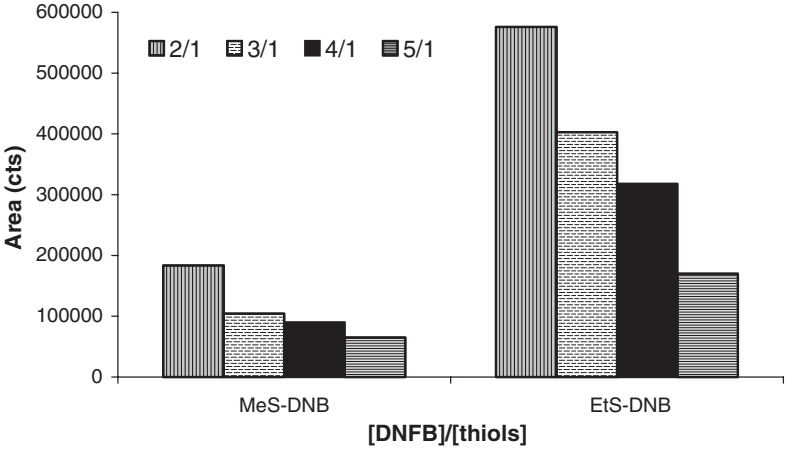

Figure 3. Influence of DNFB concentration on the derivatization yield of methyl (MeSH) and ethyl (EtSH) thiols in aqueous samples as DNB derivatives.

3.2 *Optimization of the SPME procedure*

As shown in the first part of the study, the best conditions for the derivatization reaction were with a 6.5 mL aqueous sample at pH 8–10, with agitation and at 75°C. About 60 min was sufficient to complete the derivatization reaction with a 200% derivatization reagent excess. Once the reaction parameters were fixed, different relevant parameters to the SPME procedure were evaluated. Desorption of the fibres in the injector port was performed at 230, 250 and 280°C. For all the analytes, the response increased from 230 to 250°C, but no significant improvements were obtained by increasing the injector temperature to 280°C. The optimum injector temperature was considered to be the lowest possible level at which all the derivatized analytes were totally desorbed. As no carryover effect was observed, 2 min was selected to achieve complete desorption at 250°C. Therefore, it would not be necessary to condition the fibre between each run, thus making the procedure less tedious.

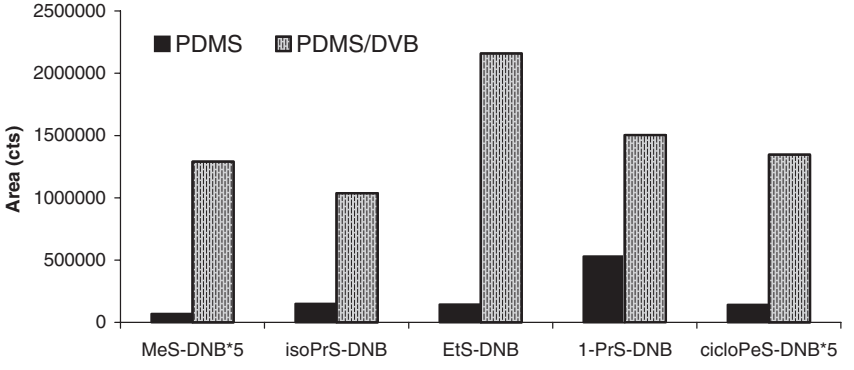

Figure 4. Comparison of the extraction efficiency of methyl (MeS), isopropyl (iso-Pr), ethyl (EtS), 1-propyl (1-Pr) and cyclopentyl (cyclo-PeS) as DNB derivatives with two different coating fibres: PDMS and PDMS/DVB, working in the direct extraction mode, at 30°C for 20 min. (The methyl and cyclopentyl thiol derivatives responses were multiplied by a factor of 5.)

3.2.1. Coating selection. The behaviour of two coating fibres for the analysis of derivatized alkylthiols, that is PDMS (100 µm) and PDMS-DVB (65 µm), was evaluated. The derivatization reaction with DNFB reduces the polarity of alkylthiols and improves the extraction efficiency. Experiments were carried out once the derivatization step was completed, exposing the fibre in direct SPME mode with agitation. The extraction time and temperature for these first experiments were initially set at 20 min and 30°C, respectively, and the fibres were desorbed for 2 min at 250°C in the injector port. The results are shown in figure 4. The responses obtained with PDMS-DVB were 10 times higher than the PDMS responses for all analytes. Consequently, PDMS-DVB fibre was selected for derivatized alkylthiols and was used for further optimization of derivatized thiol extraction.

3.2.2. Extraction temperature. Different extraction temperatures, 30, 50 and 75°C, were checked with the PDMS-DVB fibre. For all the compounds considered, responses decrease slightly as the temperature increases. Since extraction with PDMS-DVB fibre coating is an adsorption process, it is expected that an increase in the extraction temperature might have a negative influence on extraction yield. Therefore, 30°C was selected as an appropriate extraction temperature in subsequent experiments.

