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More about sampling and estimation of mercaptans in air samples

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ABSTRACT

Several strategies have been developed for sampling and determination of volatile thiols. The selectivity and sensitivity of the proposed methodologies are achieved by using a specific derivatizing reagent. The different procedures assayed are based on air sampling followed by derivatization of the analytes with OPA and isoleucine in alkaline solution. The derivatization products are separated and determined by liquid chromatography and fluorescence detection. To start, the derivatization conditions and stability of the derivates have been studied in order to establish the storage conditions. In general, the strategies studied consisted on trapping and detivatization the thiol compound on different support; a solution (Impinger) or sorbent (C_{18} cartridges or glass fiber filter). The analytical properties of the different strategies have been obtained and compared. Procedures are recommended upon specific situations.

1. Introduction

Mercaptans or thiol compounds are included in the reduced sulphur compounds (RSCs). They are introduced into the atmosphere by natural [1] (originated from the reduction of sulphate existing in aerobic waters and soils) and anthropogenic sources [2] (originated from fossil fuel burning, petrochemical industry or municipal sewage systems). These compounds have a potential role in the global atmospheric chemistry. RSCs can cause [3]: (1) environmental damage, including acid deposition and rapid acidification; (2) modifications in the sulphur flux in the atmosphere and (3) malodorous conditions in municipal sewage systems [4] or in bio industries [5]. Nowadays, odour or malodour, which refers to unpleasant smells, is considered an important environmental issue. Thus, during the last two decades it has increased the interest in the determination of thiol compounds in the atmosphere [6].

The analysis of these compounds in environmental matrices, especially in air samples, has several difficulties, including their low and broad range of concentrations, the complexity of the matrices and the highly reactive nature of the sulphur compounds [7,8]. The unstable and reactivity character of these compounds require a quicker and direct analysis; however, this is usually not possible due to their low concentrations, thus preconcentration or/and isolation steps must be included in the analytical procedure. Due to these reasons, especial precautions should be taken during the different steps of the analysis. In these analyses, the sampling and preconcentration steps play an important role. Usually, the presence of atmospheric oxidants (SO_2, O_3 and NO_x) can cause interferences, which should be considered in the sampling step. Besides that, the sampling vessels and the preconcentration materials used should be inert enough to reduce adsorptive loss and the transformation between compounds during the analysis (sampling, storage, etc). For these reasons there is a need to develop new procedures for determination of these reactive compounds.

Gas chromatography (GC) separation is generally suited for the selective determination of mercaptans in natural gas samples [7]. Different detectors, such as flame photometric detection (FPD), pulse flame photometric detection (PFPD), sulphur chemiluminescence detection (SCD), atomic emission detection (AED) o mass spectrometry (MS), have been proposed in the literature. Other separation methods such as ion chromatography [9] or HPLC (with derivatization) [10,11] are described in the literature. A gas sensor has also been proposed for the detection of *tert*-butyl mercaptan in artificial samples [12]. However the reliability of alternative methods for practical application on real environmental samples needs to be studied, in order to reach methodologies for in situ monitoring that help overcome time-consuming and tedious process of sampling or enrichment. Therefore, there is still a very strong demand for novel, simple, rapid and stable methodologies for monitoring mercaptans in the air.

The determination of thiol compounds by liquid chromatography usually requires thiol derivatization to a stable state and analyzed the derivatization products with increased sensitivity.

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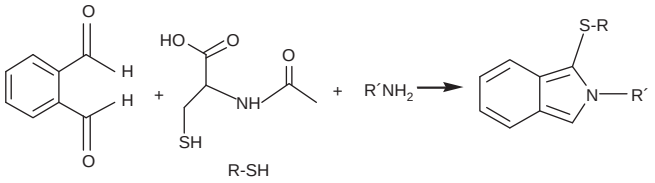

Fig. 1. The reaction scheme of mercaptans with OPA in the presence of amine.

