DEVELOPMENT OF A GAS CHROMATOGRAPHY – MASS SPECTROMETRY METHOD FOR THE DETERMINATION OF CARBON DISULFIDE IN THE ATMOSPHERE


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Abstract

Carbon disulfide (CS₂), a relevant reduced sulfur compound in air, is well-known for its malodor and its significant effect on global atmospheric chemistry. Therefore, a reliable method for determining CS₂ in atmospheric samples has been developed based on solid-phase sampling and gas chromatography - mass spectrometry (GC-MS). Two types of solid-phase sampling supports (Orbo-32 and SKC) and the elution with organic solvents - hexane and toluene - were evaluated for low-volume outdoor sampling. Recovery studies and the standard addition method were carried out to demonstrate the proper determination of CS₂ in the absence of the influence of interferences such as ozone, hydrogen sulfide or water – important atmospheric pollutants -. The proposed methodology was validated by performing experiments in a high-volume smog chamber and by comparison with two reference optical methods, Fourier Transform Infrared (FTIR) and Differential Optical Absorption Spectroscopy (DOAS). Satisfactory analytical parameters were reported: fast analysis, a correct repeatability of 6 ± 1 % and reproducibility of 14 ± 3 %, and low detection limits of 0.3 – 0.9 pg m⁻³. Finally, the method was successfully applied to industrial samples near a pulp factory area, where a high correlation between industrial emissions and reported carbon disulfide concentrations were observed.

Keywords: Carbon disulfide, atmospheric samples, solid-phase sampling, gas chromatography - mass spectrometry, pulp emissions.
1. Introduction

Considerable effort is needed for the precise determination of reduced sulfur compounds or volatile sulfur compounds (VSC) in air because of their role in global atmospheric chemistry. These compounds present a high impact due to they have a strong potential to be oxidized to secondary pollutants and they are often considered to exert influence on the Earth’s radiation budget and climate forcing [1]. Moreover, if these sulfur compounds are present in excess quantities, they can cause social and health problems due to their malodor and human toxic properties [2].

The most abundant sulfur compounds in the environment include carbon disulfide (CS$_2$), hydrogen sulfide (H$_2$S), carbonyl sulfide, methane thiol, dimethyl sulfide and dimethyl disulfide [3]. Their origin can be from natural and/or biogenic sources as volcanic activities, ocean, vegetation and from anthropogenic sources as chemical plants, oil refineries, sewage treatments, landfills, livestock facilities, industries, etc [4,5]. Although carbon disulfide (bp. 46 ºC) is a minor component, when is oxidized it produces carbonyl sulfide which contributes to the stratospheric aerosol loading. Moreover, the CS$_2$ mal odor and important effects on human health have led to restrictive regulation controlling this pollutant [2], particularly to protect areas influenced by pulp industries. The sequence of physical and chemical transformations taking place in these factories is extremely complex, but the main reaction is the regeneration of cellulose by the action of sulfuric acid, forming sodium sulfate and carbon disulfide, very significant levels. Other processes in the pulp industry produce by-products such as hydrogen disulfide and more carbon disulfide, which depend on the viscose age of pulp [6]. Due to the impact on the population by the sulfur emissions of these types of plants must to be controlled. For that, a reliable methodology for CS$_2$ sampling and analysis is required.

