

Evaluation of Adsorbent Materials for the Sampling of Chlorine Containing Volatile Organic Compounds

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The limits for industrial emissions of volatile organic compounds (VOCs) are often very low, and therefore a reliable sampling and analysis of these compounds is needed. Furthermore, VOCs are present in multicomponent gas mixtures which make both the sampling and analysis a demanding task. In this study, two adsorbents (Tenax TA and Anasorb CMS) were evaluated and compared in the sampling of chlorine containing volatile organic compounds (CVOCs) under process conditions. Emission gas included several chlorine containing volatile organic compounds (CVOCs). According to the results, Anasorb CMS adsorbent seemed to trap some of these compounds more efficiently than Tenax TA adsorbent which is commonly used in sampling of gaseous compounds at low concentrations.

Keywords: analysis, adsorbent, chlorine, sampling, volatile organic compound

1. Introduction

Halogenated volatile organic compounds (HVOCs) are a group of compounds that have aroused tremendous attention over the past two to three decades (Janssen & van Santen, 1999). HVOCs can be defined as a subgroup of VOCs, which are regulated in EU by the VOC Solvent Directive (Directive 1999/13/EC).

Recently, volatile organic compounds (VOCs) are widely studied because of their contribution to major environmental problems such as global warming, stratospheric ozone depletion, photochemical ozone formation and odour nuisance. Moreover both VOCs and their decomposition products may be significant factors in the epidemiology of respiratory disorders and cancer (Demeestere, 2007).

Wide range of definitions for VOCs can be found in the literature. According to the definition of US Environmental Protection Agency (EPA), VOCs are organic compounds taking part in photochemical ozone creation. The American Society for Testing and Materials defines VOCs as organic compounds having a vapour pressure larger than 13.3 Pa at 25°C (Test Method D3960) and the EU Solvents Directive (Directive 1999/13/EC) defines VOCs as organic compounds having a vapour pressure of at least 10 Pa at 20 °C.

Similarly to VOCs, HVOCs can be defined as organic compounds having a vapor pressure above 10 Pa at 20 °C and containing at least one halogen (fluorine, chlorine, bromine, iodine) atom. Environmentally important HVOCs or HVOCs with great environmental importance include methyl halides, halogenated solvents and freons. (Dewulf et al. 2006).

The VOC Solvents Directive is the main instrument for the reduction of VOC emissions in the European Union (EU). In the case of chlorine containing volatile organic compounds (CVOCs), Montreal Protocol (Montreal Protocol, 2000) also prevents the use of certain CVOCs.

The most widely applied technique for sampling of VOCs in indoor and outdoor air is the preconcentration of VOCs on a solid adsorbent. Air sampling and pre-concentration of HVOCs are generally performed in a single step by adsorption onto solid adsorbents, such as carbon molecular sieves, graphitized carbon blacks or porous organic polymers. The pre-concentrated analytes are then analyzed by gas chromatography (GC) after thermal desorption (Dewulf et al. 2006).

The evaluation of the ability of a sorbent to trap selected VOCs is usually determined by measuring the breakthrough volume (BTV) of a compound on the adsorbent. Several sorbent materials are available, of which Tenax TA, activated charcoal and molecular sieves are typically used in active sampling of volatile organic compounds.

Based on the results of Dewulf et al. (2006) and on our earlier studies (Heikkinen, 2006; Perttunen, 2006), it is self-evident that these conventionally used sorbent materials are not suitable adsorbents for all the sulphur and chlorine containing volatile organic compounds. E.g. SVOCs are typically adsorbed on Tenax TA and activated charcoal adsorbents. Tenax is also used in sampling of chlorine containing volatile organics, most of which are not adsorbed onto its surfaces. Carbon molecular sieves (CMS) seem to be more applicable samplers for the CVOC sampling than polymer-based adsorbents (Heikkinen, 2006; Perttunen, 2006).

Environmental authorities in Finland use Tenax TA as a sorbent material for sampling of CVOCs, but according to earlier results (Dewulf et al. 2006; Perttunen, 2006; Heikkinen, 2006), it is not suitable for this purpose. Therefore there is a need for novel sorbent systems (e.g. multibed systems) which enable the simultaneous sampling of several compounds. New sorbent materials, e.g. carbon nanotubes, should also be considered as an adsorbent for CVOCs.

