

Sampling and analysis of sulphur containing volatile organic compounds at low concentrations

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Sampling and analysis of sulphur-containing volatile organic compounds (S-VOCs) is not straightforward, since S-VOCs can be observed by human nose in very low concentrations. In addition, most of the people find these odours very unpleasant. This paper presents the results of emission measurements originating from a rendering plant and development of measurement strategy to ensure the reliability of the results. These results are needed e.g. in designing of an optimal abatement system. Three different adsorbents are tested in laboratory and industrial scales including Tenax TA, Carbograph 1 TD and Carboxen 1000 in sampling of methyl mercaptane (MM), dimethylsulphide (DMS) in dry and moist conditions. It was found that none of the adsorbents tested, was really good in sampling of methyl mercaptane and dimethyl disulphide. Tenax TA, even having a low breakthrough for tested compounds, can be used in moist conditions. A multiple-bed adsorbent showed the best performance in dry conditions.

1. Background

Sulphur containing volatile organic compounds (S-VOCs) emitted e.g. from landfills, pulp mills and rendering plants cause often odour disturbances. These mixtures contain mercaptanes and other organic sulphur compounds such as dimethyl sulphides. Olfactive nuisances are more and more frequent due to the growing urbanization and the consequent location of odorous sources nearby the municipality. (Gostelow *et al.* 2001, Davoli *et al.* 2003)

The perception levels of the human nose are often very low, even at ppt level, and the limits for industrial S-VOC emissions are more and more strict (below $\text{mg N}^{-1}\text{m}^{-3}$ air). In addition, there are plenty of natural sources for the formation of malodorous sulphur-containing emissions such as decomposition of organic matter and bacterial sulphate reduction (Black, 1978). Therefore, a reliable sampling and analysis of these compounds is needed. Furthermore, S-VOCs are present in multicomponent gas mixtures which make the analysis a demanding task. S-VOCs also tend to adsorb on the surfaces of samplers, and in the case of mercaptanes, may undergo partial oxidation. Therefore, all the materials used in sampling and analysis should be as inert as possible. (Davoli *et al.* 2003, Dewulf and van Langenhove 1999)

The most widely applied technique for sampling of VOC emissions is the pre-concentration on a solid adsorbent. There exist a number of solid adsorbents that may be used in sampling of S-VOCs including carbon molecular sieves and polymer adsorbents. For example Zemmeling *et al.* (2002) tested Tenax as an adsorbent for dimethyl sulphide (DMS). They found out that DMS is rather unstable when atmospheric oxidants are present, and the loss of DMS is significant in sampling if the oxidants are not removed before trapping. Black *et al.* (1978) have tested SO₂ and H₂S adsorption on various adsorbents. They found that adsorption capacities of Molecular Sieves 5A and 13X were quite good.

In this study, Tenax TA, Carbograph 1 TD and Carboxen 1000 were used. *Tenax* is a porous polymer resin based on 2,6-diphenylene oxide having a low polarity. It has specific surface area of 20-35 m²g⁻¹ and it has low affinity for water. Operational temperature should be below 375°C. *Carbograph* is a graphitized carbon black, which has normally a specific surface area of 12-100 m²g⁻¹. It is a non-polar adsorbent and has a low adsorption capacity for low boiling compounds and water. It has a good thermal stability. Third adsorbent used in this study is *Carboxen* – a carbon molecular sieve with high specific surface area of about 400-1000 m²g⁻¹. It has a low polarity and a very high adsorption capacity. In addition it should have better desorption of polar compounds than activated charcoal and low adsorption of water. With all these three, thermal desorption can be used in connection of analysis. (Tirkkonen *et al.* 1995) Ideally, an adsorbent should have infinite breakthrough volume for the compounds that are sampled, a complete desorption of the target compounds at reasonable temperature, no generation of artifacts and no retention of water vapor, which targets can not, however, normally be reached. (Dewulf and van Langenhove 1999) Therefore, determination of a suitable sampling time, selection of adsorbent material, evaluation of storage times and determination of desorption recoveries are crucial aspects in reliable sampling.

