Assessment of Uncertainty in Measurements of Reduced Sulfur Compounds by Active Sampling on Tenax TA® Tubes

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The interest in on-field ppbV level measurements of odorous compounds is growing over the last decade because of the olfactory annoyance related to industrial development near residential areas. The volatile reduced sulfur compounds (RSCs) are identified as the main contributors to environmental unpleasant smells because of their low olfactory thresholds and their specific odor. The active sampling through cartridges filled with Tenax TA® is recognized as the most suitable method for the RSC measurements in ambient air. However, any comprehensive qualification and validation of this method was made. That's why, this study assesses the active sampling parameters on Tenax TA® (sampling flow and breakthrough volumes), performances (detection limit, repeatability) and the uncertainties in measurement of 6 different RSCs at ppb levels. A breakthrough volume of 1L was determined for an optimal sampling flow of 40 mL/min. Storage and humidity represent the two major contributors to the global uncertainty. Indeed, the relative uncertainty on storage at -21°C was estimated between 10% for the sulfides and 38% for the mercaptans and the relative uncertainty associated to humidity was found to be 36% for the most volatile RSCs at a relative humidity of 60% (20°C).

1. Introduction

As a result of recent industrial development, nearby residents are exposed to air pollution in different forms (particles, metal, inorganic, odorous pollution…). Among environmental pollutions, the odorous emissions are a problem because of their olfactory power more or less unpleasant. This pollution can be characterized by complex mixture to different families as oxygenated compounds, sulfurs and amines. Their origins can be from biogenic sources or from anthropogenic sources (Laor *et al.*, 2014). This study targets particularly sulfur compounds due to their very low odor thresholds (ppb level) (Devos, 1990). The most abundant sulfur compounds in the environment include hydrogen sulfide (H_2S), carbon disulfide (CS_2), carbonyl sulfide (COS), methylmercaptan (MM), dimethylsulfide (DMS) and dimethyldisulfide (DMDS) (Pal et al., 2009).

The determination of sulfur compounds in environmental samples is difficult due to their low concentrations in ambient air. It's therefore necessary to concentrate the samples for a better quantification of the sulfur compounds. Several studies, reviewed by Brown *et al.*, 2015, have focused on selecting the best sorbent for sampling organic sulfur compounds and have concluded that Tenax TA® is the most suitable sorbent for the RSCs sampling. Consequently, Tenax is often preferred against other sorbents for sulfur compound active and passive sampling in research works (Schiffman et al., 2001; Gallego et al., 2012) but also in surveys carried out by engineering offices. All studies carry out at the moment highlight a lack of information concerning the performances of active sulfur sampling on Tenax TA® (oxygen or humidity effect, uncertainties…). For this purpose, this paper describes a complete qualification of analytical and sampling system as the performance (determination of optimized sampling flows, breakthrough volumes …) and the uncertainties associated with the measurement of 6 reduced sulfur compounds (RSCs) at ppb levels using active sampling on Tenax TA®. The main goal is to estimate the standard error on existing concentration data

when they results from Tenax samplings. Key parameters as detection limit, repeatability, interference effects (of humidity and oxygen) and storage were considered for this evaluation.