Several reagents such as 5,5′-dithiobis(2-nitrobenzoic acid) (Ellman's reagent) [13], 7-fluoro-4-nitro-2,1,3-benzoxadiazole (NBD-Cl) [14,15], *p*-hydroxymercurybenzoate (PHMB) [11] have been employed for derivatization of thiol compounds in several matrices (specially in biological samples). The PHMB [11] has been used as the derivatization of thiols in air sampling using an impinger system for sampling and derivatization. The *o*-phthalaldehyde (OPA) reaction for primary amines in presence of thiol is well known (Fig. 1) [16]. This reaction can also be used for thiol determination in presence of a primary amine. The suitability of isoindole formation to monitor thiols in air samples was first examined. Several procedures are described in the literature for the determination of thiol compounds in biological or food samples. The derivatization products were determined by fluorescence *o* by chemiluminescence [17,18].

Several strategies are proposed in this paper for sampling and storage of volatile thiols by trapping and preconcentration the analytes on a solution, a cartridge (C_{18} sorbent) or a glass fiber filter containing alkaline solution in presence of OPA and isoleucine. The thiol compounds are trapped by forming OPA–isoluecine–thiol derivates. First, the optimal derivatization conditions for thiols with OPA and isoleucine have been studied. The thiols-derivates, which are stable, can be separated by HPLC (C_{18} column) coupled with fluorescence detector. Different strategies have been tested and compared. The advantages and disadvantages of the different systems are explained.

2. Experimental section

2.1. Reagents and solutions

Thiophenol (phenyl mercaptan), 1-pentanethiol (amyl mercaptan), 2-methyl benzene thiol (*o*-thiocresol), ethane thiol (ethyl mercaptan), phenylmetathiol (benzyl mercaptan) and 1-propanethiol (propyl mercaptan) were obtained from Sigma (St Louis, MO, USA). 2-Propene-1-thiol (Allyl mercaptan) was from Fluka Chemike (Steinhein, Germany). *o*-Phthalaldehide was obtained from Sigma-Chemie (Steinhein, Germany), isoleucine was purchased from Guinama (Valencia, Spain). Boric acid, phosphoric acid and sodium hydroxide were from Panreac (Barcelona, Spain). Methanol and acetonitrile HPLC grade were purchased from J.T. Baker (Deventer, Holland).

Mercaptans standard solutions were prepared at different concentrations by dissolving the pure compound in methanol [11]. Dilutions at different concentration levels were obtained in methanol. Solutions of mercaptans were prepared daily and were kept in dark at 4 °C. OPA reagent (7.2×10^{-2} M) was prepared by dissolving the appropriate amount in water with 1% of methanol, and isoleucine (7.4×10^{-2} M) reagent was prepared in water. Owing to the instability OPA–isoleucine reagent, these solutions were prepared daily. All these solutions were stored in the dark at 4 °C.

Borate buffer at pH 10 was prepared by dissolving the necessary amounts of boric acid and adjusting pH with NaOH 1 M.

2.2. Apparatus

The chromatographic system consisted of a quaternary pump (1100 Series) (Hewlett-Packard, Palo Alto, CA, USA), a 100 µl sample loop injector and a high-pressure six port vale (Rheodyne model 7000). A fluorescence detector (Hewlett-Packard 1050 series) was coupled in series and link to a data system (Hewlett-Packard, HPLC Chemstation). Excitation and emission wavelengths for mercaptans derivatized OPA/isoleucine were 330 and 440 nm, respectively. The analytical column was a LiChrosphere 100 RP 18 125 mm × 4 mm i.d (5 µm) (Merk, Darmstadt Germany).

The mobile phase used was a mixture of methanol: water in gradient elution mode (25:75 at $t=0$ min, 100:0 at $t=15$ min, 100:0 at $t=17$ min and 25:75 at $t=19$ min) with a flow of 1 ml/min.

Air sampling was done with a portable Buck-Genie VSS 5-pump from A.P. Buck (USA). The pump dimensions were 146 mm height × 102 mm width × 50 deep, and its weight was 0.652 kg. For flow measurement a Multicom KS flow-meter (Dräger, Germany) was used.

SPE Bond Elut C_{18} cartridges 100 mg (Variant, Habor City, CA, USA) and Glass Fiber prefilters AP20025000 (25 × 13 mm) (Carrigtwohill, Ireland). The filters were cut in four pieces and were coupled to the syringe.