In this study, Anasorb CMS (carbon molecular sieve) adsorbent was evaluated and compared with Tenax TA adsorbent in the sampling of chlorine containing volatile organic compounds (CVOCs) under solvent-use process conditions, where the emission gas flow is a mixture of several compounds.

2. Experimental

Sampling of chlorine containing VOCs was carried out in field conditions. Emission gas from this solvent-using process was continuously analysed with Gasmeter Dx4000N FTIR analyser (Figure 1). Simultaneously to on-line gas analysis, gas samples were collected into adsorption tubes (Figure 2a), using both Tenax TA and Anasorb CMS as sorbent materials. According to previous results (Ojala et al. 2006), simultaneous sampling together with a continuous on site analysis of the gas flow gives the most reliable results. In the emission gas there were several gaseous compounds present

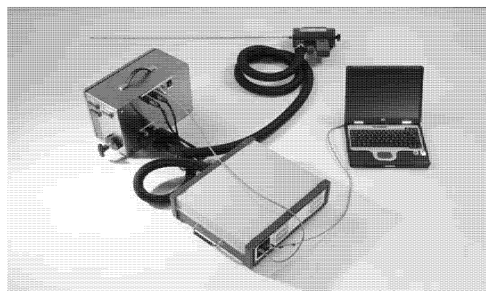


Figure 1. An on-line FTIR gas analyzer (Gaset Dx4000N) equipped with the sampling unit. (Gaset Technologies, 2006)

simultaneously, but in the following discussion only those which were calibrated with the Gaset FTIR analyser will be considered.

Gaset FTIR analyser was equipped with the automatic sampler, heated sampling lines and sampling probe. It was calibrated with 35 gaseous compounds in the concentration ranges of 0-200 ppm or 0-500 ppm depending on the compound. On these calibration areas, the reference measurements were earlier carried out with individual chlorine containing compounds as well as with the gas mixtures to confirm the reliability of the FTIR measurement method (Perttunen, 2006).

Almost every type of chemical bond absorbs infrared radiation. Only symmetric bonds, such as H_2 or Cl_2 , are not active in this respect. In FTIR spectroscopy each compound gives a characteristics FTIR spectrum. When spectra of pure compounds are known, the unknown compounds can be identified from the sample spectra by using the Gaset Dx4000N Calcmet software. The advantage of FTIR technique is a good stability of calibration. (Gaset Technologies, 2006)

Gaset Dx4000N FTIR gas analyzer is designed for on site measurements. The sample cell can be heated up to $180^{\circ}C$, and it can be flushed with nitrogen between the measurements. The absorption bath length of the sample cell is 5.0 m.

Gas samples were collected to the adsorption tubes actively with a sampling pump (Figure 2b). Two samples were collected to both adsorbents and the sample was taken from the exhaust pipe just after the Gaset FTIR analyser.

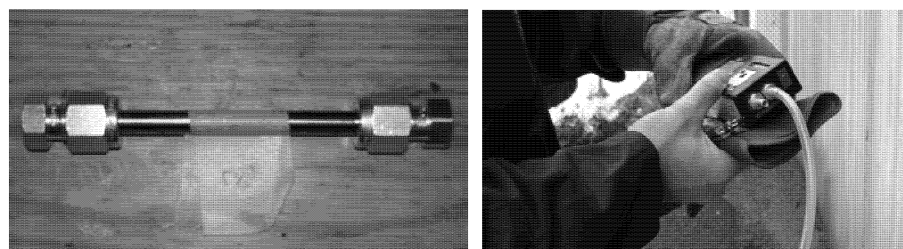


Figure 2. a) A Tenax TA adsorption tube and b) the sampling pump for active sampling

Sampling volume to the Tenax TA adsorption tubes was 1 dm³ and sampling rate 100 ml/min. To collect one sample, two Tenax adsorption tubes were attached in series to avoid overloading of the tubes. Samples were analysed with thermal desorption GC/MS (gas chromatography with mass selective detector) at Finnish Institute of Occupational Health (Helsinki). Compounds were identified with the help of pure compounds and/or Wiley or NIST-mass spectrometer database.

