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New odour sampling method: adsorption and reconstitution of odours

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This contribution deals with the aim of developing a new sampling method for odour measurements. The commonly used sampling method in polymeric sample bags has severe disadvantages. Due to adsorption, reaction and diffusion processes, the original concentrations of the species are strongly reduced. The technique of adsorptive sampling and subsequent thermal desorption has shown quantitative collection and recovery for a large number of chemical species. The aim of the research work described here is to adopt this technique for odour sampling. In order to achieve this, it is important to review the different methods used for different types of species. Only a very small degree of chemical alteration can be tolerated in odour sampling.

1. Introduction

Thermal desorption is a widely used method for sampling and pre-concentration of environmental samples. The sampling of the chemical species of interest takes place on specialized adsorbents. A large number of different adsorbents with differing advantages and drawbacks is available. The appropriate adsorbent which ensures a quantitative adsorption and a complete desorption of the compounds is required for every application.
The use of adsorptive sampling for odour measurements brings with it a change of requirements. The full scale of odorants, from low volatiles to high volatiles and through a vast range of different chemical classes has to be adsorbed and later desorbed with high efficiency and a low amount of alteration.
The recommendations for this goal are at the centre of the work of a new research project. The research is part of a greater framework of a new odour measurement scheme. Adsorptive odour sampling gives the chance of two ways of collecting odour data. The conventional method is the use of dynamic dilution olfactometry. Here, the results are odour units, i.e. the ‘dilution to threshold’. The chemical pathway means the measurement of the odorants in a sample with analytical techniques. In our project we use a measurement chain of thermal desorption, gas chromatography and time of flight mass spectrometry combined with simultaneous olfactometry (sniffing port). The thermal desorption step is the interface for the adsorptive odour samples.

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A lot of challenging work has to be done before the problems of quantitative adsorption and desorption can be solved. In this contribution we describe the main problems and the tentative solutions to them.

2. Adsorptive odour sampling

Many different methods have been published on trace analysis of gases or specific odorants using thermal desorption techniques (Harper, 2000). Low volatile analytes require strong adsorbents, whereas weak adsorbents are needed when desorption temperatures should be moderate. In some cases background water vapor leads to a competitive adsorption and thus lowers the breakthrough volume of the adsorbent. The temperature level during adsorption is a parameter which can lead to problems with condensation of water during measurements of environmental samples with high humidity levels.

Recently a method was published for odour sampling by condensation of all volatiles in an air sample with the use of liquid nitrogen without any adsorbents (Juarez-Galan, 2009). High amounts of water are usually present in environmental samples. A dew point of 20° Celsius means 23000 ppm water content. Compared to trace levels of odorants below 1 ppm, or even in the ppb or ppt range, the water interference causes a great problem for the sampling or the subsequent measurement. In the 'condensation' method the problem is tackled by a dryer with semi permeable membranes, but there is a risk that parts of the other gases are also removed.

Some adsorbents, like Tenax TA™, retain only a very small amount of water. This spares the use of special water removal techniques. Unfortunately this is not the case with all adsorbents. The use of gas coolers is a commonly applied method for the reduction of water. Inevitably those fractions of the gases which are highly miscible in water are washed out with this method (Boeker, 2001). Another technique of water removal is the use of Nafion™ gas dryers (Leckrone, 1997). The special polymeric material of these dryers is permeable for water molecules. Other polar compounds can also pass the membrane. This limits the use of Nafion™ to special measurement conditions and target compounds.

The properties of an alternative odour sampling method have to be measured against the present situation of the 'odour bag' method, and the limitations of the dynamic dilution olfactometry.

The loss of concentrations connected with the use of odour bags has been reported in some recent publications (Koziel, 2006, Trabue 2006). This adds to the measurement uncertainty which is connected to the dynamic dilution olfactometry. This measurement uncertainty is mostly due to the selection of the human panelists and their varying odour thresholds (Boeker 2007). The ongoing work for the improvement of the European norm for dynamic dilution olfactometry (EN 13725) is now focussing on the sampling and storage issues. One of the main disadvantages of the odour bags is the loss of odorants during storage. The time lag between sampling and measurement is limited in the new addendum of the norm (VDI 3880, Olfactometry, static sampling, in green print) to only 6 hours.