2.3. Procedure

2.3.1. Thiol solution derivatization

In a vial were mixed the thiol solution of known concentration, and of nanopure water up to 1.6 ml, 0.4 ml of 0.5 M buffer borate (pH=10), and in final the reagents 0.1 ml OPA (7.4×10^{-2} M) and 0.1 ml isoleucine (7.4×10^{-2} M). Analytical signals were recorded after 5 min of reaction, taking as $t=0$ the addition of last drop of reagent.

2.3.2. Active sampling with impingerflaks

Gas was trapped in an impingerflask containing 6.5 ml of water, 0.625 ml of OPA (7.4×10^{-2} M), 0.625 ml of isoleucine (7.4×10^{-2} M), and 0.4 ml of borate buffer at pH 10. Fig. 2**A** shows the schematic diagram of the air sampling system used. After connecting the pump, 10 µl of working standard solution of thiol and 50 µl of methanol solution were put in the beginning of the air path. For evaporation and sampling, the time selected was 30 min at flow rate of 260 cm^3/min.

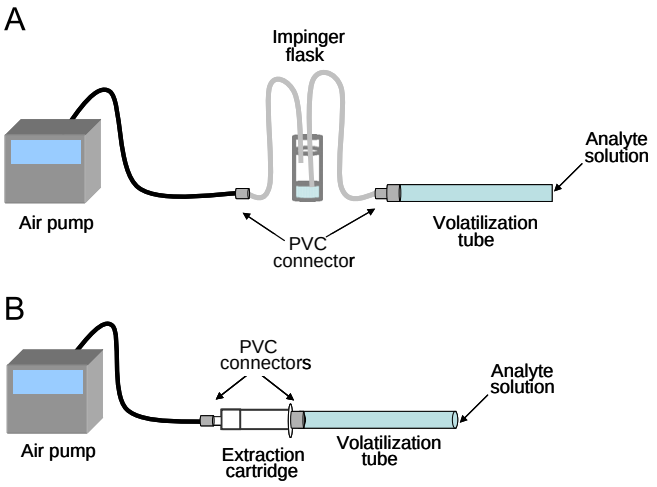

Fig. 2. (**A**) Sampling system used with the impinger flaks, (**B**) sampling system used with SPE cartridges. For both figures the volatilization tube is necessary only for calibration. (**C**) Sampling system used with glass fiber supports.

2.4. Active sampling with C_{18} SPE cartridges and derivatization

2.4.1. Procedure 1. Thiol retention followed by OPA–isoleucine derivatization

A set of six Bond Elut C18 100 mg cartridges (Varian, Habor City, CA, USA) (100 mg) were conditioned with 1 ml of methanol, followed by 1.0 ml of nanopure water, and 0.5 ml of thiol solution. These cartridges were kept at 4 °C. Each of these cartridges were derivatized at different times (2 min, 4 min and 12 min) by adding a mixture of (0.4 ml borate buffer pH 10, 0.1 ml of the OPA, 0.1 ml of isoleucine) into the cartridges. After 10 min, the derivates were eluted from the C_{18} cartridge with 0.5 ml of methanol. The final concentrations of thiols were in the range of 10 to 200 mg/ml.

2.4.2. Procedure 2. OPA–isoleucine followed by thiol addition

This procedure was performed as the procedure 1, but the reagents were introduced into the cartridges previously to the addition of the thiol (aliquots o gas sample) Fig. 2B. The procedure continued as it was described for procedure 1.

2.5. Active sampling with glass fiber filters

2.5.1. Procedure 1

A volume of 10 μl of thiol solution were spotted on a glass fiber prefilters activated with water. After, the filter was placed in a vial containing 1 ml of water, 0.4 ml of borate buffer (pH 10), 0.1 ml of OPA (7.4×10^{-2} M) and 0.1 ml of isolueucine (7.4×10^{-2} M). After 10 min the derivates were processed.

2.5.2. Procedure 2

A volume of 0.1 ml of a mixture reagent (0.4 ml of borate buffer (pH 10), 0.1 ml of OPA (7.4×10^{-2} M) and 0.1 ml of isolueucine (7.4×10^{-2} M)) was added over a glass fiber prefilters. Then aliquots o gas samples were pass through the filter. After 10 min of reaction, the filter was place in a 0.5 ml of MeOH during 3 min in agitation.