2. Materials and Methods

A certified cylinder-based primary standard of RSCs was used (Praxair, France). 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%. This primary standard was diluted to prepare test gases with RSCs concentrations ranging from 1 to 200 ppb. Moreover, the sulfur compounds are known for their high reactivity with oxygen and humidity. So, qualification experiments of this analytical method were conducted by diluting primary mixture in pure dry nitrogen to avoid possible interference. The dilution of primary mixture in dry or wet air is used for studying the influence of potential effect of oxygen or humidity. Samples were collected on Sulfinert® cartridges (l: 89 mm, o.d: 64 mm, i.d: 5 mm) packed with about 250 mg of Tenax TA® (60-80 mesh size, Sigma-aldrich). A precise volume of test gas is trapped into the cartridge with help of a mass flow controller and a pump. Then, samples were analyzed by thermodesorption (ATD) coupled with a gas chromatographic system. A double desorption was applied: first, thermal desorption of the sampling tubes was carried out at 250 °C for 5 min with helium (primary desorption). After the RSCs were refocused within the cold trap of the thermal desorber packed with 100 mg of Tenax TA (60-80 mesh) and maintained at −10 °C. Then, the cold trap was quickly heated from −10 °C to 250 °C (secondary desorption) and maintained at this temperature for 15 minutes. The analytes were injected 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 FPD. For the analysis of RSCs, the GC system was operated at the following temperature settings T (initial): 35 °C for 5 min, T (first ramping): 5 °C/min rate until 150 °C, T (second ramping): 15 °C/min rate and T (final): 250 °C for 3 min with a chromatographic RTX-1 column (105 m × 0.53 mm i.d. and 3 μm film thickness ;Restek, France) and with a flow rate of 7.2 mL/min. The detector were alimented pure H_2 = 70 and pure air = 80 mL/min (T = 300°C, photo multiplier (PMT) voltage: 500V). In addition, to allow a simple comparison of the FPD's responses among different S compounds, the peak areas of all RSCs were integrated in the linear mode with a square root function.

3. Results and discussion

3.1 Determination of sampling parameters
The linearity range of the sampling was determined at sampling flows between 10 and 200 mL/min (5 ppb of RSC mixture during 10 minutes). For TBM, linearity of the curve was broken for a flow of 50 mL/min and for MM, EM, and DMS, for a flow of 80 mL/min. On the other hand, the curves for IPM and DES are still linear until a sampling flow of 200 mL/min. So in order to avoid the influence of the flow rate on the establishment of the breakthrough curves, a sampling flow below 40 mL/min (minimal sampling flow with a flow security of 20%) could be used.

3.2 Evaluation of the breakthrough volumes
The breakthrough volume is the maximal volume that can be sampled with complete efficient adsorption. This volume corresponds to the upper limit of the linearity of the curve: linearized response in function of the sampling volume. In the present case, the concentration of the different compounds was fixed around 1 ppb and the sample flow at 40 mL/min. The sampling time was modified between 10 and 120 minutes. Two replicates were carried out for each sampling volume. Figure 2 represents the different curves obtained for the 6 targeted compounds. Except for IPM and DES that do not present any breakthrough volume, for the other compounds, a breakthrough volume of about 2L is found. In order to keep a safety volume of 50%, the sampling volume was limited to 1L.
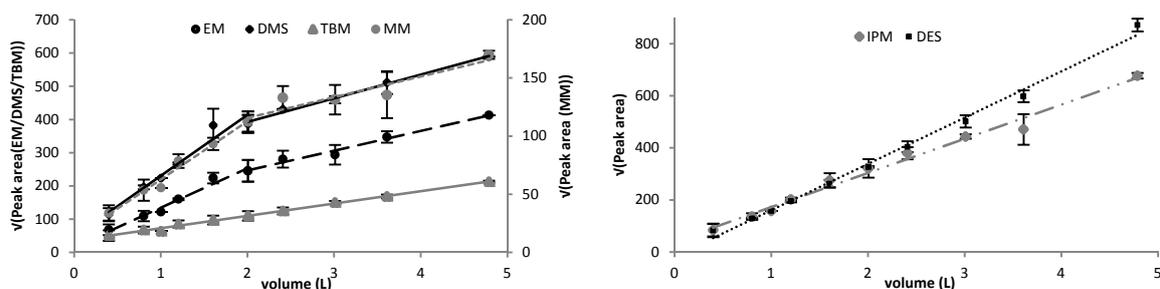

Figure 2: Breakthrough curves for RSCs sampled at 40 mL/min on Tenax TA cartridge