The determination of CS$_2$ in environmental samples is still a great challenge. The main difficulties are that this pollutant is highly reactive and it is present in the atmosphere at low concentrations - at levels of ng m$^{-3}$ to μg m$^{-3}$. For that, a pre-concentration step to achieve adequate detection limit and a suitable pre-treatment to avoid decomposition or losses are required. In addition, interferences caused by atmospheric oxidants such as SO$_2$, O$_3$, humidity, NO$_x$ and others are common in environmental air. The use of scrubbers has been proposed to control and avoid these pollutants, but they introduce more variability in the sampling process, reducing the sampling flow and altering the caption and retention of the sulfur compounds onto the sampling surface [1].
Several researchers have studied the collection of reduced sulfur compounds, including carbon disulfide, from air matrices using different types of sampling lines and different vessels such as glass bulbs, canister bags, polymer bags and Tedlar film bags [1,5,7,8]. Considering the highly reactive nature of these compounds, sampling vessels should be inert enough to reduce adsorptive loss. Careful attention should be given to length tubing and connecting materials and also the problem of storage ability should be adequately addressed. Sorption on metal surfaces has also been proposed – mainly for dimethyl sulfide determinations -, but losses can occur with them. Solid-phase micro-extraction has been applied in recent years for sampling VSC compounds [7,9]. Although excellent detection limits have been obtained with this technique, problems with the calibration of low sulfur compounds were observed, artifacts were detected as a matrix effect and poor storage stability and competitive sorption/reverse diffusion problems were identified. Cryogenic capture, also known as cryogenic trapping [1], is one of the preferred techniques for the collection of sulfur compounds in the gas phase due to the increase in trapping efficiency with decreasing temperature. Another possibility is the use of cryogenic trapping as a pre-concentration technique, applied after sampling and used before chromatographic analysis [10]. The efficiency of this technique depends on the material and the packing efficiency [11], being not suitable for samples with high humidity. It is an important limitation since environmental humidity is usually up to 70%. Finally, solid sorbent surfaces are regarded as the most general tools for the simple and cost-competitive sampling and pre-concentration of volatile species [9]. In this approach, a number of options are also available such as Tenax, activated charcoal, silica gel, aluminum oxide, graphitized carbon black, molecular sieves, and porous sorbent [12,13]. Tenax sorbent coupled with thermal desorption has traditionally been used due to the absence of interference from changes in humidity, but the trapping efficiency of Tenax tubes is often limited for organosulfur compounds with low boiling points, as is the case of carbon disulfide. Thus, to quantify low levels of sulfur compounds in environmental samples, chromatographic methods were developed due to their volatility, excellent separation capacity and ease of detection [14,15].

Our goal was the development of an easy, fast, sensitive, reproducible and efficient method for the proper determination of CS$_2$, in order to improve sampling efficiency and the extraction protocol free of artifacts. This method is based on solid-phase sampling by activated charcoal surfaces, extraction with organic solvent and separation by gas chromatography and detection by mass spectrometry. The reliable monitoring of carbon disulfide emissions implies the use of validated methods, to develop efficient abatement strategies for air pollution and to fulfill social and
environmental demands to control odor problems. Thus, an important part of this study was focused on testing the most common errors in atmospheric determinations and monitoring of CS$_2$ near a pulp industrial plant.

2. Experimental

2.1 Reagents

Solid-phase supports were activated coconut charcoal (100/50 mg) – called Orbo-32 - supplied by Supelco (St. Louis, MO, USA) and Anasorb CSC coconut charcoal (50/100 mg) combined with sodium sulfate dryers - called SKC - supplied by SKC limited (Dorset, UK). The carbon disulfide and hydrogen sulfide gas calibration were provided by Abelló-Linde (Valencia, Spain). Also, carbon disulfide as liquid state (>99%) was used supplied by Sigma Aldrich (Steinheim, Germany). HPLC grade solvents (hexane and toluene) were purchased from Scharlau (Barcelona, Spain).

2.2 Procedure

2.2.1 Optimization of analysis protocol. Carbon disulfide solutions in hexane or toluene (0.1 – 5 mg L$^{-1}$) were used for the optimization of the gas chromatographic conditions. A complete factorial design was performed for studying the retention on solid-phase supports - Orbo-32 and SKC cartridges - and organic solvent extraction - hexane and toluene -. The experiments were carried out in triplicate, passing through 60 µg m$^{-3}$ of carbon disulfide calibration gas on solid-phase cartridges using a gas-calibration instrument (Dasibi, CA, USA). This system consists of a valves system with a sampling flow of 1 L min$^{-1}$. Moreover, spiked air samples (0-60 µg m$^{-3}$) were pumped through solid-phase supports to study breakthrough volume. The total air sampling volume ranged from 0.1 to 300 m$^3$. Mixtures with pure air and calibration gas were also used for determining the detection limit. Moreover, the stability of the CS$_2$ stored on solid-phase cartridges was established by analyzing sampled supports immediately or after 1-7 days at 4 ºC and several weeks at -20 ºC.