Sampling volume to the Anasorb CMS adsorption tubes was 3 dm³ and sampling rate 100 ml/min. Accordingly to Tenax tubes, to collect one sample, two Anasorb CMS adsorption tubes were also attached in series to avoid overloading of the tubes. Samples were extracted from adsorbent and analysed with GC/FID (gas chromatography with flame ionization detector) at Finnish Institute of Occupational Health (Helsinki). Compounds were identified with the help of pure compounds. The concentration of total volatile organic compounds has been determined as toluene equivalent.

3. Results and discussion

Prior to the industrial emission measurements, the measurement and analysis of FTIR was tested under the laboratory scale with the reference measurements. Two FTIR gas analysers measured the same gas flow and results were compared. Figure 3 shows the comparison when gas flow contained only dichloromethane (DCM). As can be seen in Figure 3 the results followed each other well in the calibration areas (0-200 ppm) of both equipments. (Perttunen, 2006)

The analysis results of Tenax TA adsorption tubes and the simultaneous analysis results of Gasmeter FTIR analyzer are presented in Table 1. Concentrations measured with FTIR are presented as average gas concentrations during the sampling time of the tubes. Both the sampling tubes have the same specific surface area, and therefore, the results can be compared.

When analyzing the two adsorption tubes connected in series (one sample), it was found that the volatile organic compounds were adsorbed only in the first tube. Dichloromethane was the only compound which was found also in second Tenax TA tube (concentration presented in Table 1 is a sum of these concentrations). There is a possibility that dichloromethane has partially passed through the second Tenax TA tube. The other reason might be that the concentration of dichloromethane was clearly higher than that of other chlorine containing volatile organic compounds. The high

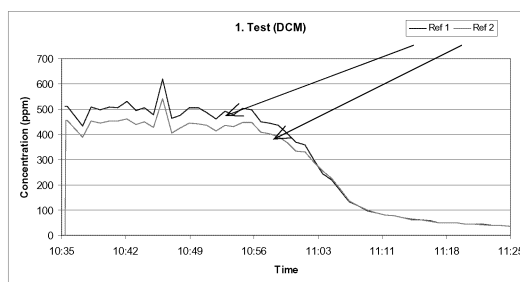


Figure 3. Verifying the gas measurements of the Gasmeter Dx4000N FTIR gas analyser. Comparison with another FTIR gas analyser was carried out by using dichloromethane (with the initial concentration of 500 ppm).

Table 1. Analysis results of Tenax TA adsorption tubes and the simultaneous analysis results of Gasmet FTIR analyzer. Gas concentrations are presented as ppms.

	<i>Tenax TA</i> (<i>Sample 1</i>)	<i>FTIR*</i>	<i>Tenax TA</i> (<i>Sample 2</i>)	<i>FTIR*</i>
Chloroform	0	0.96 ppm	0	0.79 ppm
Dichloromethane	0.95 ppm	5.86 ppm	1.66 ppm	6.74 ppm
Tetrachloroethylene	0	0.67 ppm	0.04 ppm	0.68 ppm
2-Ethoxyethanol	-	1.19 ppm	0.01 ppm	1.14 ppm

*) Concentrations measured with FTIR are presented as average gas concentrations during the sampling time of the tubes.

concentration of HCl (a product of catalytic oxidation) in the outlet gas flow was also causing interference to the analysis of the adsorption tubes, and therefore, very volatile organic compounds could not be reliably analysed.

Based on the results presented in Table 1, only dichloromethane adsorbed on the surface of polymer-based Tenax tube. At its best, only approximately 25% of dichloromethane adsorbed and therefore, this adsorption tube material cannot be considered suitable for reliable CVOC sampling.

The analysis results of Anasorb CMS adsorption tubes and the simultaneous analysis results of Gasmet FTIR analyzer are presented in Table 2. In contrast to the results obtained by using Tenax TA tubes, Anasorb CMS adsorption tubes adsorbed all the CVOCs which were considered in this study (see Table 2). The adsorption capacities of these carbon molecular sieves were also significantly higher.