3.3 Chromatographic calibration
Determination of the dynamic measurement range with the detection system
To quantify sulfur compounds, calibration curves were needed for the analytical system. For calibration experiments, gaseous standard mixtures were prepared at five different concentrations ranging from 1 to 50 ppb in order to cover a range corresponding to real ambient air concentrations. According to this range and to limit a detector saturation, sampling volume was limited to 100 mL. The calibration pattern of RSCs in Figure 3 showed that the method led to patterns quite linear for all RSCs until 20 ng.
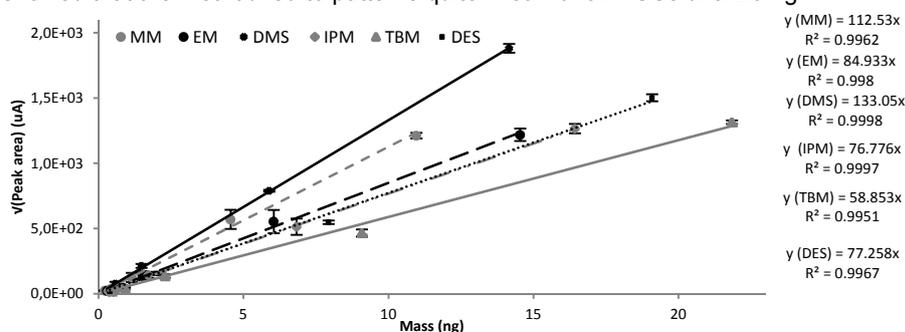

Figure 3: RSCs calibration curves obtained with the analytical system GC/FPD

Detection limits of the method
Measurements of the sulfur compounds in ambient air (concentration below 20 ppb) require the lower detection limit as possible. The detection limits for each compound are determined graphically and are summarized in Table 1. Taking into account the best sampling parameters (25 minutes at 40 mL/min), the detection limits vary from 20 ppt for DMS to 160 ppt for TBM. These values are in agreement with the concentrations of RSCs in ambient air and with their odor thresholds (around 1 ppb). These results are in the same order of magnitude comparatively to detection limits obtained by other groups (Table 1).

Table 1: Detection limits forRSCs with GC/FPD system in ng per cartridge or in ppt ([1]Susaya and al. (2011); [2]Campos and al. (2010))

	TD/GC/FPD (this work)		TD/GC/PFPD[1]	Cryogenic trap/GC/FPD[2]
Compounds	LD (ng)	LD (ppt)	LD (ppt)	LD (ppt)
MM	0.09	43	16	150
EM	0.18	71	-	-
DMS	0.05	21	-	193
IPM	0.31	98	-	-
TBM	0.59	160	-	-
DES	0.16	44	-	-

Repeatability of the measurements
A repeatability study was conducted by consecutive analysis of ten cartridges sampled in the same conditions with the same volume of working standard (100 mL at 50 ppb). The value of repeatability (% relative standard deviation (RSD)) for each RSCs as well as the collected mass on cartridges are reported on Table 2. The table highlights a relatively good RSD (< 7%) for all the compounds even the more volatile ones (i.e. MM).

Table 2: Repeatability of RSCs measurements with GC/FPD system

Compounds	Mass per tube (ng)	RSD (%)
MM	10.9	6.6
EM	14.4	3.3
DMS	14.0	1.4
IPM	16.3	1.4
TBM	21.6	1.7
DES	18.9	2.0

3.4 Storage stability
The storage of RSCs retained on the cartridges was studied. For this, seven cartridges were sampled with the same mixture of RSCs and stored in freezer (T< -21°C). After 7 days of storage, cartridges were analyzed and recovery was measured (%). Table 3 summarizes the results. An important loss was observed for MM and EM (>30%). For the others RSCs, the loss was below 10%. Haberhauer-Troyer and al. (1999) studied the storage

of MM, DMS and IPM on another support (SPME fiber) in ambient air and freezer during two days. Results showed a best storage of sulfur compounds in freezer with a maximum loss of 10%.

Table 3: Recovery of RSCs response after seven days of storage in freezer

Compounds	Average of Mass per tube (ng)	Recovery (N=7) Storage at T<-21°C (%)
MM	4.8	51 ± 6
EM	6.3	63 ± 9
DMS	6.2	91 ± 2
IPM	7.1	93 ± 2
TBM	9.5	96 ± 2
DES	8.3	95 ± 2

3.5 Influence of dilution matrix in RSCs adsorption
Influence of oxygen

To be able to conduct real measurements in ambient air, it's therefore important to quantify the influence of oxygen. For this, working standards were prepared with pure dry nitrogen and pure dry air at a concentration of 2 ppb (4 to 9 ng per cartridge assuming 25 min of sampling at 40 mL/min). These results showed a negligible effect of oxygen in RSC response (maximum 5% for MM). Any study highlights an effect of oxygen on RSCs sampled on Tenax TA®. However, effects like oxidation of mercaptans but not of sulfides have been shown by several studies made with others sorbents (mainly charcocoal sorbent). For example, Mochalski and al. (2009) quantified a loss of 50 % for MM sampled on SPME fiber (carboxen-PDMS) in the presence of oxygen and any loss for DMS.

