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Additional Information

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

7

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Abract

Carbon disulfide (CS_2), 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 CS_2 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 CS_2 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_2S), 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 type 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 occurs 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], been 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

123 environmental demands to control odor problems. Thus, an important part of this study
124 was focused on testing the most common errors in atmospheric determinations and
125 monitoring of CS_2 near a pulp industrial plant.

126

127 **2. Experimental**

128 *2.1 Reagents*

129   Solid-phase supports were activated coconut charcoal (100/50 mg) – called
130 Orbo-32 - supplied by Supelco (St. Louis, MO, USA) and Anasorb CSC coconut
131 charcoal (50/100 mg) combined with sodium sulfate dryers - called SKC - supplied by
132 SKC limited (Dorset, UK). The carbon disulfide and hydrogen sulfide gas calibration
133 were provided by Abelló-Linde (Valencia, Spain). Also, carbon disulfide as liquid state
134 (>99%) was used supplied by Sigma Aldrich (Steinheim, Germany). HPLC grade
135 solvents (hexane and toluene) were purchased from Scharlau (Barcelona, Spain).

136

137 *2.2 Procedure*

138 *2.2.1 Optimization of analysis protocol.* Carbon disulfide solutions in hexane or toluene
139 (0.1 – 5 mg L^{-1}) were used for the optimization of the gas chromatographic conditions.
140 A complete factorial design was performed for studying the retention on solid-phase
141 supports - Orbo-32 and SKC cartridges - and organic solvent extraction - hexane and
142 toluene -. The experiments were carried out in triplicate, passing through 60 µg m^{-3} of
143 carbon disulfide calibration gas on solid-phase cartridges using a gas-calibration
144 instrument (Dasibi, CA, USA). This system consists of a valves system with a sampling
145 flow of 1 L min^{-1}. Moreover, spiked air samples (0-60 µg m^{-3}) were pumped through
146 solid-phase supports to study breakthrough volume. The total air sampling volume
147 ranged from 0.1 to 300 m^3. Mixtures with pure air and calibration gas were also used
148 for determining the detection limit. Moreover, the stability of the CS_2 stored on solid-
149 phase cartridges was established by analyzing sampled supports immediately or after
150 1-7 days at 4 ºC and several weeks at -20 ºC.

151

152 *2.2.2 Smog chamber experiments.* Validation experiments were performed in a Teflon
153 – fluoropolymer – high-volume smog chamber (EUPHORE Photoreactor, Valencia,
154 Spain). For detailed information on this environmental simulation chamber, see Borrás
155 et al., 2011 [16]. The photoreactor was filled with clean air from an air purification
156 system. Carbon disulfide was injected from a calibration bottle via an air stream.
157 Together with solid-phase sampling at 1 L min^{-1}, two optical systems were used as
158 reference methods for the determination of CS_2. A Fourier Transform Infrared
159 spectrometer (FTIR, Magna-550, Nicolet Instrument, Madison, USA), coupled to a

160 long-path multi-reflection white cell with a total path length of 616 m, was used. Spectra
161 were collected with resolution of 1 cm^{-1} and a sampling time of 10 minutes.
162 Concentrations of CS_2 were determined with specific analysis software [17]. Differential
163 Optical Absorption Spectroscopy (DOAS) was also installed in the chamber. It operated
164 with the beam from a Xenon lamp (XBO, Osram) and directed into a long-path multi-
165 reflection white cell type. The total optical path-length was 128 m, frequency time was 3
166 min and the spectral resolution was 0.72 nm. Analysis of the samples was carried a
167 non-linear fitting routine.

168   The inference study consisted in injecting reduced sulfur compounds and
169 compounds that can interact with solid-phase cartridges. H_2S, O_3 and SO_2 were fed to
170 the photoreactor via an air stream and high humidity was reached by adding pure water
171 with a sprayer system. Later, all the reactants were mixed with CS_2 by high power fans
172 for 10 min in darkness, and continuous measurements were carried out for at least two
173 hours.

175 *2.2.3 Field sampling.* A low-volume pump (SIC Pocket Pump) was used at 1 L min^{-1}, for
176 24h-sampling with SKC cartridges. Firstly, possible systematic errors associated with
177 matrix interferences were evaluated using the standard addition method. Ten samples
178 from an industrial area (39º 35' 05'' N, 0º 27' 42'' W, Paterna, Spain) were fortified with
179 0, 20, 100 and 200 µL L^{-1} of carbon disulfide. Secondly, field samples were collected
180 for 13 days near to a cellulose pulp industry complex (43º 22' 3'' N, 4º 2' 34'' W,
181 Torrelavega, Spain). Fig. 1 shows the geographical location of this last study site.
182 Other pollutants (SO_2, H_2S, NO_2, NO, CO, O_3 and PM_{10}) and the meteorological
183 parameters, temperature, pressure, wind direction, wind speed and solar irradiation,
184 were monitored by a cabin air quality during this period. Samples were stored at 4 ºC
185 and analyzed by the proposed method and by an external laboratory.