2.2.2 Smog chamber experiments. Validation experiments were performed in a Teflon – fluoropolymer – high-volume smog chamber (EUPHORE Photoreactor, Valencia, Spain). For detailed information on this environmental simulation chamber, see Borrás et al., 2011 [16]. The photoreactor was filled with clean air from an air purification system. Carbon disulfide was injected from a calibration bottle via an air stream. Together with solid-phase sampling at 1 L min$^{-1}$, two optical systems were used as reference methods for the determination of CS$_2$. A Fourier Transform Infrared spectrometer (FTIR, Magna-550, Nicolet Instrument, Madison, USA), coupled to a
long-path multi-reflection white cell with a total path length of 616 m, was used. Spectra were collected with resolution of 1 cm\(^{-1}\) and a sampling time of 10 minutes. Concentrations of CS\(_2\) were determined with specific analysis software [17]. Differential Optical Absorption Spectroscopy (DOAS) was also installed in the chamber. It operated with the beam from a Xenon lamp (XBO, Osram) and directed into a long-path multi-reflection white cell type. The total optical path-length was 128 m, frequency time was 3 min and the spectral resolution was 0.72 nm. Analysis of the samples was carried a non-linear fitting routine.

The inference study consisted in injecting reduced sulfur compounds and compounds that can interact with solid-phase cartridges. H\(_2\)S, O\(_3\) and SO\(_2\) were fed to the photoreactor via an air stream and high humidity was reached by adding pure water with a sprayer system. Later, all the reactants were mixed with CS\(_2\) by high power fans for 10 min in darkness, and continuous measurements were carried out for at least two hours.

2.2.3 Field sampling. A low-volume pump (SIC Pocket Pump) was used at 1 L min\(^{-1}\), for 24h-sampling with SKC cartridges. Firstly, possible systematic errors associated with matrix interferences were evaluated using the standard addition method. Ten samples from an industrial area (39º 35’ 05’’ N, 0º 27’ 42’’ W, Paterna, Spain) were fortified with 0, 20, 100 and 200 µL L\(^{-1}\) of carbon disulfide. Secondly, field samples were collected for 13 days near to a cellulose pulp industry complex (43º 22’ 3” N, 4º 2’ 34” W, Torrelavega, Spain). Fig. 1 shows the geographical location of this last study site. Other pollutants (SO\(_2\), H\(_2\)S, NO\(_2\), NO, CO, O\(_3\) and PM\(_{10}\)) and the meteorological parameters, temperature, pressure, wind direction, wind speed and solar irradiation, were monitored by a cabin air quality during this period. Samples were stored at 4 ºC and analyzed by the proposed method and by an external laboratory.

2.2.4 Analysis of samples. CS\(_2\) retained on solid-phase cartridges was extracted with 2 mL of hexane or toluene for sacking for 30 min. 1 µL was directly injected in the gas chromatograph – mass spectrometer (GC-MS). A TRACE-DSQ II instrument system was used (Thermo Fisher Scientific Co., Waltham, MA, USA) with a TRX-5MS column of 30 m × 0.25 mm I.D × 0.25 µm film thickness supplied by Thermo Fisher Scientific. Samples were injected in splitless mode (t=0.75 s), using an on-column helium carrier gas flow of 1 mL min\(^{-1}\). The impact electron ionization was operated at 70 eV and the full scan acquisition mode ranged from m/z 30 to 300. The quantification was performed by the extraction of the base ion chromatographic peak. The ion source temperature was 200 ºC and the quadrupole temperature was 100 ºC. Two
chromatographic methods were set-up depending on the extraction solvent. The chromatograph was programmed for hexane extracts at 35 ºC for 3 min, then ramped at a rate of 10 ºC min\(^{-1}\) to 100 ºC. For toluene extracts, the chromatograph was programmed at 40 ºC for 10 min, then ramped at a rate of 10 ºC min\(^{-1}\) to 150 ºC. The injection port was held at 200 ºC and the transfer line from GC to MS was held at 280 ºC.

