

Sulphur Compounds: Comparison of Different Sorbent Tubes for their Detection

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Different techniques have been developed for the analysis of gaseous sulphur pollutants, to maximize the analytical signals. In a complex matrix, such as odorous emissions, the detection of sulphur compounds can be critical in GC analysis, due to the lower concentration of these pollutants and the disturbing effect of co-eluting hydrocarbons. However, their detection is fundamental because they have a non-negligible odour impact. In the field of gaseous emissions analytics, it is common to use sorbent tubes for the sampling step. This technology uses different adsorbent materials, with different selectivity depending on the nature of the gas to be analysed. This work aims to evaluate the ability of three different sorbent tubes to collect different sulphur compounds, belonging to the classes of mercaptans, thioethers and aromatic heterocyclic compounds. A standard solution of 10 sulphur compounds was prepared by diluting in methanol 50 μL of each liquid standard into a 10 mL flask. Subsequently, this solution was diluted in methanol to obtain sulphur standards at five different concentrations (approximately 5-500 $\text{ng}/\mu\text{L}$). The tubes were loaded with the standard solutions with an aliquot of each solution, using a gas chromatograph packed column injector and subsequently analysed by TD-GC-MS. By the results obtained - average Response Factor (RF) and its Relative Standard Deviation (% RSD), it is possible to conduct a comparison among these tubes and evaluate their performance. From the comparison of the tubes, discussing % RSD, it is possible to highlight a slightly better performance, in terms of the number of compounds with % RSD $\leq 30\%$, for tubes specific for sulphur compounds. Focusing on RF values, multi-sorbent bed tubes show slightly higher RFs for very volatile sulphur compounds, but Sulphur tubes present higher RF values for 6 compounds out of 10 compounds considered. The performance of Tenax TA tubes, instead, appears strictly correlated with the compound's volatility and therefore they don't appear useful for sorption of very volatile compounds.

1. Introduction

The use of sorbent tubes in the sampling and analysis of gaseous emissions and immission is a common practice, both in indoor air and industrial context for the collection of volatile organic compounds (VOCs) (Gallego et al., 2009). The sorbent tube method is based on the air intake in metal or glass tubes filled with appropriate sorbent/s and then an analysis by thermal desorption (TD) and gas chromatography (GC). To cover the wide range of VOCs that could be present in gaseous matrices (Invernizzi et al., 2021), different materials have been developed and used as sorbents: Tenax TA, Carbotrap, Carbopack, Carbosieve and Carboxen 569 are only some examples. Every sorbent material has a different selectivity toward different classes of VOCs (Woolfenden, 1997). In the scenario of odorous impacts, an interesting class of VOCs is *sulphur compounds*. Indeed, volatile organic sulphur compounds (VOSCs) are characterized by a non-negligible odour impact, because they are characterized by a lower odour threshold (OT) and often VOSCs are present at very low concentrations (in the ppb range) (Kim et al., 2006). In addition, these chemicals can have several health effects (Byliński et al., 2019) and their analysis is fundamental to protecting workers and citizens exposed to them

(Korhonen et al., 2004). However, due to their volatility and reactivity, these compounds are often particularly difficult to sample, retain and be detected without the application of specific precautions or the use of specific instrumentation (Haerens et al., 2016). For example, phenomena of adsorption, diffusion or degradation can occur (Higgins et al., 2006). Focusing on sorbent tube methods, different sorbent materials have been developed to sample and retain, without leaks, reactions or degradation, sulphur compounds. In the literature, numerous papers have described the application of sorbent tubes, and their chemical analysis, for a wide range VOCs analysis (Czajka et al., 2020; Gallego et al., 2012; Harper, 2000). The most diffuse analytical technique is the combination of thermal desorption with gas chromatography coupled with mass spectrometry (TD-GC-MS). In this scenario, this study aims to compare the performance of three types of sorbent tubes, filled with different sorbent materials commonly adopted when preconcentration of mixtures is required, in the analysis of sulphur compounds. In particular, the study was conducted using standard solutions of 10 different VOSCs, belonging to the classes of mercaptans, thioethers and aromatic heterocyclic compounds. To estimate the sorbent materials performances and to evaluate their usefulness in collection of sulphur compounds, the comparison between the three different sorbent tubes was conducted by calculating the average Response Factor (RF) and its Relative Standard Deviation (% RSD).