187   *2.2.4 Analysis of samples.* CS_2 retained on solid-phase cartridges was extracted
188 with 2 mL of hexane or toluene for sacking for 30 min. 1 µL was directly injected in the
189 gas chromatograph – mass spectrometer (GC-MS). A TRACE-DSQ II instrument
190 system was used (Thermo Fisher Scientific Co., Waltham, MA, USA) with a TRX-5MS
191 column of 30 m × 0.25 mm I.D × 0.25 µm film thickness supplied by Thermo Fisher
192 Scientific. Samples were injected in splitless mode (t=0.75 s), using an on-column
193 helium carrier gas flow of 1 mL min^{-1}. The impact electron ionization was operated at
194 70 eV and the full scan acquisition mode ranged from m/z 30 to 300. The quantification
195 was performed by the extraction of the base ion chromatographic peak. The ion source
196 temperature was 200 ºC and the quadrupole temperature was 100 ºC. Two

197 chromatographic methods were set-up depending on the extraction solvent. The
198 chromatograph was programmed for hexane extracts at 35 ºC for 3 min, then ramped
199 at a rate of 10 ºC min^{-1} to 100 ºC. For toluene extracts, the chromatograph was
200 programmed at 40 ºC for 10 min, then ramped at a rate of 10 ºC min^{-1} to 150 ºC. The
201 injection port was held at 200 ºC and the transfer line from GC to MS was held at 280
202 ºC.

203 **3. Results and Discussion**

204 *3.1 Optimization of analysis protocol*

205 *3.1.1 Chromatographic method.* Organic extraction solvents often generate an overlap
206 problem when reduced sulfur compounds are separated by gas chromatography.
207 Therefore, the chromatographic variables (injection parameters, working temperatures
208 and flows and detection modes) were optimized to achieve an adequate determination
209 of CS_2 using hexane or toluene as solvent. Separation was reached in a total time of 10
210 min for hexane extracts and 16 min for toluene extracts, being the retention time of CS_2
211 3.6 and 4.2 min, respectively. The relative standard deviation of the retention times was
212 lower than 1 %. Under these conditions, the resolution with the other small reduced
213 sulfur compounds was adequate since H_2S, $(CH_3)_2S$ and SO_2, eluted at 1.4, 2.9 and
214 3.2 min and 1.9, 3.2 and 3.6 min for hexane and toluene, respectively. Table 1
215 summarizes the figures of merit obtained from calibration curves (n=5) ranged from 0
216 mg L^{-1} to 5 mg L^{-1}, for both organic solvents. Good linear correlations were found using
217 splitless injection and scan detection. The instrumental sensitivity, or minimum
218 detectable amount value, was calculated as three times the standard deviation of the
219 chromatographic noise from injecting pure extraction solvents, being around 0.001 mg
220 L^{-1}. These analytical performances were adequate for the analysis of air sample
221 extracts at trace levels.

222

223 *3.1.2 Selection of solid sorbent and solvent elution.* An efficient sampling of
224 atmospheric CS_2 depends on the sampling support (material and nature, spatial
225 distribution and compaction). Thus, two solid-phase sorbents based on activated
226 coconut charcoal – Orbo-32 and SKC - were evaluated. Orbo-32 cartridge has 20-40
227 mesh particle size and a double bed (A of 100 mg and B of 50 mg) containing W,F,F
228 (glass wool, foam, foam) separators. Anasorb SKC 226-01 cartridge has a double bed
229 (A of 50 mg and B of 100 mg) containing F,F,W (foam, foam, glass wool) separators.
230 Both are extremely porous, with a large surface to volume ratio and a small diffusion
231 distance. The nature of these materials allowed the interacting and trapping of carbon
232 disulfide by an adsorption mechanism. Likewise, extraction efficiency depends on the

233 chemical nature of the elution solvent used to recover it. Two organic solvents,
234 selected for their polarity and chemical properties, were compared – hexane and
235 toluene -. The selection criteria were based on the combined capacity of the solid
236 sorbent to retain the carbon disulfide and the solvent to extract them, measured in
237 terms of the recovery percentages of the packing formats. Mean recovery percentages
238 were (89 ± 8) %, (103 ± 3) %, (84 ± 9) % and (103 ± 8) % for Orbo-32 plus hexane,
239 SKC plus hexane, Orbo-32 plus toluene and SKC plus toluene, respectively.