The aim of this study was to find an efficient adsorbent for sampling of emissions originating from a rendering plant. In this case, three adsorbents were tested. In adsorption sampling, special aspects should be considered due to sampling conditions.

2. Experimental

The S-VOC sampling was tested both in laboratory and industrial scales. Three adsorbent materials as single and multi-layered adsorbents were used as follows: Tenax TA (Ads. 1), Tenax TA + Carbograph 1 TD (Ads. 2) and Tenax TA + Carbograph 1 TD + Carboxen 1000 (Ads. 3). Adsorbents 1-3 were conditioned prior to sampling in a He flow of 100 ml/min. The adsorbents 1 and 2 were kept at 320°C for 2 hours, after which they were heated up to 335°C for 30 min. Adsorbent 3 was first treated at 100°C for 1 hour followed by 1 hour at 200°C and then 300°C, and finally, at 335°C for 30 min. The treatment with adsorbent 3 is longer, since oxygen and water should be removed carefully and without damaging the carbonised molecular sieve.

The analysis of adsorbents was carried out with TD/GC/MSD (Markes/Agilent Technologies 6890N/Agilent Technologies 5973 Network). The maximum desorption

temperature of adsorbents is 350°C, but the manufacturer recommends the use of 300-320°C in the desorption stage. 300°C was used in these analyses. In the GC analysis a capillary column (HP-5MS) with the length of 30, diameter of 250 µm and film thickness of 0.25 µm was used. Temperature of the (splitless) injector was 250°C, total flow in the column was 92.1 ml/min and carrier gas used was He (88 ml/min). The oven program for GC was started with 3 min at 40°C and then heating was started with linear heating rate of 30°C/min up to 300°C, where it was kept 30 min. The total runtime for the GC program was 41.33 min. With MSD, the scanned molecular mass range was 20-800. The scan-mode was used in order to find out also possible artefacts formed during sampling and analysis.

2.1 Laboratory experiments

Determination of breakthrough values

The adsorbents were first tested at laboratory to determine their breakthrough times (BTT) and volumes (BTV) for methyl mercaptane (MM) and dimethyl sulphide (DMS) sampling. In the determination the 'direct method' was used (see e.g. Namiesnik and Kozlowski 1982). In order to obtain the very first breakthrough values, the breakthrough time was evaluated by sensory impression. This is possible, because the tested compounds have very low odour levels, 2-8 ppb and 1-20 ppb for MM and DMS, respectively. This means that in a present state, a nose is a very sensitive detector for these compounds. (Young 2005) The effect of other odours possibly present in laboratory atmosphere was minimized by using a ventilated laboratory mask where the outlet gas from an adsorbent was introduced during the odour sensation.

The model emission gases (~40 ppm MM in air and ~80 ppm vaporized DMS in air) were introduced into adsorption tubes with a rate of ~100 ml/min at room temperature. The outlet gas was then monitored by smelling and when the compound was observed at the outlet, adsorption was stopped and the tubes were tightly capped to wait for the analysis. When the odour was observed, the time was recorded. All these tests were done at least twice to make the evaluation more reliable. In addition, odour appearance at the outlet of a sampling tube was tested with several (2-3) persons. During the experiment, the feed concentrations were also checked with FTIR-analysis (Gasmeter Dx4000N).

Testing the effects of moisture and mixture

After testing the breakthrough values, the effect of moisture and mixture of the model compounds were tested for all adsorbents. A known amounts of MM, DMS, water vapour or their mixtures in air were introduced into adsorbents with a sampling rate of 100 ml min⁻¹. The analyses of the tubes were carried out in a similar way than described before.

