Odour Measurement: Focus on Main Remaining Limits Due to Sampling

Jean-Michel Guillot[a]

[a] Industrial Environment Engineering Laboratory, Ecole des mines d'Alès, 6 av. de Clavières, 30319 Alès, France
jean-michel.guillot@mines-ales.fr

Odour and odorous compound measurements depend on the first analytical step: the sampling. This first step could be considered as the most important because the global results are dependent on sampling and analytical procedures but the second part (analysis) is globally more controlled. As example, olfactometric measurement procedures are well described by EN 13725 standard. But, if panel selection and all smelling parts allow limiting uncertainty for the dilution to threshold measurement, the sampling part is not as well described. Because of several approaches on sampling especially sampling from area sources, a lot of variations can be obtained by this step.

Typically, several experiments on area sources have shown that a factor 10, 100 or more can be attributed to the sampling step. In such a case, the uncertainty of the olfactometric part is negligible comparatively to the sampling part. That's why, it is important to keep in mind that hoods or flux chambers as devices to sample on an active or a passive area respectively must be considered with strict procedures. Even if a lot of teams follow rigorously their own procedure or a regional or a national standard, the lack of international standard on this point is still a problem. Some results cannot be compared with others due to great differences on sampling.

The problem could be increased by the sample collection and storage in bags. A lot of studies showed that storage of some compounds or odours are very problematic (losses) and therefore can lead to wrong results. Of course, limitation of time storage can minimize such an impact but it's important to consider this potential problem by taking some warranties. The present paper gives an overview on the main drawbacks linked to sampling and that affect the global response of odour measurement.

1. Introduction

For all analysis, the sampling step is crucial for the quality of results. Odour analysis is also concerned by the necessity to control, as well as possible, the sampling step. For that, protocols have been established by laboratories and by countries. Some aspects of the odorous atmosphere sampling are well accepted around the world such as use of bags to collect samples. But, if a global protocol can be used, it does not imply that any interference or problems can be due to this protocol. Other aspects are more specific such as area sampling for witch different protocols can be found in different countries. This introduction indicates the standards, guidelines or protocols used to collect odorous atmospheres. The two main points (bags and area sources) are then described in paragraphs 2 and 3. These two main points are illustrated in Figure 1 which shows a sampling protocol. The sample can de diluted before the introduction in the bag in case of very high humidity and risk of condensation, or just before the analysis typically in the case of very odorous sample in order to be in the range of dilution factors of the olfactometer. The steps of main drawbacks linked to sampling are the sampling device if necessary

(typically the use of hoods of flux chamber for area source) and the collection and storage atmosphere in bags. This second aspect is common for all odour samples as shown in Figure 1.
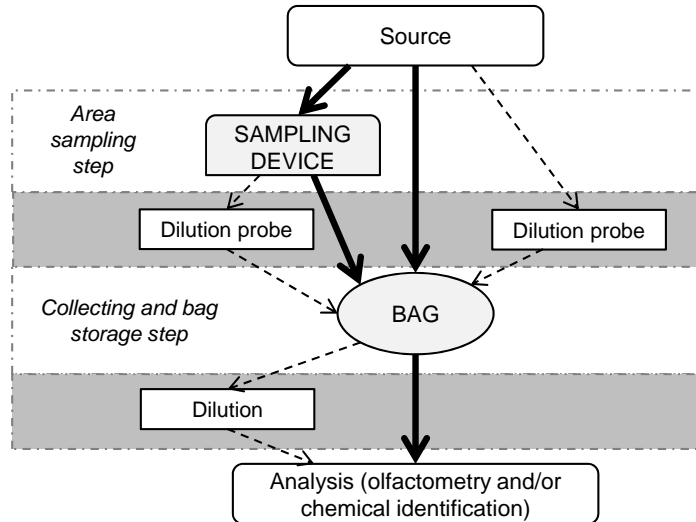

Figure 1: Description of a sampling protocol (The bag is placed in a sampling drum and connected to the atmosphere to be sampled).

Some countries elaborated their own methods for odour measurement as example, Australia (AS/NZS 4323.3:2001), but also several European countries for which the national standard has been supplanted by the European Standard approximately 10 years ago (EN 13725: 2003). In this standard the measurement by dynamic olfactometry is well described but the sampling protocol doesn't give a lot of details about all possibilities depending of source type. France will produce a guide for the end of year 2012 to orientate area sampling. Germany has elaborated a complete guideline on sampling (VDI 3880, 2011) to define protocols to apply before analysis with olfactometry. Of course, some choices were made like for example: "The dividing line between an active and a passive source is defined by convention as a flow velocity of 30 m/h as the arithmetic mean over the entire source interface ». In order to complete, devices with dimension criteria are also described for each type of source.

2. Atmosphere sampling with bags

The odour measurement needs firstly collection and storage of an air volume in a container and secondly the connection of this storage to the olfactometer. Figure 2 shows the different containers classically used for air samples when pollutants are not concentrated by adsorption or absorption processes.
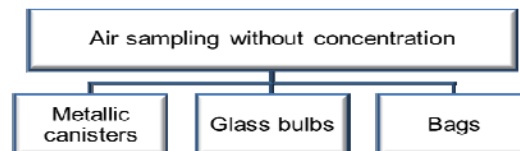

Figure 2: Containers for air samples.