3. Results and Discussion

3.1 Optimization of analysis protocol

3.1.1 Chromatographic method. Organic extraction solvents often generate an overlap problem when reduced sulfur compounds are separated by gas chromatography. Therefore, the chromatographic variables (injection parameters, working temperatures and flows and detection modes) were optimized to achieve an adequate determination of CS\(_2\) using hexane or toluene as solvent. Separation was reached in a total time of 10 min for hexane extracts and 16 min for toluene extracts, being the retention time of CS\(_2\) 3.6 and 4.2 min, respectively. The relative standard deviation of the retention times was lower than 1 %. Under these conditions, the resolution with the other small reduced sulfur compounds was adequate since H\(_2\)S, (CH\(_3\))\(_2\)S and SO\(_2\), eluted at 1.4, 2.9 and 3.2 min and 1.9, 3.2 and 3.6 min for hexane and toluene, respectively. Table 1 summarizes the figures of merit obtained from calibration curves (n=5) ranged from 0 mg L\(^{-1}\) to 5 mg L\(^{-1}\), for both organic solvents. Good linear correlations were found using splitless injection and scan detection. The instrumental sensitivity, or minimum detectable amount value, was calculated as three times the standard deviation of the chromatographic noise from injecting pure extraction solvents, being around 0.001 mg L\(^{-1}\). These analytical performances were adequate for the analysis of air sample extracts at trace levels.

3.1.2 Selection of solid sorbent and solvent elution. An efficient sampling of atmospheric CS\(_2\) depends on the sampling support (material and nature, spatial distribution and compaction). Thus, two solid-phase sorbents based on activated coconut charcoal – Orbo-32 and SKC - were evaluated. Orbo-32 cartridge has 20-40 mesh particle size and a double bed (A of 100 mg and B of 50 mg) containing W,F,F (glass wool, foam, foam) separators. Anasorb SKC 226-01 cartridge has a double bed (A of 50 mg and B of 100 mg) containing F,F,W (foam, foam, glass wool) separators. Both are extremely porous, with a large surface to volume ratio and a small diffusion distance. The nature of these materials allowed the interacting and trapping of carbon disulfide by an adsorption mechanism. Likewise, extraction efficiency depends on the
chemical nature of the elution solvent used to recover it. Two organic solvents, selected for their polarity and chemical properties, were compared – hexane and toluene -. The selection criteria were based on the combined capacity of the solid sorbent to retain the carbon disulfide and the solvent to extract them, measured in terms of the recovery percentages of the packing formats. Mean recovery percentages were (89 ± 8) %, (103 ± 3) %, (84 ± 9) % and (103 ± 8) % for Orbo-32 plus hexane, SKC plus hexane, Orbo-32 plus toluene and SKC plus toluene, respectively.

Applying a statistical ANOVA test at 95 %, three of the four of the combinations support-solvent were similar, discarding Orbo-32 plus toluene. These recovery percentages were similar to the ones obtained by Ras et al., 2008 [9] for other VSC compounds using Tenax TA and Unicarb and thermal desorption coupled with gas chromatography–mass spectrometry. However, the trapping efficiency of Tenax tubes is often limited for organosulfur compounds with low boiling points, as is the case of CS₂, if used at room temperature [1]. For that, the use of the proposed analysis methodology will improve the correct CS₂ determinations. Moreover, the study of the extraction volume (tested volume ranged between 1 – 10 mL) indicated that 2 mL of solvent provides the best results.