2.2 Industrial sampling

S-VOC samples were collected at a rendering plant that uses ~30 000 tonnes of raw material per year to produce animal fats and proteins. The rendering process consists of crushing and heating animal remains to produce the mentioned products. The company has a problem with a pungent odour spreading to the surroundings. It is known from our

previous experience that the part of the odour is coming from sulphur-containing compounds, such as methyl mercaptane.

The sampling was carried out outside the rendering plant directly from above the bio-filter that is used to reduce the odour problem. The outside temperature was +2.8°C, but the temperature measured next to the sampling site was 22.5°C. The sampling was carried out in moist conditions, however, the exact level of atmospheric moisture was not measured. The samples were taken with a double-tubing system, when the possible breakthrough could be observed from a second adsorbent tube. The sampling pump was calibrated to work with a sampling rate of 100 ml/min.

3. Results and discussion

3.2 Determination of break through values

The breakthrough volume is related to the sampling capacity of an adsorbent, and can be defined as the gas volume which passes through the sampler before a given compound begins to be eluted from the adsorbent. This occurs when the concentration ratio of effluent gas to incoming gas reaches a pre-defined value. Similarly, breakthrough time BTT is the time needed in the determination of BTV. It is known that the BTV value of a given adsorbent/adsorbate system is often an exponential function of the adsorbate concentration. So, when concentration increases the values of BTV and BTT decrease. This indicates that the precise determination of BTV value can't be a general measure of a sampling capacity of an adsorbent. (Bertoni and Tappa 1997) Therefore, BTV values should be considered as case-dependent and in our case, the breakthrough values were determined in such a way that is suitable to the measurement of these special emissions. Table 1 presents the results of the evaluation of breakthrough values.

Table 1. Breakthrough values of different adsorbents at room temperature; BTT breakthrough time, BTV volume of gas flow/mass of adsorbent.

Ads.	MM			DMS		
	Feed concentration [ppm]	BTT [min:s]	BTV [$l\ g^{-1}$]	Feed concentration [ppm]	BTT [min:s]	BTV [$l\ g^{-1}$]
1	35	8:30	4.38	80	1:00	0.50
2	35	14:50	4.23	80	15:00	4.31
3	35	57:30	14.04	80	47:00	11.09

The results show that in general, the BTT is increasing in the following order: adsorbent 1, 2 and 3 independent of the model compound used. This is probably related to the specific surface area of the adsorbents which is increasing in the same order. BTT values presented in Table 1 are determined slightly differently than normally, *i.e.*, the breakthrough point was observed by sensory impression. Therefore, in the experiments, the level of odour (concentration of model compound at break through moment) might be slightly different than normally presented in the literature related to the determination of breakthrough values. In the repeated experiments, the BTT:s were surprisingly close to each other, and the BTT values presented in Table 1 are averaged values from 2-3

repetitions. In addition to the selected concentration level at the outlet, it is good to notice that the BTT value is also dependent on the mass and surface area of the adsorbent. The determined BTT values were used in selection of suitable sampling time for further testing in laboratory and industrial scales. The sampling times in further experiments were 0:30 min, 10:00 min and 30:00 min for adsorbents 1, 2 and 3, respectively. Breakthrough volumes were calculated by using the information of the sampling pump flow rate, sampling time and adsorbent mass. In general, BTV values seem to be quite low, but in an acceptable level compared to the values published by the adsorbent supplier. In addition, BTVs determined for SO₂ and H₂S on Tenax GC and different Molecular Sieves were quite similar to the values shown above (Black *et al.* 1978).

According to analysis results, the adsorbent 3 seems to be the best-one for MM sampling. In other adsorbents, MM seems to convert to DMDS, since the amount of DMDS found in all the adsorbents was exceptionally high while the amount of MM was very low. Actually, adsorbent 3 was the only-one where MM could have been detected with good quality, and therefore, Carboxen 1000 should be tested alone in MM adsorption to avoid the effect of Tenax TA and Carbograph 1 TD. All the tested adsorbents are more suitable in DMS sampling. Probably due to better adsorption capacity, the adsorbent 3 seems, once again to be the best. In addition, adsorbent 2 is significantly better than adsorbent 1. In summation, it looks like when MM is adsorbed on adsorbents 1 and 2 significant partial oxidation of MM to DMDS occurs. This may be due to the air matrix used in sample preparation, and present in real conditions as well. The results allow us to consider, that Tenax TA is not a good adsorbent for MM and DMS sampling. This is consistent with the results of Black *et al.* (1978), since they considered that due to low adsorption capacities of porous polymer and graphitized carbon for sulphur containing gases, they are not very suitable for field testing.