2. Materials and methods

2.1 VOSCs and standard solutions

In the study, 10 target sulphur compounds were selected, according to their interest in the scenario of odorous emissions. The list of the VOSCs analysed in this experiment is shown in Table 1. In the table, for every sulphur compound considered, its CAS, formula, molecular weight (MW, expressed in g/mol), boiling point (T_b , expressed in °C) and odour threshold (OT, expressed in mg/m³) are reported.

Table 1: Target VOSCs considered

| VOSC | CAS | Formula | MW [g/mol] | T_b [°C] | OT [mg/m ³] |
|-----------------------|----------|--|---------------|---------------|----------------------------|
| Ethyl mercaptan | 75-08-1 | C ₂ H ₆ S | 62 | 35 | 2.21E-05 ^[a] |
| Dimethyl sulphide | 75-18-3 | C ₂ H ₆ S | 62 | 37 | 7.62E-03 ^[a] |
| Carbon disulphide | 75-15-0 | CS ₂ | 76 | 46 | 6.54E-01 ^[a] |
| Propyl mercaptan | 107-03-9 | C ₃ H ₈ S | 76 | 67 | 4.05E-05 ^[a] |
| Ethyl methyl sulphide | 624-89-5 | C ₃ H ₈ S | 76 | 66 | 2.20E-02 ^[b] |
| Isobutyl mercaptan | 513-44-0 | C ₄ H ₁₀ S | 90 | 88 | 2.51E-05 ^[a] |
| Thiophene | 110-02-1 | C ₄ H ₄ S | 84 | 84 | 1.93E-03 ^[a] |
| Diethyl sulphide | 352-93-2 | C ₄ H ₁₀ S | 90 | 92 | 1.22E-04 ^[a] |
| Dimethyl disulphide | 624-92-0 | C ₂ H ₆ S ₂ | 94 | 109 | 8.48E-03 ^[a] |
| Benzothiazole | 95-16-9 | C ₇ H ₅ NS | 135 | 227 | n.d. |

[a] (Nagata, 2003); [b] (Gemert, 2011); "n.d.": not defined

The VOSCs used were purchased as commercial neat chemicals from Sigma Aldrich (Milwaukee, WI, USA), with purity greater than or equal to 96%. They are liquids at room temperature. From these neat chemicals, stock standard solutions were prepared by diluting in methanol 50 µL of each liquid standard (via pre-weighted 100 µL Hamilton syringe) into a 10 mL flask. After that, this solution was diluted in methanol to obtain sulphur standards at five different concentrations (approximately 5-500 ng/µL). The five standard solutions were freshly prepared, transferred to locked vials and stored at 4 °C in darkness, until the use.

2.2 Sorbent tubes

Different sorbent materials exist, according to the type of compounds researched and the user's analytical needs (research of specific compounds or wide-ranging).

In the study, three types of tubes, packed with different adsorbent materials and characterised by different properties, were tested (Figure 1):

- Multi-sorbent bed (Carbotrap 20/40, 70 mg; Carboxen 569 20/45, 90 mg) obtained from Supelco (Bellefonte, PA, USA);
- Tenax TA (60/80, 200 mg, obtained from Supelco (Bellefonte, PA, USA));
- Tubes specific for sulphur and odorous compounds (Tenax TA+ SulfiCarb) (Markes International Ltd., UK).

Tubes A (Multi-sorbent bed), developed and described in (Ribes et al., 2007), are designed for the determination of both polar and non-polar VOCs, to be adopted in different scenarios and obtain the collection of different classes of compounds. For A and B types, sorbent materials were inserted manually inside glass tubes, obtained from Supelco (Bellefonte, PA, USA). On the contrary, types C, and inert-coated stainless-steel tubes were adopted.



Figure 1: Sorbent tubes used in this study

Before the use, tubes were conditioned by thermal cleaning (350 °C for 60 min for type B and C and 400 °C for 60 min for type A), under a flow rate of helium, using Markes Sorbent tube conditioner TC-20. After conditioning, tubes were immediately closed with Swagelok end caps fitted with PTFE ferrules and stored at 4 °C.