Influence of humidity

To determine the influence of humidity on RSCs measurements, working standards of RSCs were prepared with pure air at a Relative Humidity of approximately 60 % (20 °C). For this, working standard was generated at 2 ppb (4 to 9 ng per cartridge with a sampling flow of 40 mL/min during 25 minutes). Calibrated temperature and humidity probes measure both parameters during the experimentation. The average relative humidity is estimated at 59.3 % for a temperature of 20°C (water concentration = 14000 ppm). The responses were compared to the same experimentation in dry air (Figure 4). Humidity was shown to cause a significant decrease of the adsorbed amount of all RSCs. Losses ranged from 17 % (DES) to 48 % (MM). The same conclusions were obtained by Haberhauer-Troyer et al. (1999) with losses between 20 and 40 % in function of RSCs with a relative humidity of 60% (Haberhauer-Troyer et al., 1999). One explanation could be a decrease in the efficiency of Tenax TA sorbent due to the adsorption of water molecules instead of RSCs or sulfur reactivity on the sorbent.
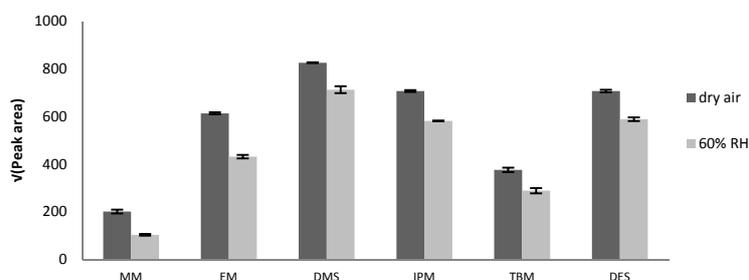

Figure 4: Comparison of RSCs response in two different dilution matrix: dry air and wet air (RH 60 % at 20°C)

3.6 Uncertainty of measurements of RSCs by using Tenax TA cartridge

The determination of measurement uncertainties allows the identification of the uncertainties sources and so, the identification of the more efficient improvement of the method. To our knowledge, no calculation of uncertainty exists for RSCs in literature. In order to quantify measurement uncertainties of RSCs concentrations in ambient air, two standards: EN 14662-1 (2005) and NF EN 1076 (2010), were used.

As shown on Equation 1, the global uncertainty on the concentration of RSCs depends of two parameters: one term related to analytical parameters $(U^2(C_{analytical}))$ and one term related to the sampling $(U^2(C_{sampling}))$. These two terms are explained in Equation 2 and 3. Two others parameters are also considering in uncertainties: the humidity effect (U^2_h) and the storage of the samples (U^2_{st}). The Equation 2 highlights parameters used to quantify the analytical uncertainties including: uncertainty related to the desorption efficiency (u^2D/D^2), the uncertainty on the mass measured for a compound on the cartridge $(u^2 (m_{meas})/m_{meas}^2)$ including uncertainties of repeatability, system drift, linearity, selectivity. The uncertainty of the sampling volume $(u^2 (V_{sam,STP})/V_{sam,STP})$ is

explained in Equation 3 and is composed to the uncertainty on the sampling flow and on the sampling duration.

$$\frac{u^2(C_m)}{(C_m)^2} = U^2(C_{analytical}) + U^2(C_{sampling}) + U^2{}_h + U^2{}_{st}$$ (1)

$$U^2 (C_{Analytical}) = \frac{u^2(m_{meas})}{(m_{meas})^2} + \frac{u^2(D)}{D^2} = w_F{}^2 + w_{selectivité}{}^2 + w_{anal}{}^2 + w_{cs}{}^2 + w_d{}^2 + \frac{u^2(D)}{D^2}$$ (2)

$$U^2(C_{sampling}) = \frac{u^2(V_{sam,STP})}{(V_{sam,STP})^2} = \frac{u^2(\varphi_{start,STP})}{(\varphi_{start,STP})^2} + \frac{u^2(t)}{t^2} + \frac{(\Delta\varphi_{STP})^2}{3 \times \varphi_{start,STP}{}^2}$$ (3)