3.3 Effect of moisture and mixture

The moisture may affect the adsorption of the compounds but it may also cause problems in thermal desorption of the samples. The problems arise due to possible ice formation in the cooling-trap –phase of desorption, which may plug the gas flow. Therefore, it is important that the adsorbents used in industrial measurements have a low affinity to water. All the tested adsorbents should have rather low adsorption capacity for water. Especially Tenax is reported to be suitable for sampling in moist conditions. It is also possible, that certain compounds affect the adsorption of other compounds when they are present as mixtures. For example, the atmospheric oxidants may affect the sampling of methyl mercaptane, since it is a rather reactive compound. Table 2 shows how the moisture and mixture of model compounds affect the tested adsorbents 1-3.

Table 2. Comparison of the adsorption of the model compounds in dry and moist conditions on adsorbents 1-3 (n.d. not detected).

Adsorbent 1				
Compounds	Feed [ppm]	Adsorbed adsorbed dry [%]	wet / dry [%]	DMDS formed wet / DMDS formed dry [%]
MM	39			
MM+H ₂ O	39+1.5%	40		60
DMS	80			
DMS+H ₂ O	80+1.5%	120		-
MM+DMS	39+80			
MM+DMS+H ₂ O	40+80+1.5%	n.d. dry + 200		120
Adsorbent 2				
Compounds	Feed [ppm]	Adsorbed adsorbed dry [%]	wet / dry [%]	DMDS formed wet / DMDS formed dry [%]
MM	35			
MM+H ₂ O	35+1.5%	n.d. wet		150
DMS	80			
DMS+H ₂ O	80+1.5%	80		-
MM+DMS	35+80			
MM+DMS+H ₂ O	35+80+1.5%	n.d. wet + 180		160
Adsorbent 3				
Compounds	Feed [ppm]	Adsorbed adsorbed dry [%]	wet / dry [%]	DMDS formed wet / DMDS formed dry [%]
MM	35			
MM+H ₂ O	35+1.5%	n.d. wet		80
DMS	80			
DMS+H ₂ O	80+1.5%	30		-
MM+DMS	35+80			
MM+DMS+H ₂ O	35+80+1.5%	n.d. wet + n.d. wet		50

On all adsorbents moisture affects the adsorption of MM *i.e.* the amounts of MM detected from an adsorbent after adsorption in the presence of water are significantly smaller. The results show also that MM is not detected in the analysis of adsorbent 2 and 3 in moist conditions at all. This is surprising, since the water feed was not very high, only 1.5%. This may be either due to competitive adsorption of water on the adsorbent or due to the effect of water on thermal desorption-phase of analysis. The adsorption of DMS on adsorbent 1 is slightly enhanced in moist conditions even if in the case of adsorbents 2 and 3 adsorption is decreased. In addition, in the cases of adsorption of the mixture of MM and DMS, DMS adsorption is again enhanced in moist conditions on adsorbent 1 and 2. It can be seen that in moist conditions, adsorbent 1, *i.e.* Tenax TA is the best choice, even if it was considered worse based on the adsorption capacity. Furthermore, it seems that the molecular sieve is not a good adsorbent in moist conditions.

When the effect of mixture is considered, it can be seen that MM is rarely detected in analysis, except from adsorbent 1 in moist conditions. It means that in a mixture, MM is either not adsorbed or it reacts to DMDS. The results show also, that DMS adsorption is somewhat enhanced in the mixture with MM in both wet and dry conditions. However, adsorbent 2 makes an exception, the mixture is affecting negatively in both adsorption of MM and DMS in dry conditions.