The day after conditioning, sorbent tubes were loaded with the standard solutions with an aliquot (1 µL) of each solution, using a gas chromatograph packed column injector (heated at 30°C and with a flow of 100 mL min⁻¹ of nitrogen during 5 minutes), according to a previous study (Ribes et al., 2007), and subsequently analysed by TD-GC-MS. During the period between injections of standard solutions in sorbent tubes and TD-GC-MS analysis (two days), the tubes were stored at 4°C to preserve the analytes correctly.

2.3 Analytical instrumentation

Analysis of tubes was performed by automatic thermal desorption (ATD) coupled with capillary gas chromatography (GC)/mass spectrometry detector (MS), using a Markes Unity Series 2 (Markes International Ltd., Llantrisant, UK) via Thermo Scientific Focus GC fitted with a Thermo Scientific DSQII MSD (Thermo Fisher Scientific, Austin, Texas, USA). Thermal desorption of the tubes was conducted at 300 °C with a flow rate of 53 mL/min for 10 min (primary desorption). After primary desorption, the cold trap was maintained at -30 °C, applying a flow rapidly heated from -30°C to 300 °C (secondary desorption) and then maintained at this temperature for 10 min. During the secondary desorption, the VOCs were submitted to a flow split of 11 ml/min and were injected onto the capillary column (DB-624) via a transfer lined heated at 200 °C. The column oven temperature started at 40 °C for 1 min, increased to 230 °C at a rate of 6 °C min⁻¹ and then maintained at 230 °C for 5 min. GC interface temperature was set at 250 °C. Mass spectral data were acquired over a mass range of 30–300 amu. The integrated area of the qualifier ion was obtained for each target compound for data manipulation (Xcalibur 1.2 validated software package). Qualitative identification of target VOCs was based on the match of the retention times and qualifier ions, shown in Table 2.

2.4 Performance parameters

The discussion of the performances of different sorbent tubes was conducted by comparing two principal parameters: the Average Response Factor (RF_{average}) and its Relative Standard Deviation (% RSD). The RF_{average} for each VOC was calculated as the average of the RF calculated for each of the five calibration levels (Eq.1)

$$RF_i = \frac{A_{\text{qual. ion}}}{C_{th}} \quad (1)$$

where the $A_{\text{qual. ion}}$ is the response area of the qualifier ion and C_{th} is the theoretical concentration of every calibration level (expressed in ng). Therefore, RF is expressed in Counts/ng. As acceptability criteria, the % RSD of the RF_{average} for each target VOC should be $\leq 30\%$, which accomplished EPA performance criteria (US EPA, 2019).

Table 2: Retention time (RT) and qualifier ions used for the identification of VOSCs considered

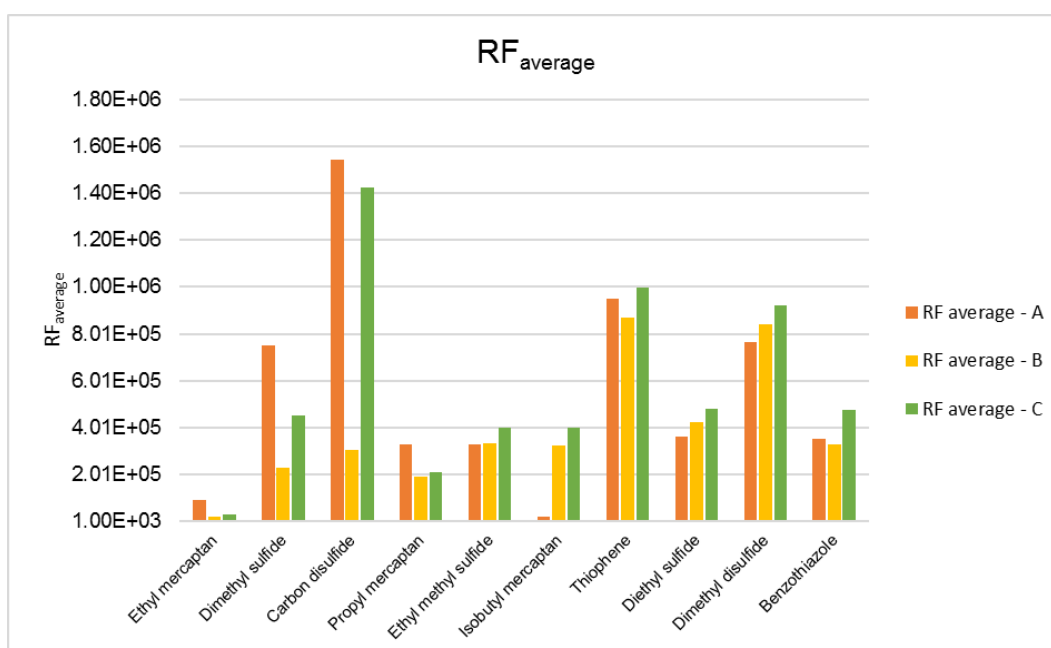
| VOSC | RT [min] | Qualifier ion <i>m/z</i> |
|-----------------------|-------------|-----------------------------|
| Ethyl mercaptan | 5.8 | 62 |
| Dimethyl sulphide | 6.2 | 62 |
| Carbon disulphide | 6.4 | 76 |
| Propyl mercaptan | 8.6 | 76 |
| Ethyl methyl sulphide | 8.8 | 76 |
| Isobutyl mercaptan | 10.85 | 90 |
| Thiophene | 10.88 | 84 |
| Diethyl sulphide | 11.6 | 90 |
| Dimethyl disulphide | 13.7 | 96 |
| Benzothiazole | 30.8 | |