240   Applying a statistical ANOVA test at 95 %, three of the four of the combinations
241 support-solvent were similar, discarding Orbo-32 plus toluene. These recovery
242 percentages were similar to the ones obtained by Ras et al., 2008 [9] for other VSC
243 compounds using Tenax TA and Unicarb and thermal desorption coupled with gas
244 chromatography–mass spectrometry. However, the trapping efficiency of Tenax tubes
245 is often limited for organosulfur compounds with low boiling points, as is the case of
246 CS_2, if used at room temperature [1]. For that, the use of the proposed analysis
247 methodology will improve the correct CS_2 determinations. Moreover, the study of the
248 extraction volume (tested volume ranged between 1 – 10 mL) indicated that 2 mL of
249 solvent provides the best results.

250

251 *3.1.3 Breakthrough and sampling flow.* In solid-phase sampling it is very important to
252 determine the breakthrough. This refers to the appearance of sampled molecules in the
253 outlet stream due to saturation within the bed or displacement by another chemical.
254 Since breakthrough depends mainly on the total air volume of sample passed, tests
255 were carried out at a fixed sampling air flow of 1 L min^{-1}. Recovery percentages of both
256 types of solid-phase supports, mounted each one in tandem, were obtained by testing
257 the CS_2 gas calibration. The results were totally satisfactory since carbon disulfide was
258 completely recovered from the top layer of the solid-phase sorbent, up to 300 m^3 of air
259 volume sampled. For a 24h-period (total air volume of 1.44 m^3), the breakthrough
260 corresponded to a carbon disulfide concentration approximately 300 times higher than
261 conventional thresholds. EU legislation has set a limit of 10 µg m^{-3} of carbon disulfide -
262 average concentration in 24 hours – and the levels allowed by U.S.A legislation are
263 less than 10 µg m^{-3} - average concentration in 8 hours.

264

265 *3.1.4 Detection limits and precision.* The detection limits calculated, including all steps
266 of the analytical procedure, are listed in Table 2. This table also lists the detection limits
267 obtained from the analysis of the blank and spiked air-samples prepared by serial
268 dilution. The ranges of values were 0.3 – 0.8 pg m^{-3}, being similar to the instrumental
269 LOD (0.2 - 0.9 pg m^{-3}, considering the sampled air volume), and demonstrating that no

8

270   contamination occurred during the extraction protocol. These values are quite similar to

271   the ones obtained for CS_2 by Catalán et al., 2006 [18] using permeation tube sampling

272   and GC with pulsed flame photometric detection (0.8 pg compared with our 0.2 – 0.6

273   pg of method LOD), and better than those achieved by Campos et al., 2010 [10] - 3.4

274   ng corresponding to 1.1 pg m^{-3} for 20 min sampling at 150 mL min^{-1} obtained by air

275   cryogenic sampling with argon or nitrogen and determined by gas chromatography with

276   flame photometric detection - and Kim et al., 2006 [15] – 4.3 ng corresponding to 5.4

277   pg m^{-3} for sampling volume of 800 mL obtained by vacuum sampling systems and

278   determined by gas chromatography with pulsed flame photometric detector -. Even

279   better LODs (0.1 – 0.3 pg m^{-3}) were obtained by operating the GC–MS in selected ion

280   monitoring (SIM) mode - main fragment of CS_2 was m/z 76 -. However, this would lead

281   to losing some of the additional information necessary for confirming the identity of

282   other possible unknown interferences in industrial emissions.

283   Replicate analysis - from ten fractions of an air sample - confirmed the good

284   precision of the method. The relative intra-day reproducibility ranged 4.2 – 5.9 % and

285   the relative inter-day reproducibility ranged 9.6 – 14.0 %. These values are suitable for

286   CS_2 determination of environmental samples and similar or better than the values

287   obtained by similar studies in Ras et al., 2008 [9].

288

289   *3.1.5 Stability in storage.* The stability of the carbon disulfide retained on the tested

290   solid-phase supports was studied to guarantee applicability for atmospheric analysis.