3.2.3. Extraction time. To investigate the extraction kinetics of the SPME process for the derivatized thiols from water, different extraction times (5, 10, 15, 30, 45 and 60 min) were tested at 30°C using the PDMS-DVB fibre. The extraction time profiles are shown in figure 5(a). For all the compounds investigated, the yields increased with increasing extraction time and the derivatized alkylthiols studied reached equilibrium in 45 min. The SPME process seemed to be a slightly slower for the derivatized EtSH, but considering that responses obtained at 45 min were close to those obtained in 60 min for further experiments, 45 min was selected as a suitable extraction time. The same kinetic study was performed with the same conditions but using the PDMS fibre coating instead of the PDMS-DVB. In this case, the

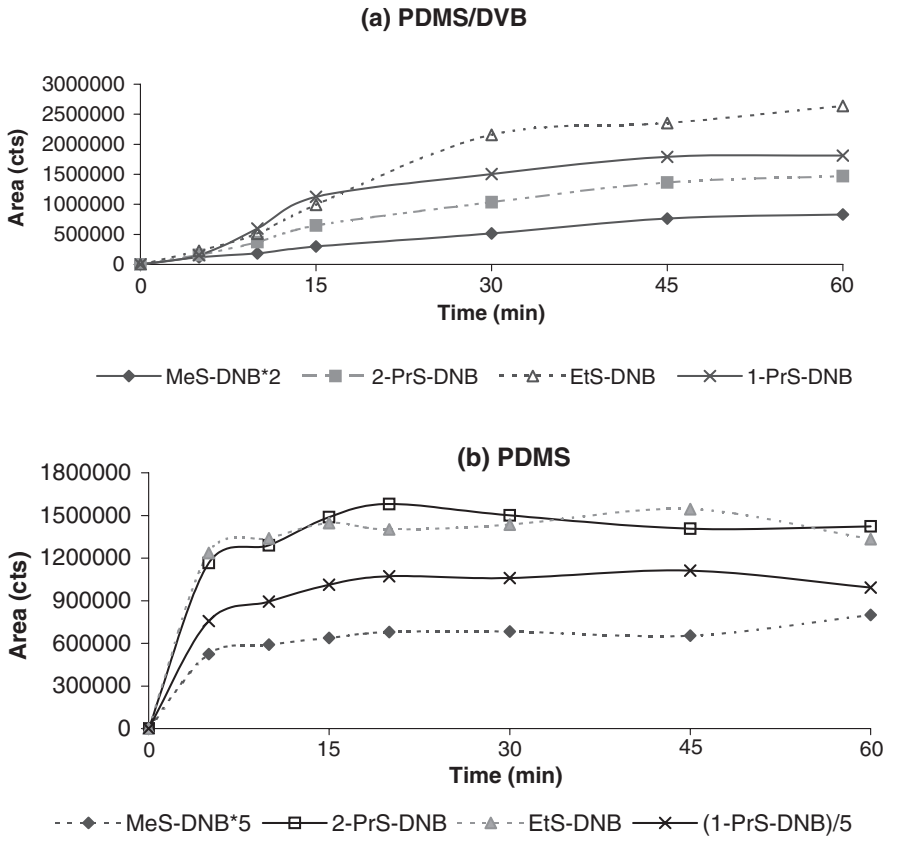

Figure 5. Extraction time profiles for the four derivatized alkylthiols using a (a) PDMS/DVB and (b) PDMS fibre coatings (immersion, 30°C, with agitation).

equilibrium was reached faster, as shown in figure 5(b), and 20 min was sufficient for all the target analytes. Although faster extraction processes were reached when a PDMS coating was used, the PDMS-DVB was finally selected as a more suitable fibre coating because it yields much higher responses, as mentioned in section 3.2.1.

3.2.4. Performance evaluation of the proposed method. Linearity, repeatability and detection limits were evaluated with a GC coupled to a dual detector: ECD/NPD in order to assess the performance of the *in situ* derivatization SPME method. The correlation coefficients (r^2) and the slopes of the calibration curves are shown in table 1, and an ECD chromatogram for a spiked water sample with $5\,\mu g\,L^{-1}$ is shown in figure 6, working under optimal conditions. The response was found to be linear with both detectors ($r^2 = 0.9903-0.9991$ for ECD and $r^2 = 0.9946-0.9994$ for NPD) over two orders of magnitude ($0.1-10\,\mu g\,L^{-1}$) for all compounds.