3. Results and discussions

In this section, the statistical parameters used to evaluate the performance of the three considered tube types, when applied to the sampling and analysis of sulphur compounds, are reported.

Figure 2 shows the $RF_{average}$ calculated for each target compound, for each of the three types of sorbent tubes (A – Multi-sorbent bed, B- Tenax TA, C – Sulphur).

In Figure 3 a graphical representation of the % RSD calculated for every VOSC considered, divided by three different tubes type tested, is reported. A red line evidences the acceptability criteria adopted (% RSD \leq 30%).

Figure 2: $RF_{average}$ calculated for each VOSC considered

From Figure 2, it is possible to notice that the Tenax TA tube (B – yellow column) has, in general, lower RF values if compared with Multi-sorbent bed and Sulphur tubes. This is particularly evident observing RF values obtained for very volatile compounds (Ethyl mercaptan, Dimethyl sulphide, Carbon disulphide and Propyl mercaptan). On the contrary, by increasing of boiling point temperature and reaching close to 100 °C, a reduction in the difference between the Tenax TA and the other two types of tubes can be observed. This observation could be explained by the specific properties of Tenax TA adopted as sorbent material: the boiling point of 100 °C is often considered as a lower limit value below which the adsorption properties of compounds are not satisfying for Tenax TA (Gallego et al., 2010). Focusing on the comparison between Multi-sorbent bed and Sulphur tubes, in general, RF values for these two types of tubes are usually similar. However, focusing on discussing the slight differences observed, Multi-sorbent bed tubes show slightly higher RFs for very volatile sulphur compounds (Ethyl mercaptan, Dimethyl sulphide, Carbon disulphide and Propyl mercaptan).