3.1.3 Breakthrough and sampling flow. In solid-phase sampling it is very important to determine the breakthrough. This refers to the appearance of sampled molecules in the outlet stream due to saturation within the bed or displacement by another chemical. Since breakthrough depends mainly on the total air volume of sample passed, tests were carried out at a fixed sampling air flow of 1 L min⁻¹. Recovery percentages of both types of solid-phase supports, mounted each one in tandem, were obtained by testing the CS₂ gas calibration. The results were totally satisfactory since carbon disulfide was completely recovered from the top layer of the solid-phase sorbent, up to 300 m³ of air volume sampled. For a 24h-period (total air volume of 1.44 m³), the breakthrough corresponded to a carbon disulfide concentration approximately 300 times higher than conventional thresholds. EU legislation has set a limit of 10 µg m⁻³ of carbon disulfide - average concentration in 24 hours – and the levels allowed by U.S.A legislation are less than 10 µg m⁻³ - average concentration in 8 hours.

3.1.4 Detection limits and precision. The detection limits calculated, including all steps of the analytical procedure, are listed in Table 2. This table also lists the detection limits obtained from the analysis of the blank and spiked air-samples prepared by serial dilution. The ranges of values were 0.3 – 0.8 pg m⁻³, being similar to the instrumental LOD (0.2 - 0.9 pg m⁻³, considering the sampled air volume), and demonstrating that no
contamination occurred during the extraction protocol. These values are quite similar to the ones obtained for CS$_2$ by Catalán et al., 2006 [18] using permeation tube sampling and GC with pulsed flame photometric detection (0.8 pg compared with our 0.2 – 0.6 pg of method LOD), and better than those achieved by Campos et al., 2010 [10] - 3.4 ng corresponding to 1.1 pg m$^{-3}$ for 20 min sampling at 150 mL min$^{-1}$ obtained by air cryogenic sampling with argon or nitrogen and determined by gas chromatography with flame photometric detection - and Kim et al., 2006 [15] – 4.3 ng corresponding to 5.4 pg m$^{-3}$ for sampling volume of 800 mL obtained by vacuum sampling systems and determined by gas chromatography with pulsed flame photometric detector - . Even better LODs (0.1 – 0.3 pg m$^{-3}$) were obtained by operating the GC–MS in selected ion monitoring (SIM) mode - main fragment of CS$_2$ was m/z 76 -. However, this would lead to losing some of the additional information necessary for confirming the identity of other possible unknown interferences in industrial emissions.

Replicate analysis - from ten fractions of an air sample - confirmed the good precision of the method. The relative intra-day reproducibility ranged 4.2 – 5.9 % and the relative inter-day reproducibility ranged 9.6 – 14.0 %. These values are suitable for CS$_2$ determination of environmental samples and similar or better than the values obtained by similar studies in Ras et al., 2008 [9].

3.1.5 Stability in storage. The stability of the carbon disulfide retained on the tested solid-phase supports was studied to guarantee applicability for atmospheric analysis. CS$_2$ concentrations were determined after storage at 4 ºC and -20 ºC.

Carbon disulfide was stable for time intervals of less than a week. However, after 7 days important losses were observed, for Orbo-32 solid phase sampling supports stored at 4 ºC (see Fig. 2). No changes were detected for samples stored at – 20 ºC for a time interval of 4 weeks. Nielsen et al., 2002; Kim et al., 2005; Kim et al., 2006 and Pal et al., 2009 [4,7,14,15] analyzed their Tedlar samples before 12h or 24h, respectively, after sampling to minimize losses reported previously by volatilization. For other types of supports, like Tenax, Carbopack, Carbotrap X and Carboxen 569 cartridges, analysis were carried out before a week to avoid losses of VSCs [2,9].

Thus, using our proposed sampling solid-phase supports improved storage properties of carbon disulfide.

3.2 Validation experiments

3.2.1 Smog chamber experiment. Validation of the correct CS$_2$ determination and gaseous interference study tests were carried out under well-controlled conditions in a large simulator chamber. The large volume atmospheric simulator (200 m$^3$) was filled...
with carbon disulfide diluted in clean dry air. Blanks and samples were collected at a sampling flow of 1 L min\(^{-1}\) for 30 min. Firstly, the presence of systematic errors from the reactor were evaluated, since reactor walls can be a source of gas and/or particles due to the off-gassing of compounds. No interferences appeared along the chromatogram.

