



# Quantitative or only qualitative measurements of sulfur compounds in ambient air at ppb level? Uncertainties assessment for active sampling with Tenax TA®



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## ABSTRACT

In the past two decades there has been increasing interest in monitoring volatile reduced sulfur compounds (RSCs) in the atmosphere relatively to their unpleasant smell and their low olfactory threshold. The olfactory annoyance is considered as an important environmental issue, especially since the industrial development near residential areas. The volatile reduced sulfur compounds including mercaptans (RSH) and sulfides (RSR') are emitted from different sources as sewage, waste treatment plant and chemical industry. A preconcentration step before analysis is required in case of odor nuisance at low concentration (a few ppb). While active sampling through cartridges filled with Tenax TA® is recognized as the most suitable method for the measurements of RSCs in ambient air, any comprehensive qualification and validation of this sampling method was carried out. In this work, breakthrough volumes were determined for 6 different RSCs (methylmercaptan, ethylmercaptan, dimethylsulfide, isopropylmercaptan, tertbutylmercaptan, diethylsulfide) at ppb levels on active sampling tubes packed with 250 mg of Tenax TA®. Breakthrough volumes range from 1 to >5 L, for an optimal flow of 25 mL min<sup>-1</sup>. Except for methylmercaptan, for which it was estimated to <0.2 L at 20 ppb and around 2 L at 1 ppb. No quantitative measurement could be assured for methylmercaptan due to low breakthrough volume; whereas for the 5 others RSCs, the global measurement uncertainties linked to the active sampling (matrix interferences, storage), and to the analytical performances of TD-GC-FPD/FID analysis were calculated. Analytical uncertainties don't exceed 25%: the accuracy of the standard preparation and the lack of fit of calibration are the two major contributors. However, taking into account the sampling uncertainties, global relative concentration uncertainties reach maximal values of 74 and 59% for mercaptans and sulfides respectively considering a storage at -21 °C and a relative humidity of 85% (at 20 °C). Storage contribution was estimated to 2% for sulfides and 34% for mercaptans and relative humidity contribution between 55% and 85% for the sulfides and mercaptans at a relative humidity of 85% (at 20 °C).

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## 1. Introduction

As a result of recent industrial developments, nearby residents are exposed to air pollution under different forms (particles, metal, inorganic, odorous pollution...). Among environmental pollution, the olfactory annoyance, referring to the occurrence of compounds with unpleasant smell and low olfactory threshold, is an important issue: they can involve chronic health concerns as a result of their malodorous and toxic properties [1]. Besides, these compounds show a high impact on atmospheric chemistry due to their strong potential of oxidation to secondary pollutants contributing to global warming [2–6]. “Olfactory

pollution” can be characterized by a complex mixture of compounds belonging to different chemical families as the oxygenated compounds, sulfides and amines [7] coming from natural and/or biogenic sources such as volcanic activities, ocean, vegetation and from anthropogenic sources such as chemical plants, sewage treatments, landfills, agricultural activities and industries [8–11].

The odor nuisance can be qualified combining three approaches: (i) a sensory approach using olfactory analysis, (ii) a physico-chemical approach associated to instrumental measurements or (iii) a senso-instrumental approach related to measurement by “electronic noses”. Olfactory analysis, time-consuming and involving human panels, allows a lexical description of the odor in terms of intensity or quality, whereas electronic noses could give in a short time (second) a global pattern corresponding to the response of the sensors to chemicals; this response is non-specific and subjected to interferences (humidity). Nevertheless, to

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fulfill the growing need of odorous compounds quantification in ambient air, chromatographic methods associated to enrichment sampling are generally used for environmental monitoring [12,13]. With the help of selective detectors, this approach allows a specific qualification of odorous mixtures.

This study targets particularly sulfur compounds due to their very low odor thresholds (below 1 ppb) and their specific unpleasant smell for nearby residents [14]. The most abundant sulfur compounds in the environment include hydrogen sulfide (H<sub>2</sub>S), carbon disulfide (CS<sub>2</sub>), carbonyl sulfide (COS), methylmercaptan (MM), dimethylsulfide (DMS) and dimethyldisulfide (DMDS) [15–17]. Several previous works report surrounding or on-site sulfur compounds concentrations with a large magnitude from a few tens of ppt to tens ppm in function of the distance from the source (Table 1) [15,18–20].

To reach a ppb-quantification level, the preconcentration step is inescapable requiring the use of various commercial sorbents. Organic sorbent (silica gel) are preferentially used with chemical desorption while activated carbon, carbon molecular sieve (Carboxen 1000), graphitized carbon (Carbotrap), porous organic polymer (Tenax TA®) are rather employed with thermal desorption and concern the majority of the ambient air applications [21]. Mochalski et al. (2009) compares the adsorption of six sulfur compounds (H<sub>2</sub>S, CS<sub>2</sub>, COS, MM, ethylmercaptan (EM) and DMS) on eight typical sorbents (Tenax TA, Carboxen 1003, Unicarb and Chomosorb), to conclude on best sulfur adsorption (MM/EM) on Tenax TA® [22]. In others studies [22–25], similar conclusions were found and recognized Tenax TA® as the most suitable for the RSCs sampling.

