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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 derivatives have been studied in order to establish the storage conditions. In general, the strategies studied consisted on trapping and derivatization the thiol compound on different support; a solution (Impinger) or sorbent (C₁₈ cartridges or glass fiber filter). The analytical properties of the different strategies have been obtained and compared. Procedures are recommended upon specific situations.

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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 (SO₂, O₃ 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) or 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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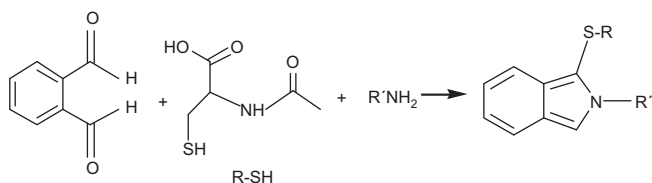


Fig. 1. The reaction scheme of mercaptans with OPA in the presence of amine.

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 or 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–isoleucine–thiol derivatives. 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 (Steinheim, Germany). *o*-Phthalaldehyde was obtained from Sigma-Chemie (Steinheim, 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 μ l sample loop injector and a high-pressure six port valve (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 \times 4 mm i.d (5 μ m) (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 \times 102 mm width \times 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, Harbor City, CA, USA) and Glass Fiber prefilters AP20025000 (25 \times 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. 2A shows the schematic diagram of the air sampling system used. After connecting the pump, 10 μ l of working standard solution of thiol and 50 μ l 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 .

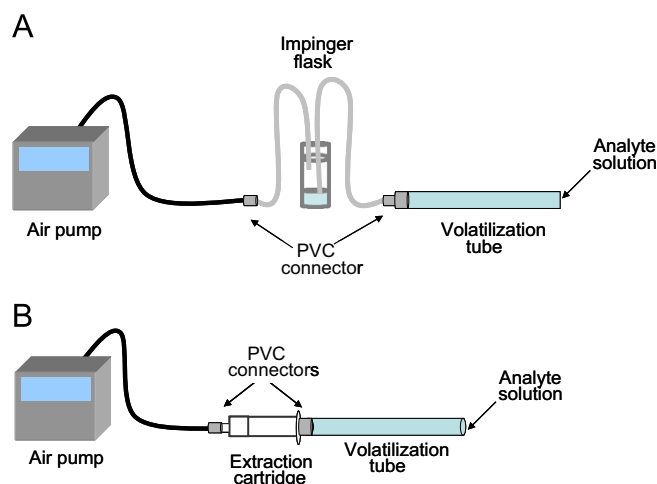


Fig. 2. (A) Sampling system used with the impinger flaks, (B) sampling system used with SPE cartridges. For both figures the volatilization tube is necessary only for calibration. (C) Sampling system used with glass fiber supports.

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