291   CS_2 concentrations were determined after storage at 4 ºC and -20 ºC.

292   Carbon disulfide was stable for time intervals of less than a week. However,

293   after 7 days important losses were observed, for Orbo-32 solid phase sampling

294   supports stored at 4 ºC (see Fig. 2). No changes were detected for samples stored at –

295   20 ºC for a time interval of 4 weeks. Nielsen et al., 2002; Kim et al., 2005; Kim et al.,

296   2006 and Pal et al., 2009 [4,7,14,15] analyzed their Tedlar samples before 12h or 24h,

297   respectively, after sampling to minimize losses reported previously by volatilization. For

298   other types of supports, like Tenax, Carbotrap, Carbopack X and Carboxen 569

299   cartridges, analysis were carried out before a week to avoid losses of VSCs [2,9].

300   Thus, using our proposed sampling solid-phase supports improved storage properties

301   of carbon disulfide.

302

303   *3.2 Validation experiments*

304   *3.2.1 Smog chamber experiment.* Validation of the correct CS_2 determination and

305   gaseous interference study tests were carried out under well-controlled conditions in a

306   large simulator chamber. The large volume atmospheric simulator (200 m^3) was filled

307   with carbon disulfide diluted in clean dry air. Blanks and samples were collected at a
308   sampling flow of 1 L min^{-1} for 30 min. Firstly, the presence of systematic errors from the
309   reactor were evaluated, since reactor walls can be a source of gas and/or particles due
310   to the off-gassing of compounds. No interferences appeared along the chromatogram.
311   Secondly, carbon disulfide calibration experiments – working at different concentration
312   levels – checked the correct injection system of CS_2 and the mixing and dilution
313   processes in dark conditions. For that, two different optical reference instruments (FTIR
314   and DOAS) were employed to obtain a good time resolution data and to study the
315   absence of interferences. Both optical instruments provided a good correlation factor >
316   0.997, for the range of 7 - 3110 µg m^{-3}. Thirdly, an intercomparison of CS_2 sampling
317   and analysis was carried out. Carbon disulfide was injected into the high-volume
318   chamber at different concentration levels and its concentration was determined by GC-
319   MS using solid-phase cartridges sampling and solvents extraction and by reference
320   FTIR and DOAS systems (see Table 3). The results showed an excellent agreement
321   demonstrating that the sampling and analysis efficiency was not influenced by the level
322   of CS_2 concentrations. The best correlation was obtained for the combination of SKC
323   as cartridge and hexane as extraction solvent. These results definitely confirmed the
324   advantages of using this combination for ambient air analysis.

325   Fourthly, the influence of interferences in the correct determination of CS_2 was
326   studied. High concentrations of hydrogen sulfide, sulfide oxygen, SF_6, $(CH_3)_2S$ and
327   humidity were injected into the high-volume chamber: H_2S at 3100 µg m^{-3}, SO_2 at 1500
328   µg m^{-3}, SF_6 at 500 µg m^{-3}, $(CH_3)_2S$ at 1500 µg m^{-3} and a relative humidity of 40%. The
329   results showed that no interference was observed in the determination of carbon
330   disulfide (test t at 95 %).

331   It is worth mentioning that smog chamber provided more reliable results on the
332   validation of analytical methods than other type of reactors or field campaigns. In fact,
333   the EUPHORE simulator chamber has already been used for the validation of pesticide
334   sampling systems [19] and for checking the design and the effect of interferences in
335   correct gaseous determinations using prototype sampling systems [20]. In the present
336   study, their high volume improved the representativeness of CS_2 determinations since
337   low concentrations, a wide range of relative humidity and the presence of interferences
338   were studied in gas-phase sampling. Meteorological conditions driving dispersion were
339   totally avoided. These facilities also avoid problems like interactions of CS_2 with vessel
340   or other wall materials since they are made of inert Teflon – fluoropolymer – which
341   does not react with the carbon disulfide; moreover, absorption, adsorption and
342   deposition processes were extremely reduced. Different interference compounds
343   and/or mixtures of these were added without interactions. According to our

344   experiences, the conclusions about the effect of interferences are more reliable when
345   the study was performed by mixing in the simulation chamber than when using spiking
346   cartridges.

347

348   *3.2.2 Standard addition method.* Field air samples are complex, matrix effect can be
349   produced and present several different kinds of potential interferences. The accuracy
350   and reliability of the proposed method were tested by the use of fortified samples. Air
351   samples from an industrial area (Paterna, Valencia, Spain) were analyzed. CS_2 was not
352   detected in eight samples and the concentrations reported in the two positive samples
353   were lower than 0.2 μg m^{-3} (below to EU limit of 10 μg m^{-3}). Then, the standard addition
354   method (explained on section 2.2.3) was applied to estimate the presence of
355   proportional systematic error. No interferences appeared along the chromatogram and
356   the slope values obtained in the standard addition method agreed with the slope values
357   in the gas phase carbon disulfide calibration (test t at 95 %). Thus, the statistical
358   analysis of results indicated that air pollutants of industrial sources did not provide
359   proportional systematic errors in the determination of CS_2.