3.4 Industrial measurements

The industrial sampling was carried out in moist conditions. Furthermore, the exact temperature of sampling is easily less than room temperature due to weather conditions during the sampling. Both the sampling temperature and weather conditions affect the results. Table 3 shows the main compounds detected in adsorption samples for the pre-adsorbent (major sampling tube) and the post-adsorbent (breakthrough detection tube).

Table 3. Main compounds detected from adsorbents 1-3 after industrial sampling (n.d. not detected).

Adsorbent 1 (pre)	Adsorbent 2 (pre)	Adsorbent 3 (pre)
n,n-dimethylamine	n,n-dimethylamine	n.d.
DMDS	DMDS	DMDS
Adsorbent 1 (post)	Adsorbent 2 (post)	Adsorbent 3 (post)
n,n-dimethylamine (equal amount)	n.d.	n.d.
DMDS (very little)	DMDS	DMDS (very little)

The results show firstly, that the concentrations of the emissions are extremely low. Therefore, the sampling time could have been longer. In previous measurements, it was found that emission contains MM and DMS (see Figure 1). Neither of these compounds was detected at this time. However, detection of rather high amounts of DMDS in the pre-adsorbents suggests that MM could have been present during the sampling, but it has reacted to DMDS. It is possible, since previous direct measurements have not shown the presence of DMDS in the sampled gas. In addition, the sampling was carried out in moist conditions, which according to laboratory results, may hinder MM adsorption. Wet conditions may also enhance DMDS formation from MM when adsorbents 1 and 2 are used. Adsorbent 3, which was found to be best in laboratory testing, seems to be a poor adsorbent for n,n-dimethylamine. In addition, it has also been seen that it is quite poor when used in moist conditions.

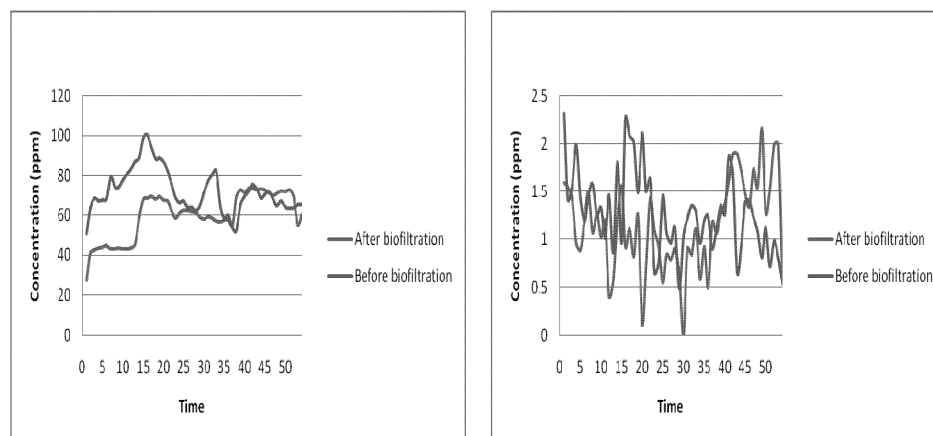


Figure 1. Results of industrial FTIR-measurements from the rendering plant above a biofilter: a) methyl mercaptane, b) dimethyl disulphide.

4. Conclusions

According to the results, simultaneous sampling together with a continuous on-site analysis of the gas flow gives most reliable results in the case of SVOCs. Multi layered adsorbents seem to be more applicable samplers for the SVOC sampling, but in the presence of water vapour the polymer-based Tenax TA adsorbent is the most useful. The way of determination the breakthrough values used in this case, is maybe not the most accurate or analytical one, even if the odour breakthrough was evaluated with several persons, but it is a simple and fast way to resolve the suitable sampling times in industry.

5. References

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