The overall uncertainty of the RSCs concentration $U(C_m)$ and of analytical parameters $U(C_{analytical})$ calculated on Tenax TA® cartridges was determined with help of Equation 4. The global uncertainties U(C) for the six compounds are listed in Table 4.

$$U(C) = 2 \times \sqrt{u^2(c)}$$ (4)

Table 4: Global uncertainties for RSCs measurements made by active sampling of ambient air on Tenax TA

Compounds	Global concentration uncertainties (%)	Global Analytical uncertainties (%)
MM	86	9
EM	60	8
DMS	36	21
IPM	33	14
TBM	40	18
DES	33	17

The contribution of each parameters to the overall uncertainty was estimated (Figure 5).
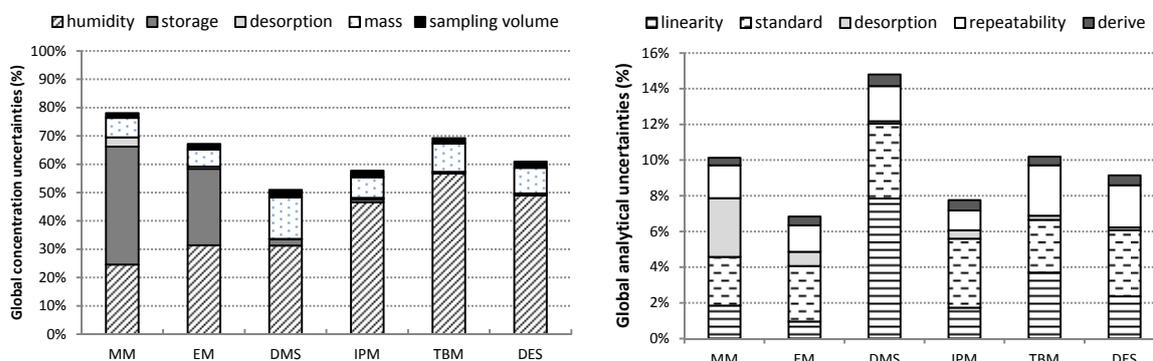

Figure 5: Contribution of each uncertainty parameters on global uncertainty of RSCs measurements made by in active sampling of ambient air on Tenax TA and analyzed by GC/FPD

The global uncertainty of RSCs concentration determined by active sampling of ambient air on Tenax TA® cartridge was led by two main parameters: the storage of samples and the humidity of the mixture. For storage, an uncertainty up to 28 % was found for the lightest sulfur compounds: MM, EM. For the other compounds, storage uncertainties are negligible. For the global analytical uncertainties, the linearity and the working standard represented the maximal uncertainties for all compounds (between 4 and 12 %). But the global analytical uncertainties did not exceed 21%. This value was in agreement with uncertainties give by analytical laboratory for other hydrocarbons compounds.

4. Conclusion

Although sulfur compounds are generally considered as being non-toxic at low concentrations, they may induce an odor annoyance for people living near sources. Many approaches and techniques exist for the measurements of sulfur compounds but, the sampling on sorbent is generally regarded as the best method for the low concentrations. In this study, we characterized the complete performance of a method based on active

sampling on Tenax TA cartridge coupled with GC/FPD analyze. This work highlights that this method is characterized by two principal biases for RSCs measurements: the storage and the impact of humidity for the lightest compounds as MM and EM. Storage and humidity uncertainties were estimated to a maximal value of 30% respectively. To measure the lightest compounds, the best way should be to use online chromatographic method with maximal uncertainty of 21% for DMS or to change the sorbent for reduce the uncertainties related to the storage and humidity effect. The current method could be applied for the measurements of other sulfur compounds studied here but a storage in freezer was required to limit the losses.

Acknowledgments

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