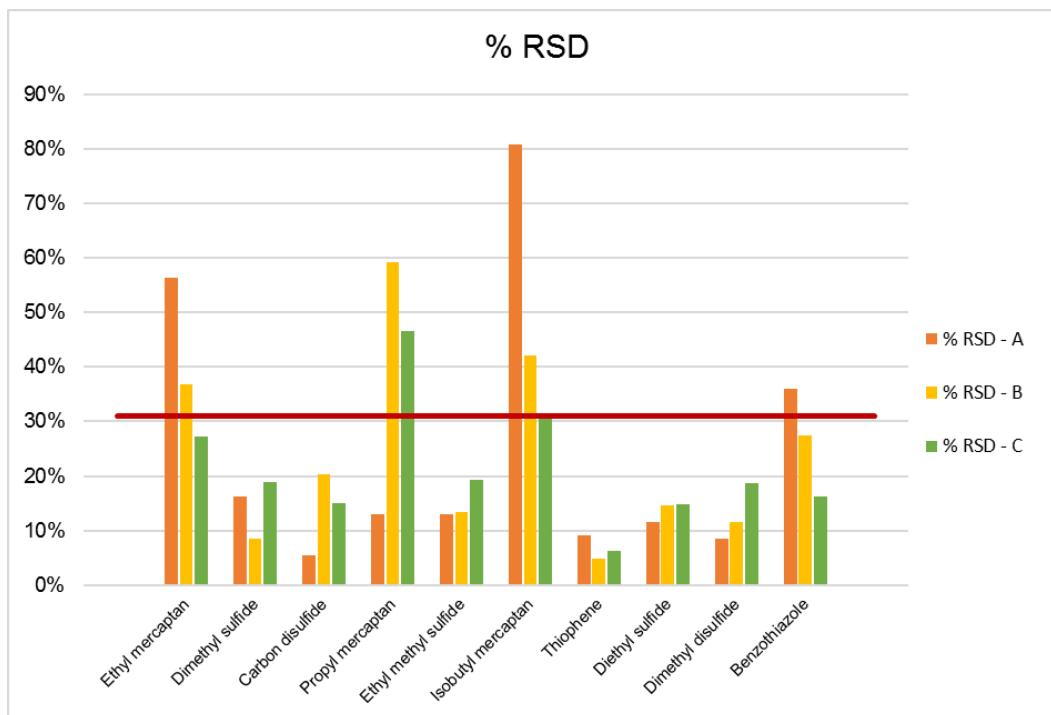


Figure 3: %RSD calculated – the red line represents the acceptability criteria (%RSD \leq 30%)

On the contrary, Sulphur tubes present higher RF values for the other 6 out of 10 VOSCs considered. Compared to that observed for the Multi-sorbent bed tubes, these 6 compounds are characterized by higher values of boiling point: in particular, Ethyl methyl sulphide, Isobutyl mercaptan, Thiophene, Diethyl sulphide, Dimethyl disulphide, Benzothiazole. It is therefore preliminarily possible to affirm that Multi-sorbent bed tubes show better performance for very volatile sulphur compounds. Discussing the RF values obtained for different compounds, Ethyl mercaptan shows the lowest RF for all the types of tubes: having observed similar performance for the different sorbent materials considered, it is possible to correlate this result with the high volatility of the compound ($T_b = 35\text{ }^\circ\text{C}$) resulting in difficult handling and retention of this compound. Focusing on Figure 3, it is possible to highlight a slightly better performance, in terms of the number of compounds with % RSD \leq 30%, for tubes specific for sulphur compounds (Sulphur tubes – type C). Indeed, the %RSD values of Multi-sorbent bed and Tenax TA tubes are above the selected acceptability criterion, with % RSD values up to 80% (Isobutyl mercaptan – Multi-sorbent bed tube, type A). However, considering the several manual operations during the preparation phase of the standard, the % RSD value could be also a parameter strictly correlated and influenced by the operator's manual skills: for this reason, these differences in performance could be explained and related more to operation procedure than to the intrinsic characteristics of the sorbent materials investigated and particular attention should be paid to assessing and reducing this possible source of error.

4. Conclusion

The selection of sorbent materials could be a critical point for the chemical analysis of odorous emissions, due to the different sorbent materials available for the retention of the wide range of VOCs potentially present in odorous emissions and immission. The presence of specific compounds, such as VOSCs, can drastically influence the selection of specific sorbent materials due to the critical aspects associated with their detection and storage. To better investigate the performance of different sorbent materials applied to the analysis of VOSCs, a comparison of different sorbent tubes applied to the analysis of sulphur compounds was discussed in this study. From the preliminary results obtained, Sulphur tubes, specific for the collection of VOSCs, present slightly better performances compared to other tubes, in terms of the number of compounds with % RSD \leq 30%. Focusing on the resulted RF, Multi-sorbent bed and Sulphur tubes present similar performance. However, slightly better performances for very volatile sulphur compounds can be observed for Multi-sorbent bed tubes. Discussing Tenax TA tubes, they show the influence of volatility of compounds on the sorption performance that could enable Tenax TA material to be applied in other analytical contexts.

By the presented analysis, this material appears not appropriate for the adsorption of very volatile sulphur organic compounds (boiling points lower than 100 °C). However, with compounds with boiling points close to 100 °C, Tenax TA tubes show similar performances to Sulphur and Multi-sorbent bed tubes. It is important to note that this study is a first attempt to evaluate the different performance of sorbent materials for the detection of sulphur compounds and further evaluations could be conducted to deepen the quality assurance (additional repetitions, influence of STD concentration, operator bias).