In all procedures, the extracted derivates were injected in the chromatographic system (100 μl). Blanks solutions were prepared for the different procedures.

3. Results and discussion

3.1. Thiol derivatization procedure

–SH containing species can react with *o*-phthalaldehide (OPA) in the presence of an amine and basic pH, to produce highly fluorescent isoindole fluorophores. The suitability of isoindole formation to monitor thiols was first examined. In previous papers, we have studied the determination of amines by using OPA and *n*-acetyl-cysteine (NAC) as derivatization reagent [19,20]. Based on the conditions established for amines, the optimization reaction for thiol compounds have been developed using isoleucine as amine. Several thiols (see Section 2) were used in the optimization procedure. The tested parameters were the OPA concentration and OPA/thiol ratio, formation time and stability. The response (analytical signal) of the formed derivates in solution were monitored with a diode array spectrophotomer or/and with HPLC coupled with fluorescence detector. The best sensibility was obtained with OPA 4.6×10^{-3} M and ratio OPA: isoleucine (1:1). As can be seen in Fig. 3, the reaction time was studied between 2, 5, 15 and 30 min. It was observed that the formation of derivates reach the maximum between 2 and 5 min. According to these results 5 min were selected as the optimum time. These conditions are already an improvement regarding others proposed in the literature which normally take longer reaction times [21].

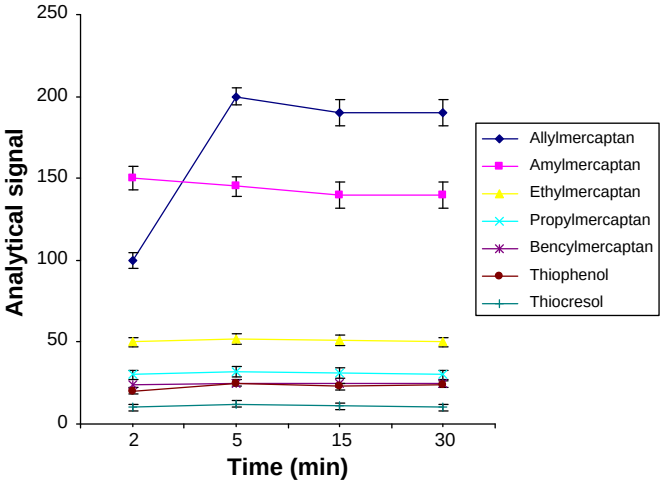

Fig. 3. Analytical signal (area) of the isoindole derivate at different reaction times. Conditions: OPA (4.6×10^{-3}) M:isoleucine (4.6×10^{-3}) M (1:1), analyte concentrations: thiocresol 6 ppm, thiophenol 50 ppm, bencylmercaptan 250 ppb, propylmercaptan 50 ppb, ethylmercaptan 70 ppb, amylmercaptan 250 ppb, allylmercaptan 400 ppb.

Taking into account that one of the main disadvantages of the derivatización procedures is the instability, the derivate stability was studied from 10 min to 14 days after the reaction (maximum time studied). The thiol derivatized solutions were stored at 4 °C. Working at these conditions, the derivates were formed in 5 min and were stables within the working day if kept at room temperature, or for 14 days (maximum time studied) if stored at 4 °C. This represents an important feature of the analytical method considering the problems involved in sampling and storage of thiols [7,8]. Table 1 shows the calibration graphs, the limit of detection, the precision obtained in the optimized conditions. As it can be seen several thiol compounds were assayed and the sensitivity was higher for alkylthiol such as ethanethiol, propanethiol and pentathiol. Thus, fluorogenic reaction gave intense fluorescence for aliphatic thiols while aromatic thiols exhibit weaker fluorescence (other thiols, such as thiophenol and thiocresol were assayed and they presented low sensitivity). No differences were observed when the compounds were processed individually or in presence of other thiol compounds.