Secondly, carbon disulfide calibration experiments – working at different concentration levels – checked the correct injection system of CS\(_2\) and the mixing and dilution processes in dark conditions. For that, two different optical reference instruments (FTIR and DOAS) were employed to obtain a good time resolution data and to study the absence of interferences. Both optical instruments provided a good correlation factor > 0.997, for the range of 7 - 3110 µg m\(^{-3}\). Thirdly, an intercomparison of CS\(_2\) sampling and analysis was carried out. Carbon disulfide was injected into the high-volume chamber at different concentration levels and its concentration was determined by GC-MS using solid-phase cartridges sampling and solvents extraction and by reference FTIR and DOAS systems (see Table 3). The results showed an excellent agreement demonstrating that the sampling and analysis efficiency was not influenced by the level of CS\(_2\) concentrations. The best correlation was obtained for the combination of SKC as cartridge and hexane as extraction solvent. These results definitely confirmed the advantages of using this combination for ambient air analysis.

Fourthly, the influence of interferences in the correct determination of CS\(_2\) was studied. High concentrations of hydrogen sulfide, sulfide oxygen, SF\(_6\), (CH\(_3\))\(_2\)S and humidity were injected into the high-volume chamber: H\(_2\)S at 3100 µg m\(^{-3}\), SO\(_2\) at 1500 µg m\(^{-3}\), SF\(_6\) at 500 µg m\(^{-3}\), (CH\(_3\))\(_2\)S at 1500 µg m\(^{-3}\) and a relative humidity of 40%. The results showed that no interference was observed in the determination of carbon disulfide (test \(t\) at 95\%).

It is worth mentioning that smog chamber provided more reliable results on the validation of analytical methods than other type of reactors or field campaigns. In fact, the EUPHORE simulator chamber has already been used for the validation of pesticide sampling systems [19] and for checking the design and the effect of interferences in correct gaseous determinations using prototype sampling systems [20]. In the present study, their high volume improved the representativeness of CS\(_2\) determinations since low concentrations, a wide range of relative humidity and the presence of interferences were studied in gas-phase sampling. Meteorological conditions driving dispersion were totally avoided. These facilities also avoid problems like interactions of CS\(_2\) with vessel or other wall materials since they are made of inert Teflon – fluoropolymer – which does not react with the carbon disulfide; moreover, absorption, adsorption and deposition processes were extremely reduced. Different interference compounds and/or mixtures of these were added without interactions. According to our
experiences, the conclusions about the effect of interferences are more reliable when
the study was performed by mixing in the simulation chamber than when using spiking
cartridges.

3.2.2 Standard addition method. Field air samples are complex, matrix effect can be
produced and present several different kinds of potential interferences. The accuracy
and reliability of the proposed method were tested by the use of fortified samples. Air
samples from an industrial area (Paterna, Valencia, Spain) were analyzed. CS$_2$ was not
detected in eight samples and the concentrations reported in the two positive samples
were lower than 0.2 $\mu$g m$^{-3}$ (below to EU limit of 10 $\mu$g m$^{-3}$). Then, the standard addition
method (explained on section 2.2.3) was applied to estimate the presence of
proportional systematic error. No interferences appeared along the chromatogram and
the slope values obtained in the standard addition method agreed with the slope values
in the gas phase carbon disulfide calibration (test t at 95 %). Thus, the statistical
analysis of results indicated that air pollutants of industrial sources did not provide
proportional systematic errors in the determination of CS$_2$.

3.3. Analysis of environmental samples

The method was applied to gaseous samples collected in an area affected by
emissions from a pulp industrial plant. Therefore, a total of 13 blind samples sampled in
duplicate during winter were analyzed. Fig. 3 shows the concentration of CS$_2$ obtained
by the proposed method and those obtained for the external reference laboratory. A
total agreement was observed (CS$_2^{\text{proposed method}} = (0.50 \pm 0.06) + (0.98 \pm 0.02) \text{ CS}_2^{\text{external laboratory}}, R^2 = 0.998$).