The precision of the experimental procedure was also evaluated with a time series of five consecutive determinations. The results were very repetitive with a relative standard deviation (RSD) ranging from 3.7 to 6.8% (table 1) calculated for a concentration level of $1\,\mu g\,L^{-1}$. Detection limits (signal-to-noise ratio of 3) and quantification

Table 1. Linearity, repeatability and limits of detection (LOD) and quantitation (LOQ) for the derivatizated thiols obtained by dual GC-ECD/NPD.

Compound	MeS-DNB		2-PrS-DNB		EtS-DNB		1-PrS-DNB	
DETECTOR	NPD	ECD	NPD	ECD	NPD	ECD	NPD	ECD
Slope	0.0941	0.1227	0.0246	0.0498	0.1239	0.2121	0.3423	0.4651
R^2	0.9962	0.9991	0.9952	0.9903	0.9946	0.9932	0.9994	0.9923
RSD (%) ($n=5$)	3.95	–	4.17	–	6.81	–	3.70	–
LOD (ng L^{-1})	14.3	11.4	27.2	22.4	18.3	18.4	28.0	6.8
LOQ (ng L^{-1})	47.7	38.1	90.6	74.8	61.1	61.4	93.4	22.6

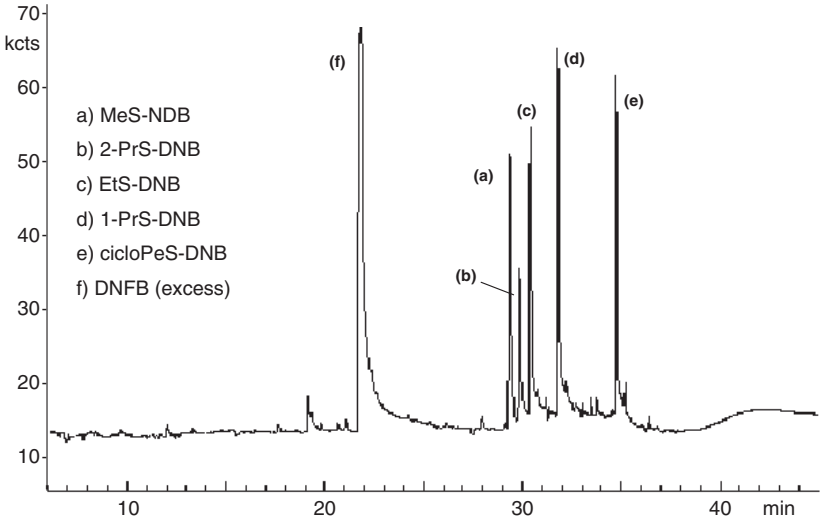

Figure 6. GC-ECD chromatogram showing the five derivatized thiols under optimized conditions (i.e. derivatization reaction at pH 8–10, in 60 min at 75°C adding an excess of DNFB of twice the total alkylthiol concentration; SPME using PDMS-DVB stable-flex fibres in immersion, at 30°C for 45 min and with agitation).

limits (signal-to-noise ratio of 10) were also evaluated and are presented in table 1 (in ng L^{-1} for all target compounds).

3.3 *Application to real samples and evaluation of matrix effects*

Wastewater samples, both influent and effluent collected from a constructed wetland serving a small community ≈200 habitants [14], were analysed to evaluate the method performance. Dimethylsulphides have already been detected in these wetlands, which is attributable to a prevailing sulphate reducing conditions [15]. Target analytes were below their detection limits, and so, the same aqueous samples were spiked, first with 5 and then with 100 μg L^{-1} of the studied analytes. Even though the high concentration of the target compounds was spiked to the samples, they were not detected, thus highlighting the strong matrix effects of these wastewater samples. Similar behaviour was also obtained when other real wastewater samples were analysed, in the influent and tertiary effluents (i.e. UV and chlorine disinfection) from an urban wastewater treatment plant and spiked groundwater samples.

As the method performance does not provide satisfactory results for the environmental applications evaluated, further research is needed to solve the matrix effects reported. The identification of alkyldisulfides in the spiked aqueous matrices could indicate that some matrix components could catalyse a fast alkylthiol oxidation reaction preventing the formation of the corresponding DNFB derivatives. The application of the developed procedure to other matrices such as food and fragrances that might contain alkylthiols should be evaluated to confirm the former hypothesis.

4. Conclusions

An *in situ* derivatization SPME procedure has been developed and optimized for the determination of alkylthiols in aqueous samples. Parameters that might affect the method performance have been optimized. Thus, a simple derivatization reaction was carried out at pH 8–10, in 60 min at 75°C and with a 2 : 1 DNFB/alkylthiol molar concentration ratio. Extraction of the derivatized analytes was finally carried out with a PDMS-DVB fibre coating for 45 min at 30°C. Desorption in the injector port was selected at 250°C for 2 min. The method provided good linearity and precision, and the detection and quantification limits were in the $\mu g\,L^{-1}$ level but limited to simple matrices.

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