3.2. Active sampling with impinger flasks

The stability of mercaptans in water solutions is strongly affected by the temperature and storage time. This stability is also dependent on the pH solutions being more unstable at neutral and basic pH. On the other hand, the pK_as of these compounds are around 10, and basic conditions will be needed to trap them into the solution. Taking into account all these factors, we propose to pass the gas through a solution containing 10 ml of OPA:isoleucine and boric acid at pH 10 in an impinger flask for sampling. Working at these conditions, 30 min were required to recover the thiol in the derivatization solution. Gaseous standard of thiols, each one generated according to the conditions described in Section 2, were processed in order to obtain relevant analytical data. For quantification purposes the fluorescence signal of the derivates was registered. Lineal calibration graphs were obtained over the tested concentration (Table 2). It can be observed that calibration curves for gaseous and aqueous samples were statistically equivalent (at the confidence level of 95%) This proves that under the proposed conditions, the thiols assayed

Table 1
Calibration graphs and some analytical parameters corresponding for different thiols by performing solution derivatization.

Compound	Calibration graphs equations ($y=a+b\times x$ μg/l)	LODs (ppb)	Intra-day ($n=3$)	Inter-day ($n>7$)
Ethane thiol (ethylmercaptan)	$a\pm Sa$: $0.1009\pm1.8\times10^{-04}$ $b\pm Sb$: 0.4782 ± 0.005 $R^2=0.9999$	0.6	1.2	1.7
1-Propanethiol (propylmercaptan)	$a\pm Sa$: $0.1103\pm1.5\times10^{-04}$ $b\pm Sb$: 0.591 ± 0.07 $R^2=0.999$	0.6	1.4	1.8
1-Pentanethiol (amylmercaptan)	$a\pm Sa$: $0.1511\pm3\times10^{-04}$ $b\pm Sb$: 0.8138 ± 0.008 $R^2=0.998$	0.25	1.09	1.2
2-Proprane-1-thiol (alylmercaptan)	$a\pm Sa$: $0.1213\pm1.6\times10^{-04}$ $b\pm Sb$: 0.666 ± 0.017 $R^2=0.999$	0.6	0.2	0.7
Phenylmethathiol (bencylmercaptan)	$a\pm Sa$: $0.1578\pm2\times10^{-05}$ $b\pm Sb$: 0.2047 ± 0.0008 $R^2=0.997$	1	1.2	1.7

Table 2
Calibration graphs corresponding to different thiols by performing solution derivatization in aqueous solution and in air (expressed in μg).

Compound	Calibration graphs equations (area vs μg of thiol) ($y=a+b\times x$)	
	Aqueous standards	Air standards
Ethane thiol (ethylmercaptan)	$a\pm Sa$: $0.1009\pm1.8\times10^{-04}$ $b\pm Sb$: 0.4782 ± 0.005 $R^2=0.9999$	$a\pm Sa$: $0.0984\pm2.5\times10^{-04}$ $b\pm Sb$: 0.4851 ± 0.04 $R^2=0.998$
1-Pentanethiol (amylmercaptan)	$a\pm Sa$: $0.1511\pm3\times10^{-04}$ $b\pm Sb$: 0.8138 ± 0.008 $R^2=0.998$	$a\pm Sa$: $0.209\pm5\times10^{-03}$ $b\pm Sb$: 0.805 ± 0.05 $R^2=0.995$

Table 3
LODs in solution and in air samples of the different mercaptans assayed.

Compound	$LODs_{(in\ solution\ \mu g)}$	$LODs_{(\mu M*10^{-4})}$	$LODs_{air\ \mu g/m^{3(*)}}$
Ethane thiol	0.06	9.7	0.77
1-Propanethiol	0.06	7.9	0.77
1-Pentanethiol	0.025	5.8	0.32
2-Propane-1-thiol	0.06	3.4	0.77
Phenylmetathiol	0.1	4.8	1.28

* Considering a flow rate of 260 cm^3/min during 30 min.

were volatilized and derivatized in the OPA–isoleucine solution. Thus, it demonstrated that aqueous standards could be used to determine thiols in air samples. This methodology has been already proposed by this research group for determination of amines in air samples [22]. This is also the case where silica gel is the adsorbent [23]. In Table 3 are shown the detections limits corresponding to processing 260 cm^3/min of air during 30 min.