Fig. 1 shows the sources of measurement uncertainty. It is not only the final step in the measurement process - the real odour measurement by dilution to threshold - which defines the uncertainty, but also the preceding steps of sampling and storage.

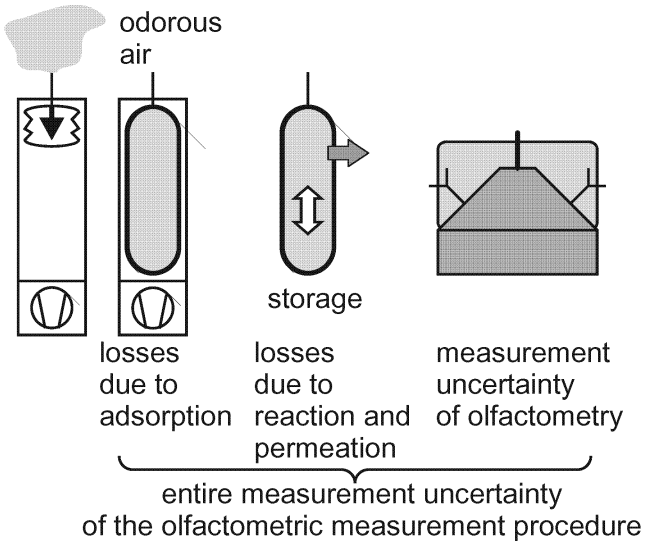

Fig.1: Measurement uncertainty of the complete olfactometric measurement procedure

Multibed adsorbents are commonly used to trap volatiles with differing chemical properties (Ribes 2007). The recommendations regarding odour sampling are very exact. The biogenic odorants ammonia and hydrogen sulfide are especially critical (Devai, 1997, Rechenbach, 1999, Pandey, 2009). Fig 2 shows a hypothetical three bed adsorption. The first bed is silica gel for the trapping of water, ammonia and hydrogen sulfide. The following two beds are made of one weak and one strong adsorbent, Tenax™ and Carbosieve S3™. Tenax has proved to be an efficient adsorbent for the semi volatiles. Carbosieve, on the other hand, can trap the low boiling, high volatile compounds. Hydrogen sulfide, which may have passed the silica gel, is also trapped in the Carbosieve bed to a certain extent.

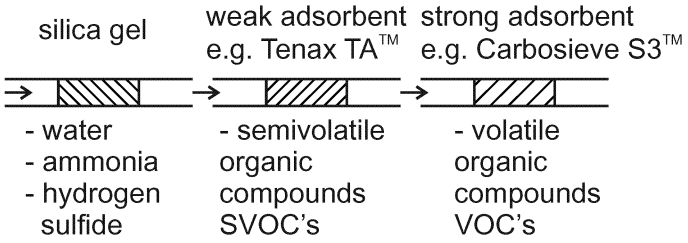

Fig.2: Adsorption of odour samples with multiple adsorbents

3. Reconstitution of odour samples

The trapping of the odorous volatiles is only the first step of the new sampling method. The desorption also requires an accurate procedure. The aims for the reconstitution of the original odorous air to sample bags are:

1. Reconstitution of the exact volume, hence the same concentrations of odorants as in the sampled air.
2. Reconstitution of the same matrix, hence the desorption of the odorants in the air.
3. Reconstitution of the same humidity as in the air.

Some of these requirements are mainly technical tasks, some involve critical limitations, e.g. the danger of oxidation connected with oxygen during the desorption step at high temperatures.

We recommend the use of a multi step desorption and reconstitution method (Fig. 3). Inert carrier gas is used in the desorption process. This avoids the danger of oxidation reactions of the trapped compounds, and of the adsorbents respectively. The carrier gas volume during the desorption step can be much lower than the original sampling gas volume, e.g. only 1 liter compared to a 10 liter sampling volume. To reconstitute the original matrix, the rest of the volume can be complemented with synthetic odorless (humidified) air.