Some tested the performance of active sulfur sampling on Tenax TA® in terms of breakthrough volume and qualify the analytical system (TD-GC-MS) in terms of linearity, and repeatability [24,26]. But, the effect of storage and moisture had never been studied while these parameters could introduce important bias mainly due to heterogenous reactivity of these compounds on sampling supports. This phenomenon has already been highlighted for sampling in Tedlar bag or canister. Indeed, Brown et al. (2015) studied the storage of a dry sulfur mixture in canister. He notes some sulfur losses estimated to around 20% after

**Table 1**  
Concentration of sulfur compounds in ambient air on industrial site and in surrounding complex areas.

Sampling place	Compounds	Concentration (ppb)	Reference
Surrounding complex area	H <sub>2</sub> S <sup>a</sup>	1.06 (average) ± 2.07 (SD)	R. Pal et al. (2009) – Korea [15]
	MM <sup>b</sup>	0.11 ± 0.23 ppb	
	DMS <sup>c</sup>	0.24 ± 0.83 ppb	
	CS <sub>2</sub> <sup>d</sup>	0.84 ± 0.54 ppb	
	DMDS <sup>e</sup>	0.36 ± 1.21 ppb	
Surrounding complex area	H <sub>2</sub> S	0–7.887 ppb	K.-H. Kim et al. (2007) – Korea [28]
	MM	0–0.128 ppb	
	DMS	0–3.421 ppb	
	DMDS	0–0.249 ppb	
On industrial site	EM <sup>f</sup>	ND - 37.6 ppb	M. R. Ras et al. (2008) – Spain [18]
	PropM <sup>g</sup>	ND - 127.0 ppb	
	BM <sup>h</sup>	ND - 24.7 ppb	
	PentM <sup>i</sup>	ND - 209.0 ppb	
	DMS	1.0–1548.7 ppb	
	CS <sub>2</sub>	ND - 2053.7 ppb	
	DMDS	0.8–3311.7 ppb	

<sup>a</sup> Hydrogen sulfide.

<sup>b</sup> Methylmercaptan.

<sup>c</sup> Dimethylsulfide.

<sup>d</sup> Carbon disulfide.

<sup>e</sup> Dimethyldisulfide.

<sup>f</sup> Ethylmercaptan.

<sup>g</sup> Propylmercaptan.

<sup>h</sup> Butylmercaptan.

<sup>i</sup> Pentylmercaptan.

4 days storage. The storage of the same sulfur mixture in wet matrix in canister showed 60% of losses after 4 h. Moreover, Mochalski et al. (2009) shows an impact of the nature of Tedlar bag (transparent or black layered Tedlar bag) on sulfur storage. Some losses (≈30% before 24 h of storage) were found with all Tedlar bag studied [17,27,28].

This paper aims to assess the performances of Tenax TA® active sampling followed by a TD-GC-FID/FPD analysis for the quantification of sulfur compounds in ambient air. It describes the optimization of sampling parameters (determination of optimized sampling flows, breakthrough volumes...), the performances of the analytical method (repeatability, detection limit...), the interference effect of humidity and oxygen and the effect of storage. This paper concludes on the global uncertainties associated with the measurement of 6 reduced sulfur compounds at ppb levels.

## 2. Materials and methods

### 2.1. Chemicals

A certified cylinder-based primary standard of RSCs (Praxair, France) was used. Standard was made up in pure nitrogen at about 1 ppm of each following compounds: methylmercaptan (MM), ethylmercaptan (EM), isopropylmercaptan (IPM), tertbutylmercaptan (TBM), dimethylsulfide (DMS) and diethylsulfide (DES). It was certified at ±5%. The basic properties (chemical formula, molecular weight, concentration in cylinder and odor threshold) of all these RSCs are summarized in Table 2.

### 2.2. RSCs sample preparation

#### 2.2.1. Generation of the RSCs mixture

In order to prepare working standards (from 1 to 500 ppb), the primary standard gas was mixed with the selected matrix gas (dry or wet air, nitrogen). The dilution of primary mixture in dry or wet air is used for studying the influence of potential effect of oxygen or humidity. Fig. 1 below illustrates the generation system for working standards.

#### 2.2.2. Sampling cartridges

Brown et al. (2015) highlight in their review a best adsorption of sulfur compounds on Tenax TA® cartridge in comparison with other sorbent [23]. Tenax TA®, chosen for the present work is a macroporous, semi-crystalline polymer manufactured from diphenyl-*p*-phenylene oxide (DPPO) [4,17] showing a relatively low surface-specific area (about 15 m<sup>2</sup> g<sup>-1</sup>). Samples were collected on Sulfinert® cartridges (89 mm length, 6.4 mm outer diameter, 5 mm internal diameter) packed with about 250 mg of Tenax TA® (60–80 mesh size, Sigma-Aldrich). An accurate volume of test gas was sampled into the cartridge with help of a mass flow controller (MFC) and a pump respectively from MKC (Germany) and KNF (France). Then, cartridges were analyzed by the thermodesorption/chromatographic system.

#### 2.2.3. Sample analysis

Samples were analyzed by a thermo-desorber (ATD: Automated Thermo Desorber) coupled with a gas chromatographic system. A double desorption was applied: first, thermal desorption of the sampling cartridges was carried out at 250 °C for 5 min with helium at about 7.2 mL min<sup>-1</sup> (primary desorption). Then, the RSCs were refocused within the cold trap of the thermos-desorber packed with 100 mg of Tenax TA (60–80 mesh) and maintained at –10 °C by a Peltier system. Then, the cold trap was quickly heated from –10 °C to 250 °C (secondary desorption) in <10 s and maintained at this temperature for 15 min. The analytes were injected (splitless) onto a capillary column via a transfer line heated at 200 °C. The GC system used in this study was a Clarus 580 model (Perkin Elmer) interfaced with a double detection system (split of the column exhaust by 50:50 for both detectors): a Flame Ionization Detector (FID) and a Flame Photometric Detector (FPD). For

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