This reagent solution (OPA–isoleucine at pH 10) was used to analyse several air samples by flushing (with syringe) the air samples into the solution. Different sample volumes (ranged from 15 μl to 10 ml) of the head space of a bottle containing thiol were processed and a good reactivity was observed. A linear behaviour was observed between the analytical signal (area) and the volume of sample processed (up to 1 ml). At higher volumes the chart was non-linear due to the high concentration. The calibration graphs obtained were: for ethylmercaptan (area: 20+9977 vol (ml) (ethylmercaptan) $R^2=1$ $n=4$), and for propylmercaptan (area: 8.36+3080 vol (ml) (propylmercaptan) $R^2=0.9971$ $n=4$). Fig. 4**A** are shown the chromatograms corresponding to the a blank (flushing 1 ml of clean air into the solution (A), a volume of the head space of solutions of ethylmercaptan 4300 mg/l (B) or propylmercaptan (C) and standard solution (D). The first peak of all the chromatograms corresponds to the free reagent (blank peak). Although

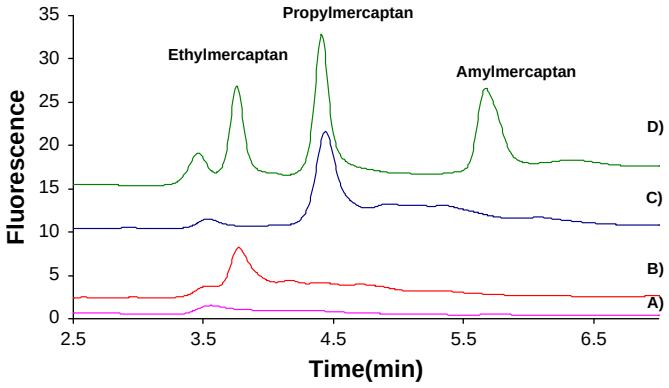

Fig. 4. Chromatograms corresponding to absorption of thiols in a solution of OPA–isoleucine–borate buffer. (A) Air blank (flushing 1 ml of clean air in the solution), (B) processing 15 μl of the head space of a ethylmercaptan solution, (C) processing 25 μl of the head space of propylmercaptan solution, (D) standard with ethylmercaptan (0.10 μg m^{-3}), propylmercaptan (0.12 μg m^{-3}) and amylmercaptan (0.10 μg m^{-3}); for conditions see text.

methylmercaptan has not been included in the analyzed thiols, it is expected that this thiol will react with OPA:isoluecine and gave a peak in the first part of the chromatogram. As can be seen in the samples (chromatogram B and C) appear the peak corresponding to the ethylmercaptan or propylmercaptan and the blank peak. The concentration of ethylmercaptan in the sample was 0.196 ± 0.05 mg/l and 0.173 ± 0.08 mg/l for propylmercaptan.

3.3. Active sampling with SPE C_{18} cartridges

Air sampling into SPE cartridges can be used for a variety of compounds provided that they can be efficiently retained in the extractive phase. However, it is particularly useful for analytes

that require chemical transformation before the measurement step, because the derivatization can be carried out inside the cartridge. This form of derivatization, originally developed for the analysis of amino-compounds in aqueous matrices, is compatible with different reagents commonly used in UV/vis spectroscopy and spectrofluorimetry, and offers some advantages over conventional solution derivatizations such as improved reaction yields and simplification of the entire analytical process.

In order to test the capabilities of SPE in sampling of thiols and derivatization, several alternatives were tested using C_{18} as sorbent. The aim of this study was to test the possibilities of using C_{18} in the sampling and derivatization of thiol compounds by using OPA–isoleucine. First, the retention and elution of the isoindole derivate from the sorbent was studied. These derivates were eluted from the cartridges by passing 0.5 ml of MeOH. The recoveries obtained were: 72 ± 5, 85 ± 4 and 86 ± 7 for ethylmercaptan, propylmercaptan and amylmercaptan, respectively.