A step by step desorption with separate adsorbent tubes for the different adsorbents to avoid interferences between the trapped compounds is technically possible. With this technique the temperature levels of desorption can be set independently.

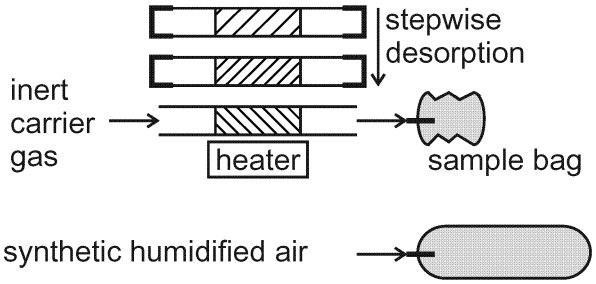

Fig.3: Multistep desorption and reconstitution of odour samples

4. Advantages and Disadvantages

When proposing a new odour sampling method, the performance should not be measured against an ideal, but against the present status of sampling, with all its disadvantages. A closer look unveils the disadvantages of the commonly used odour sampling bags (Table 1). At the precise moment of sampling, huge parts of the components are adsorbed onto the large surface area of the bags. Additional parts of the components permeate through the polymeric walls during the time lag between sampling and measurement. Reactions can also take place inside the bags. The composition is altered by all these processes, and is not identical to the original composition, when measured with dynamic olfactometry.

The sampling with adsorbents also has disadvantages. These disadvantages are less known as yet, and thus less quantifiable due to the lack of knowledge of them.

Table 1 Comparison of advantages and disadvantages

Drawbacks	Sample bags	Adsorptive sampling
Losses	Adsorption onto surface	Incomplete adsorption (breakthrough)
	Permeation through polymer	Incomplete desorption
	Reactions (photo induced, with water)	Reactions adherent to desorption (high temperature)
Storage	Variable losses, time lag sampling/measurement < 6 hours	High stability over month
Complexity	Low	High (adsorption + desorption)
Composition	Change compared to original odorous air	Change compared to original odorous air

5. Outlook on new methods for odour measurements

Adsorptive odour sampling opens up two ways for the evaluation of odour.
The first one is the conventional organoleptic testing with dynamic olfactometry. Here, the reconstitution of the original composition to nearby 100% is recommended.
To reduce the relative amount of losses due to adsorption on the surface area it is possible to reconstitute e.g. only 10% of the original sampled volume, thus getting a sample with tenfold the original concentration.

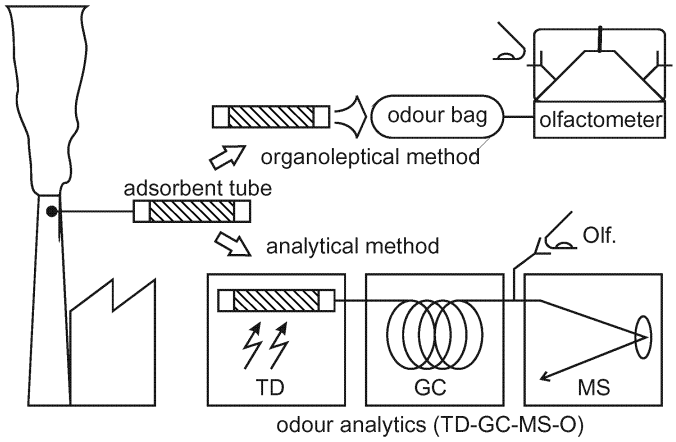

Fig. 4: The two ways for odour measurements with adsorptive samples

The conventional olfactometers require the use of sample bags. In future, this technology has to be revised. New types of olfactometers with an interface for adsorption tubes, without the use of sample bags, would avoid the shortcomings of the bags.

The second way aims at analytical odour data. The adsorption tubes are processed in a thermal desorber, with subsequent gas chromatography and mass spectrometry. If useful also simultaneous odour information of the separated components are accessible via a sniffing port. For specific applications, the analytical data can replace the olfactometric data with its huge measurement uncertainty, by the use of correlations of concentration data and odour activity factors.

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