Table 2. Analysis results of Anasorb CMS adsorption tubes and the simultaneous analysis results of Gasmet FTIR analyzer. Gas concentrations are presented as ppms.

	<i>Anasorb CMS</i> (<i>Sample 1</i>)	<i>FTIR*</i>	<i>Anasorb CMS</i> (<i>Sample 2</i>)	<i>FTIR*</i>
Chloroform	0.09 ppm	0.32 ppm	0.09 ppm	0.31 ppm
Dichloromethane	1.58 ppm	3.06 ppm	0.79 ppm	2.89 ppm
Tetrachloroethylene	0.14 ppm	0.2 ppm	0.14 ppm	0.18 ppm
2-Ethoxyethanol	0.12 ppm	0.73 ppm	0.12 ppm	0.78 ppm

*) Concentrations measured with FTIR are presented as average gas concentrations during the sampling time of the tubes.

4. Conclusions

In this study two sorbent materials (Tenax TA and Anasorb CMS) were evaluated and compared in the sampling of chlorine containing volatile organic compounds (CVOCs) under solvent-using process conditions. According to the results, Anasorb CMS seems to be a more suitable adsorption material for the sampling of chlorinated volatile organic compounds than polymer-based Tenax TA.

Environmental authorities (e.g. in Finland) use Tenax TA as a sorbent material for sampling of chlorine containing VOCs. Tenax TA, however, seems to be unsuitable for this purpose. The applicability of Anasorb CMS for sampling of CVOCs is also not

well-known in the gas mixtures, and therefore, there is a need for novel sorbent materials and systems (e.g. multibed systems) which enable the simultaneous and reliable sampling of several CVOCs. New sorbent materials, e.g. carbon nanotubes, should also be considered as potential adsorbents for CVOCs. Sampling should also be carried out with the simultaneous gas analysis due to the fluctuating gas flow. Only this way the reliable qualitative and quantitative information can be obtained.

In our further study, different adsorbent materials will be compared. Sampling and simultaneous FTIR gas analysis will be carried out both during the laboratory experiments as well as in process conditions. In the former case the conditions are well known, whereas in the latter case the process conditions are not well known, i.e. emission gases are fluctuating and they are mixtures of several gaseous compounds. The effect of parameters such as flow-rate, amount of the sorbent and vapour concentration on break-through volumes (BTVs) will also be clarified.

5. References

- Demeestere, K., Dewulf, J., De Witte, B., Van Langenhove, H. (2007) Sample preparation for the analysis of volatile organic compounds in air and water matrices, *Journal of Chromatography A* (2007), doi:10.1016/j.chroma.2007.01.012.
- Dewulf, J., Huybrechts T., Van Langenhove, H. (2006) Developments in the analysis of volatile halogenated compounds, *Trends in Analytical Chemistry* 25, pp 300-309.
- Directive 99/13/EC. Council Directive 1999/13/EC of 11 March 1999 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations [website]. Official Journal of the European Communities. The council of the European Union, 29.3.1999 [referred to 24.8.2005].
- Gasmet Technologies (2006) Gasmet DX-Series Instruction & Operating manual (E1.3).
- Heikkinen, M. (2006) Raportti vertailumittauksista 190606 (unpublished data).
- Janssen, F.J.J.G. & van Santen, R.A. (1999) *Environmental Catalysis*. London, Imperial College Press. 369 p. ISBN 1-86094-125-7.
- Montreal Protocol (2000) The Montreal Protocol on Substances that Deplete the Ozone Layer. Available at: <http://hq.unep.org/ozone/Montreal-Protocol/Montreal-Protocol2000.shtml>.
- Ojala, S., Lassi, U., Keiski, R. L. (2006) Testing VOC emission measurement techniques in wood-coating industrial processes and developing a cost-effective measurement methodology, *Chemosphere* 62, pp 113-120.
- Perttunen, A-S. (2006) Implementation and verification of in situ FTIR analysis in VOC measurements, B.Sc. thesis, Central Ostrobothnia University of Applied Sciences, Department of Technology.