Several strategies were tested: (1) retention of thiol compounds in the sorbent followed by the derivatization step (by adding the reagents OPA–isolucine and borate buffer), (2) inmovilization of the reagents on the C_{18} followed by the addition of the analytes (see Section 2 for further details). In both situations the reaction takes place into the cartridges. Following the first procedure, the thiol compounds are retained into the cartridges, although they were instable. Respect the second strategy, the reagents also presented instability in the cartridges depending on the time. Fig. 5 compares the signals obtained for propylmercaptan by using the two different procedures. The behaviour observed was similar for the other thiols assayed. The thiols are quickly degraded, being its degradation higher than the reagents. The reagents in the cartridges are stable for 1 h. In terms of sensitivity, this was higher when the cartridges contained the reagents previously to the addition of the analytes. According to these results, it is convenient to trap the analytes after the immobilization of the reagent into the cartridges. This procedure can be applied for active sampling and derivatization if the reagent addition is performed just before the sampling. The derivates were stable in the cartridges for 1 h. After the elution from the cartridges, the derivates can be stored at -20 °C. If this procedure is compared with impinger sampling and derivatization, the chromatograms corresponding to the blank solutions presented more impurities than those obtained by using impinger. According to this, although the sensitivity obtained was higher (ranged between 1.6 and 2 higher than that corresponding to the impinger procedure) the detection limits obtained were higher.

3.4. Active sampling on glass fibre filter

Two different procedures were assayed. In *procedure 1*, thiol compounds were retained on a glass fiber filter. As in the C_{18} cartridges-based method, the thiols were unstable when the filter was pre-conditioned in neutral medium. Consequently, in *procedure 2*, the reagent solution (OPA–isoleucine–borate buffer of pH 10.0) was sorbed in the filter, and then, exposed to the samples. In order to perform the standard calibration graphs, a small amount of thiol solution was deposited on the filter. After 10 min of reaction time, the filter was immersed in 0.5 ml of MeOH during 3 min with agitation. The extraction solution was injected in the chromatographic system. The sensitivity obtained with this procedure was lower than that obtained with the other procedures (solution derivatization or derivatization into the cartridges), being 17 ± 1, 20 ± 1 and 64 ± 2, for ethylmercaptan, propylmercaptan and amylmercaptan, respectively (calculated by comparing the slope of the calibration graphs between this procedure and solution derivatization–impinger).

Similar to the other procedures, different gas volumes of the sample (head space of amylmercaptan solution) were passed though the filter and a linear relation was obtained between the analytical signal and the sample volume processed. Fig. 6 shows the chromatograms obtained under such conditions for a standard solution (A) and 30 ml of the head space of amylmercaptan solution (B) and a blank (30 ml of an air sample (C). As can be seen in this figure, the peak corresponding to the amylmercaptan appears in the sample and the found amount was of 0.09 μg.

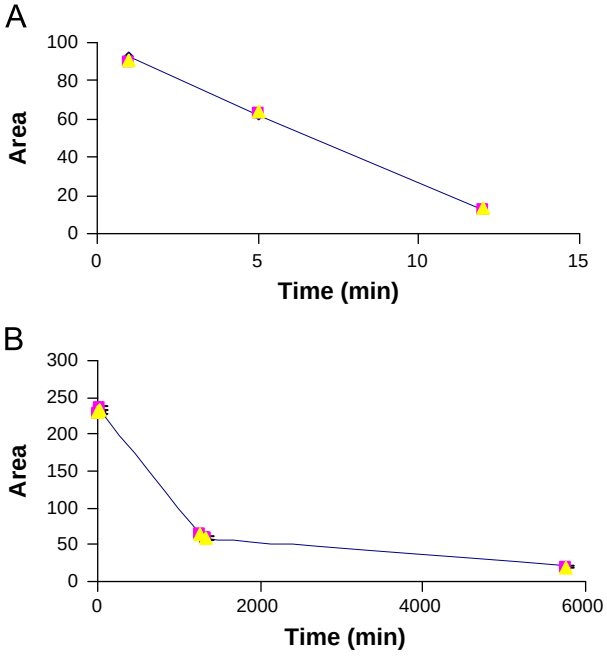

Fig. 5. Analytical response of propylthiol (100 ppb) vs time (min): (A) sampling and latter derivatization into the C_{18} cartridges (B) retention of the reagent into the cartridges followed by sampling at different times (several replicates).