The environmental implications of the obtained results were also analyzed. The
carbon disulfide concentration levels measured (1 – 141 $\mu$g m$^{-3}$) exceeded European
regulations in 75% of the cases studied (threshold level: 10 $\mu$g m$^{-3}$). The values were
significantly higher than the results obtained by Guo et al., 2010, Pal et al., 2009 and
Kim et al., 2006 [4,15,21] for urban locations or industrial areas without pulp industry.
Moreover, in order to help gain some insights into potential source processes, the
correlation of CS$_2$ concentrations with atmospheric conditions or concentrations of
other pollutants was studied. Highest concentrations of CS$_2$ were obtained for samples
4, 5, 7, 8, 11 and 13, as can be observed in Fig. 3. The analysis of wind patterns
showed that this pollution peaks coincided with south-west wind direction was
predominant. Under these conditions, the emission from pulp industry impacted on our
sampling site (see Fig. 1). The lowest concentrations of CS$_2$ were detected when winds
came from south directions and the emission of pulp industry was directed far from the city. Also upper limits were associated with high value emissions of H$_2$S and SO$_2$ (Fig. 3). The sources of these both pollutants are several, but they are also secondary products of the chemical processes of pulp-industry. These high concentrations of H$_2$S and SO$_2$ are correlated with high levels of CS$_2$, confirming that our proposed sampling and analysis methodology can be used properly for environmental monitoring. As summary, during this field sampling campaign, the high CS$_2$ levels suggest the dominance of the industrial source together with lower wind recirculation and a poor vertical exchange of air as the main causes that implied a great population impact of reduced sulfur compounds.

4. Conclusions

Identification of potential sources of VSCs should be considered prerequisites for controlling their emissions from point sources and for their maintenance at acceptable ambient concentration levels (below to legislation limits). Analytical efforts to characterize odor pollution will help us to protect human and environmental health from possible adverse effects generated by the diverse source activities of malodorous and/or hazardous compounds. In this sense, we proposed a new method for the selective monitoring of carbon disulfide, a key pollutant in specific industrial areas, e.g. the pulp industry is still a worldwide environmental problem. The combination of SKC solid-phase cartridge sampling, hexane as an organic extraction solvent and GC–MS analysis has allowed its correct determination. This method provides adequate sensitivity, good linearity and a fast and easy analysis protocol for the routine quality control and monitoring of trace carbon disulfide in air. Although other cartridges or extraction solvents provided good results, the proposed combination is the best in terms of accuracy and precision under atmospheric conditions. The control VSC emissions, including CS$_2$, also require reliable monitoring methods. For that, the validation has been the most important goal of this study. Experiments carried out in a high-volume simulation chamber and the comparison with optical reference methods has demonstrated the high accuracy of the proposed method. The absence of effects due to interference compounds such as ozone, water or other VSCs was also confirmed. Moreover, the absence of systematic errors was demonstrated with data from a sampling campaign in industrial areas. Finally, this study reinforced the need for CS$_2$ monitoring to qualitatively upgrade current regulations and controls, since its presence was detected in a high concentration levels and a high number of samples.
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References


Figure captions

Fig. 1 Geographical location of the study site in Torrelavega, Spain.

Table 1 Figures of merit for GC-MS determination of CS$_2$ solutions.

Table 2 Detection limits and precision by coconut charcoal cartridge sampling, solvent extraction and GC-MS determination

Fig. 2 Storage stability at 4 ºC of CS$_2$ retained in solid-phase cartridges.

Table 3 Concentration of CS$_2$ (µg m$^{-3}$) obtained in smog chamber experiments

Fig. 3 Temporal evolution of carbon disulfide—obtained by our method and by external laboratory-, sulfur oxide and hydrogen sulfide, including wind rose for critical samples.