References

- Byliński, H., Gębicki, J., Namieśnik, J., 2019, Evaluation of Health Hazard Due to Emission of Volatile Organic Compounds from Various Processing Units of Wastewater Treatment Plant, *International Journal of Environmental Research and Public Health*, 16(10).
- Czajka, M., Fabisiak, B., Fabisiak, E., 2020, Emission of Volatile Organic Compounds From Heartwood and Sapwood of Selected Coniferous Species, *Forests*, 11(1).
- Gallego, E., Roca, F. J., Perales, J. F., Guardino, X., 2010, Comparative study of the adsorption performance of a multi-sorbent bed (Carbotrap, Carbopack X, Carboxen 569) and a Tenax TA adsorbent tube for the analysis of volatile organic compounds (VOCs), *Talanta*, 81(3), 916–924.
- Gallego, E., Roca, F. J., Perales, J. F., Sánchez, G., Esplugas, P., 2012, Characterization and determination of the odorous charge in the indoor air of a waste treatment facility through the evaluation of volatile organic compounds (VOCs) using TD-GC/MS, *Waste Management*, 32(12), 2469–2481.
- Gallego, E., Roca, X., Perales, J. F., Guardino, X., 2009, Determining indoor air quality and identifying the origin of odour episodes in indoor environments, *Journal of Environmental Sciences*, 21(3), 333–339.
- Gemert, L. J. van, 2011, *Flavour Thresholds: Compilations of Flavour Threshold Values in Air, Water and Other Media*, Oliemans Punter Partners BV, The Netherlands.
- Haerens, K., Segers, P., Van Elst, T., 2016, Sampling and stability of mercaptans: Comparison between bags, canisters and sorbent tubes, *Chemical Engineering Transactions*, 54, 31–36.
- Harper, M., 2000, Sorbent trapping of volatile organic compounds from air, *Journal of Chromatography A*, 885(1–2), 129–151.
- Higgins, M. J., Chen, Y.-C., Yarosz, D. P., Murthy, S. N., Maas, N. A., Glindemann, D., Novak, J. T., 2006, Cycling of Volatile Organic Sulfur Compounds in Anaerobically Digested Biosolids and Its Implications for Odors, *Source: Water Environment Research*, 78(3), 243–252.
- Invernizzi, M., Roveda, L., Polvara, E., Sironi, S., 2021, Lights and Shadows of the Voc Emission Quantification, *Chemical Engineering Transactions*, 85, 109–114.
- Kim, K. H., Jeon, E. C., Choi, Y. J., Koo, Y. S., 2006, The emission characteristics and the related malodor intensities of gaseous reduced sulfur compounds (RSC) in a large industrial complex, *Atmospheric Environment*, 40(24), 4478–4490.
- Korhonen, K., Liukkonen, T., Ahrens, W., Astrakianakis, G., Boffetta, P., Burdorf, A., Heederik, D., Kauppinen, T., Kogevinas, M., Osvoll, P., Rix, B. A., Saalo, A., Sunyer, J., Szadkowska-Stanczyk, I., Teschke, K., Westberg, H., Widerkiewicz, K., 2004, Occupational exposure to chemical agents in the paper industry, *International Archives of Occupational and Environmental Health*, 77(7), 451–460.
- Nagata, Y., 2003, Measurement of Odor Threshold by Triangle Odor Bag Method, *Odor Measurement Review*, 118–127.
- Ribes, A., Carrera, G., Gallego, E., Roca, X., Berenguer, M. J., Guardino, X., 2007, Development and validation of a method for air-quality and nuisance odors monitoring of volatile organic compounds using multi-sorbent adsorption and gas chromatography/mass spectrometry thermal desorption system, *Journal of Chromatography A*, 1140(1–2), 44–55.
- US EPA, 2019, *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Method TO-15*.
- Woolfenden, E., 1997, Monitoring VOCs in Air Using Sorbent Tubes Followed by Thermal Desorption-Capillary GC Analysis: Summary of Data and Practical Guidelines, *Journal of the Air & Waste Management Association*, 47(1), 20–36.