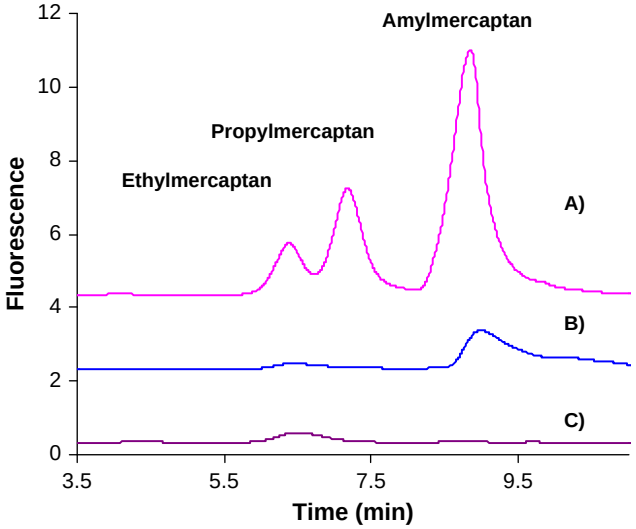

Fig. 6. Chromatogram corresponding to thiols sampling in a glass fiber filter impregnated with a mixture of OPA–isoleucine–borate buffer. (A) Standard with ethylmercaptan (0.45 μg), propylmercaptan (0.6 μg) and amylmercaptan (0.5 μg), (B) air sample (injecting 30 ml of air sample (head space of a amylmercaptan solution (25 mg/l)) in the absorbent solution) and (C) air blank (flushing 30 ml of clean air in the solution). For experimental conditions see text.

Table 4
Comparison of different properties of the procedures assayed.

Steps	Impinger	Solid support C_{18}[a]	Glass fibre[b]
In situ	Mixing reagents, sampling, derivatization	Cartridge preparation, sampling, derivatization, extraction	Fiber preparation, Sampling derivatization, extraction
Transport	Keep at 4 °C	Keep at 4 °C	Keep at 4 °C
Laboratory	Determination	Determination	Determination
LOD ($\mu g/m^3$)	1	–	100
Working range	μg/l–10 mg/l	μg/l–10 mg/l	1 mg/l–100 mg/l
Sensitivity	++	+++	+
Rapidity	+	++	+++
Cost	++	+	+++
In situ	+++	+++	+++

[a] Considering a flow rate of 260 cm^3/min during 30 min.
[b] Considering a sample volume of 30 cm^3.

3.5. Comparative study of the different strategies

In Table 3 are compared the main analytical properties for the different strategies assayed. The lowest limit of detection can be reached by using the impinger system, followed by derivatization in the cartridges C_{18} and glass fiber filter Table 4. Although, all procedures can be used for sampling and derivatization in situ, the recommended methodology is the impinger procedure, based on solution derivatization, due to the higher stability of the derivates. The glass fiber filter is the most economical and quicker procedure, however the sensitivity and LODs are higher, respect to the other procedures. Thus, the procedure to select will be depending on the concentrations expected in the sample. All the procedures can be used for active sampling. However, the glass fiber procedure could be an alternative for passive sampling that will require further experiments.

4. Conclusions

The reaction of thiol (R-SH) compounds with OPA and isoluecine represents a useful improvement in the analysis of sulphur compounds in air. The strategy of trapping/preconcentration/derivatization forming stable complexes allows minimizing some of the analytical problems of this analysis (their volatility and their instability). The material used avoids any losses due to the adsorption onto metal surfaces, or oxidation process.

In this paper it has been established the optimal conditions for derivatization of thiol compounds with OPA and several alternatives have been studied in order to perform a procedure for sampling and derivatization of these compounds in air samples. The study of the analytical procedures has been focussed on the development of effective active sampling. Active sampling system using impinger flasks has been successfully. The use of C_{18} SPE cartridges has also been tested showing good results as active sampling systems when the reagents were previously retained in the cartridges. The success on the application of the proposed procedures also came from the use of selective derivatization reactions that provided the selectivity and sensitivity required for the analysis of the target analytes. Detection limits at low μg have been achieved with impinger and SPE procedures. These studies could help to resolve the difficulties existing in the sampling and determination of thiol compounds, and show new strategies in this field.

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