360

361   *3.3. Analysis of environmental samples*
362   The method was applied to gaseous samples collected in an area affected by
363   emissions from a pulp industrial plant. Therefore, a total of 13 blind samples sampled in
364   duplicate during winter were analyzed. Fig. 3 shows the concentration of CS_2 obtained
365   by the proposed method and those obtained for the external reference laboratory. A
366   total agreement was observed ($CS_{2proposed\ method}$ = (0.50 $\pm$ 0.06) + (0.98 $\pm$ 0.02) $CS_{2external}$
367    $_{laboratory}$, R^2 = 0.998).
368   The environmental implications of the obtained results were also analyzed. The
369   carbon disulfide concentration levels measured (1 – 141 μg m^{-3}) exceeded European
370   regulations in 75% of the cases studied (threshold level: 10 μg m^{-3}). The values were
371   significantly higher than the results obtained by Guo et al., 2010, Pal et al., 2009 and
372   Kim et al., 2006 [4,15,21] for urban locations or industrial areas without pulp industry.
373   Moreover, in order to help gain some insights into potential source processes, the
374   correlation of CS_2 concentrations with atmospheric conditions or concentrations of
375   other pollutants was studied. Highest concentrations of CS_2 were obtained for samples
376   4, 5, 7, 8, 11 and 13, as can be observed in Fig. 3. The analysis of wind patterns
377   showed that this pollution peaks coincided with south-west wind direction was
378   predominant. Under these conditions, the emission from pulp industry impacted on our
379   sampling site (see Fig. 1). The lowest concentrations of CS_2 were detected when winds

380 came from south directions and the emission of pulp industry was directed far from the
381 city. Also upper limits were associated with high value emissions of H_2S and SO_2 (Fig.
382 3). The sources of these both pollutants are several, but they are also secondary
383 products of the chemical processes of pulp-industry. These high concentrations of H_2S
384 and SO_2 are correlated with high levels of CS_2, confirming that our proposed sampling
385 and analysis methodology can be used properly for environmental monitoring. As
386 summary, during this field sampling campaign, the high CS_2 levels suggest the
387 dominance of the industrial source together with lower wind recirculation and a poor
388 vertical exchange of air as the main causes that implied a great population impact of
389 reduced sulfur compounds.

390 **4. Conclusions**

391   Identification of potential sources of VSCs should be considered prerequisites
392 for controlling their emissions from point sources and for their maintenance at
393 acceptable ambient concentration levels (below to legislation limits). Analytical efforts
394 to characterize odor pollution will help us to protect human and environmental health
395 from possible adverse effects generated by the diverse source activities of malodorous
396 and/or hazardous compounds. In this sense, we proposed a new method for the
397 selective monitoring of carbon disulfide, a key pollutant in specific industrial areas, e.g.
398 the pulp industry is still a worldwide environmental problem. The combination of SKC
399 solid-phase cartridge sampling, hexane as an organic extraction solvent and GC–MS
400 analysis has allowed its correct determination. This method provides adequate
401 sensitivity, good linearity and a fast and easy analysis protocol for the routine quality
402 control and monitoring of trace carbon disulfide in air. Although other cartridges or
403 extraction solvents provided good results, the proposed combination is the best in
404 terms of accuracy and precision under atmospheric conditions. The control VSC
405 emissions, including CS_2, also require reliable monitoring methods. For that, the
406 validation has been the most important goal of this study. Experiments carried out in a
407 high-volume simulation chamber and the comparison with optical reference methods
408 has demonstrated the high accuracy of the proposed method. The absence of effects
409 due to interference compounds such as ozone, water or other VSCs was also
410 confirmed. Moreover, the absence of systematic errors was demonstrated with data
411 from a sampling campaign in industrial areas. Finally, this study reinforced the need for
412 CS_2 monitoring to qualitatively upgrade current regulations and controls, since its
413 presence was detected in a high concentration levels and a high number of samples.

414

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498   **Figure captions**

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

500   Table 1 Figures of merit for GC-MS determination of CS_2 solutions.

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

503   Fig. 2 Storage stability at 4 ºC of CS_2 retained in solid-phase cartridges.

504   Table 3 Concentration of CS_2 ($\mu g\ m^{-3}$) obtained in smog chamber experiments

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

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