If metallic canisters are mainly used for VOC analysis (especially in Northern America) the price of these samplers limits their use. Glass containers are also limited but mainly by their low volume and

their weakness during transportation. Polymer bags are cheap, without main risk for transport and easy to fill with a vacuum chamber avoiding contact of the sample with a pump. That's the reason why odour samples are commonly based on use on such polymer bags. First of all, it must be considered that different polymers are used for air (or odour) sampling and depending on the film properties, the sample stability could be affected.

2.1 Different types of bags
Different polymer films are used to make sampling bags. Probably one of the most popular films is polyvinyl fluoride, trade name Tedlar. Other films are also used like fluorinated ethylene propylene copolymer, trade name Teflon, 4-plyfoil material named flexfoil and poly(ethylene terephtalate), trade name Nalophan. Three of these films, Teflon, Nalophan and Tedlar are considered as suitable materials for sample bags in the European standard (EN13725, 2003). New films are found on the market but few studies have been carried out with these new bags.

2.2 Stability of sulphur compounds in bags
Several studies have shown the limitations of bags. One work (Mochalski et al., 2009) compare the behaviour of 5 films (Nalophan, transparent Tedlar, black layered Tedlar, Teflon and FlexFoil) with sulphur compounds (H_2S, MeSH, EtSH, COS, DMS and CS_2). The example of H_2S behaviour is shown in Figure 3. It proves that for a short time (<5h), the samples are relatively stables even if 30 % and 20 % are lost during 5 h storage in Nalophan and transparent Tedlar respectively. This fact confirms a recommendation of VDI 3880 guideline that considers 6h as a maximum storage time in bags for odour analysis if longer stability is not proven.
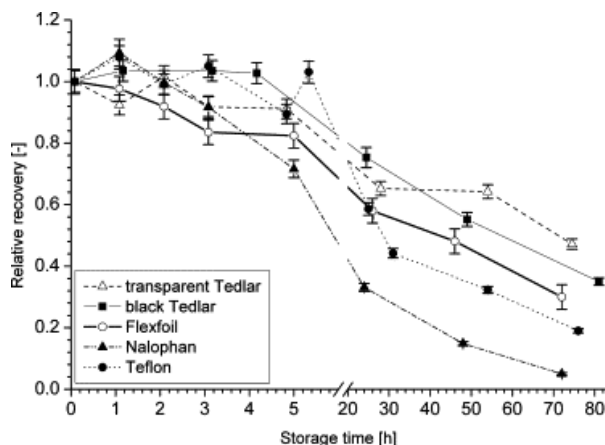

Figure 3: Recovery of H_2S as a function of time in different types of bags (initial conc. 61.8 ppbv) from Mochalski et al. (2009)

Another work (Dong et al.2009) is also based on odorous sulphur gas in Tedlar for 20 to 350 min. In this work, Methane-thiol and hydrogen sulphide are stable in the bag for 6 h but other sulphur components decrease during the same period of time. Because odorous compounds are very odorous and found in a lot of industrial or WWTP atmospheres, their decrease in bags (instability, reaction or diffusion) can modify the odour intensity. Such data that proves the instability of odorous compounds in samples is fundamental to demonstrate a limitation of the analytical protocol.

2.3 Other characteristics of the bags
If losses can be due to reactivity or adsorption, the phenomenon of diffusion also exists. It can be considered that diffusion needs time but taking into account the thickness of the films (in general 50µm for Tedlar and twice thinner for Nalophan), some compounds can diffuse very quickly. Beghi and Guillot (2006, 2008) showed the fast diffusion of humidity through films, this fact is illustrated by Figure 4. Such a diffusion property allows the removal of water from a sample. This aspect could be

important for complementary chemical measurement because trace analysis is still difficult to achieve in humid atmosphere.
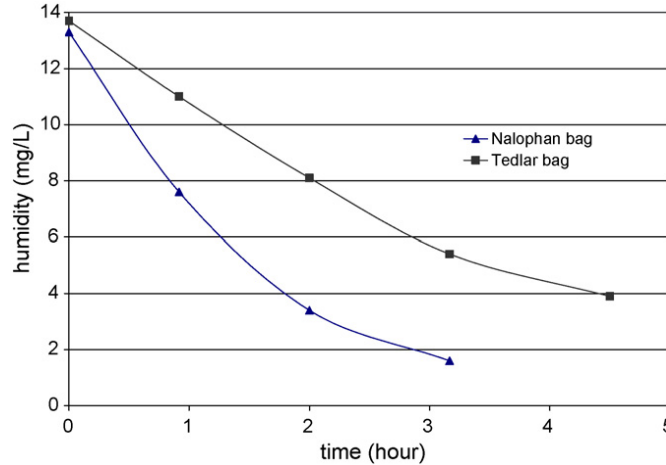

Figure 4: Water diffusion through Nalophan and Tedlar bags (humid air inside and dry air outside) from Beghi and Guillot (2008)

3. Sampling from area sources

Depending on the type of source, a sampling device must be used to isolate one part of area source. This device must collect the emission from the source and of course the number of sampling points to consider, in order to be representative of the whole surface, is an important factor for result quality. In case of aerated surface, devices are hoods covering generally one square meter and presenting a chimney to force the emission through this exhaust where sampling can be carried out. For non-aerated sources (passive area sources), devices are more complex. Globally two main types can be distinguished: isolation or flux chamber with a low air flow and wind tunnel with higher air flow.

3.1 Source with flow (active source)

On aerated surface, a typical hood could be the example given in the recent German guideline (VDI3830, 2011) as shown in Figure 5. Globally, this type of hood is largely used on active source. One limitation still remaining concerns the definition of active source *i.e.* the minimum flow from the surface to consider a source as no-passive.
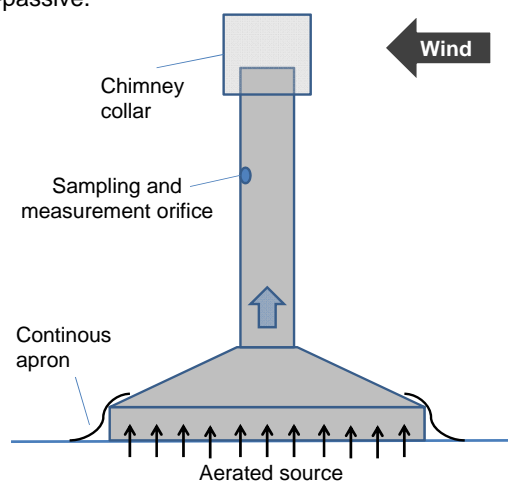

Figure 5: Sampling hood for aerated sources adapted from VDI3880 (2011).

3.2 Source without flow (passive source)

This part is related to several studies with different devices that illustrate the difficulty to sample on a passive area. A lot of devices are described in literature and others aren't because correspond to lab-made device to measure odour concentration. Globally, two main types can be distinguished as show in Figure 6. The first type allows the concentration of pollutants in the chamber and then induces high concentration and high odour intensity. The second type simulates the wind speed over the surface and tries to represent real conditions but such device can also dilute a lot the emission to the limit of detection or limit of precise quantitation of emitted odour.
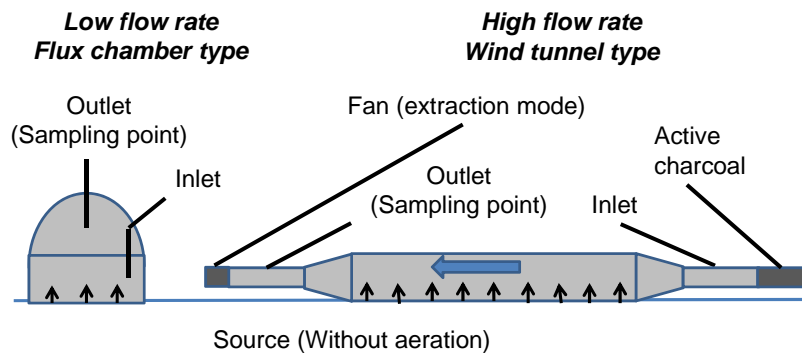

Figure 6: Sampling devices (flux chamber and wind tunnel types) for passive area sources.

The difference of results is shown by comparative studies like Hudson et al. (2009) where two devices are compared on different sources. In this study a low flow chamber (flux chamber) and a high flow chamber (wind tunnel) are tested on different passive source. If the odour concentration can be different between chambers, the mean difference is lower than a factor 5. Concentrations are always higher in a flux chamber due to the low flow-rate. But considering the emission factor (based on odour concentration, sweep air flow rate and covered surface by the sampling device) can vary in a range from 60 to 240 times. Higher values are always obtained with the wind tunnel. Same kinds of results are obtained in a French study (ADEME, not published yet). It clearly shows that the emission rate depends, of course, on the source but also on the device itself. All simulation shows that it's difficult to have the real odour emission rate because sampling chamber influences a lot the emission and then values are linked to a sampling conditions and don't correspond to real emission. Some results are probably close to the reality while others are very far. The main limitation is to consider that emission rates are relative values and that comparison of values can be carried out only if the same sampling protocol was used (same chamber and same conditions of use). Actually, a lot of people try to find a chamber that could represent the emission. The chamber (push-pull tunnel) described in VDI3880 (2011) is one approach. In US, recent studies about emission from agriculture had shown the necessity to consider with more precision area sampling (Parker et al., 2012).

4. Conclusion

Sampling is still a limiting step for environmental measurement. This limitation can be linked to the number of samples, the variability of the source or the sample transportation and storage before analysis. The case of area source also implies questions about homogeneity or heterogeneity, passive or active source. So, because the final result depends on the sampling step, improvements are still necessary and typically for odour sampling. This aspect will be one part of the revision of EN 13725 standard.

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