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Stability assurance of odour concentration by cryocondensation sampling

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The sampling of odours and volatile organic compounds by means of universal containers such as polymeric bags and canisters is a widely used method. However, problems regarding sample stability during storage can arise, even within the period established by EN-13725, leading to the analysis of a non-representative sample of the odour emitted at the source. The CRYOCORE (cryocondensation and reconstitution) device allows the condensation of the sample under cryogenic conditions (-196ºC) and is presented as a promising alternative to the current methodologies. The present paper evaluates this new approach by comparing the stability of samples stored under EN-13725 requirements versus samples obtained by means of CRYOCORE. The results obtained showed a great improvement of representativeness when samples where cryocondensed. Samples maintained during 24 h under EN conditions showed a deviation of 41% from the target value while, on the other hand, the new cryocondensation method showed a deviation of 12% for the same samples.

1 Introduction

The term odour, refers to the perception experienced when the whole mixture of chemical substances in the air comes in contact with the various human sensory systems. This is the main reason why the entire sample must be collected (universality of the method is mandatory) and sensory methods should be used for the analysis. Among the methods for determining the odour concentration in the laboratory, the European Standard EN-13725 and the American Standard ASTM E679-04 are widely accepted (the first one even outside Europe). Both methods specify the use of polymeric bags for taking samples for their later analysis in the laboratory by means of dynamic olfactometry. Nevertheless, one very important limitation to this methodology is the chemical instability of many of the compounds, despite the rigorous application of the maximum storage time established for these methods (Richter et al, 2001; Sluis and Vossen, 2008). Stability of volatile organic compounds and odours, not only with sampling bags but also when using canisters or sorbent media, is a critical aspect that has been under discussion in recent years (Batterman et al, 1998; Trabue et al, 2006; Ribes et al, 2007; Ochiai et al, 2002; Dettmer et al, 2000; Volden et al, 2005; Prado et al, 2006; Koziel et al, 2005). The new VDI 3880-Sampling for olfactometric measurement, tackles this important problem stating that "storage times of more than

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six hours are to be avoided at all costs. If not, a source-specific test is to be carried out to ensure that the odour concentration in the samples has not altered" (Richter and Frechen, 2008).

In 2009 a new universal, integrative air sampler, named CRYOCORE (CRYOgenic COndensation and REconstitution) was developed with the aim of overcoming many of the limitations of current methodologies for the sampling of airborne VOCs and odours. The papers (Juarez-Galan and Valor, 2009; Juarez-Galan and Valor, 2008) describe in depth this new device. One of the main objectives was to develop a sampling method allowing the possibility of sample integrity for long periods of time. With CRYOCORE, the samples are condensed in a silanized stainless steel condenser and kept under cryogenic conditions until their analysis in the laboratory. The present paper describes the validation of the condensation storage and reconstitution processes with the CRYOCORE system by comparing the odour concentration obtained with different real environmental samples maintained under EN-13725 requirements versus cryocondensation by means of CRYOCORE.

2 Experimental

2.1 Sample collection

Different types of samples have been used to test the cryocondensation technique in order to assess the effect of the condensation, storage and recovery, on the odour concentration of the samples. A preliminary selection of typical odour-types involved in odour nuisance episodes (waste water smell (WW), biogas, sludge and landfill leachate) was made. A subsequent selection of corn pulp (starch smell), coffee aroma and exhaust gas was included on the basis of previous information about stability or "sticky" behavior (Vance, 2008)).

WW samples were collected from an urban waste water treatment plant. Several waste water samples were placed into 50 ml glass bottles, capped and stored at 4ºC until their use (one bottle for each sample). Landfill leachates were sampled from a landfill pond following the same methodology. One kilogram of sludge was obtained from a waste water treatment plant, another kg of corn pulp from a starch (glucose and fructose) manufacturing company and, one kg from a coffee roasting company. Each raw material was sealed into a glass bottle and stored at 4ºC. Biogas samples were obtained daily from a local landfill and collected into nalophan bags. Biogas was sampled by using a dilution probe (former model 797, Thermo Scientific, USA) and diluting 1/203 times, in order to adjust the odour concentration of the sample to the dilution range of the olfactometer (model TO-8 ECOMA GmbH, Germany). Exhaust gases were obtained daily using a fuel-fed AC power generator and collecting the sample into a nalophan bag. Both biogas and exhaust gases were sampled one hour (maximum) before the analysis and the condensation process.

2.2 Procedure

Sample preparation and condensation

Samples prepared from liquid sources (WW and leachate) were generated by purging the liquids with an impinger. A 50 mL room temperature liquid sample was purged (*Figure 1)* with synthetic air (Air Liquide, France) at 5 L/min and a Nalophan bag was used to collect a final volume of 50 L. Odorous samples from solid sources (sludge, pulp and coffee) were prepared filling the impinger with 50 g of raw material and using the same set-up (Fig. 1). The biogas and exhaust gases were directly prepared from the sampled bags.

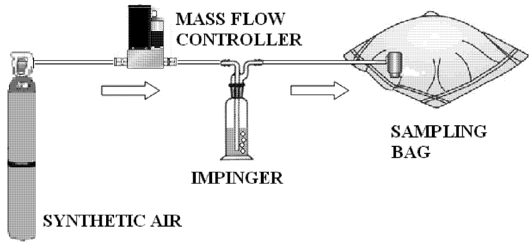

Figure 1. *Scheme of the set-up used to prepare odorous samples in laboratory.*

Nalophan bags were made by cutting the appropriate length of commercial 1000 m long Nalophan rolls (Kalle, Germany). To eliminate background interferences from the polymer, the deodorized protocol at 60ºC during 24h described in a previous work (Juarez-Galan et al. 2008) was used. Once the gas sample was prepared (or collected) into a 50 L Nalophan bag (bag A) it was then separated into three different 15 L aliquot bags (B, C and D). The scheme of the procedure is shown in Fig. 2. Bag B was analyzed immediately (T0) by Dynamic Olfactometry. Bag C was stored at room temperature during 24 h and, bag D was immediately condensed at -196ºC into a 50 mL fused-silica-coated stainless-steel condenser (Fig. 3) and kept under cryogenic conditions (-196ºC) during 24 h.

Condensation of the samples was carried out by placing the condenser in a liquid nitrogen bath and connecting the bag to the inlet port of the condenser (1/4” valve). Then, the sample is spontaneously sucked in by the pressure drop caused by the gas contraction (Juarez-Galan and Valor, 2009). After 24 h storage, both samples C and D were analyzed by Dynamic Olfactometry (T24 and T24CRYO respectively), comparing the results with the odour concentration obtained for the reference sample B (T0).

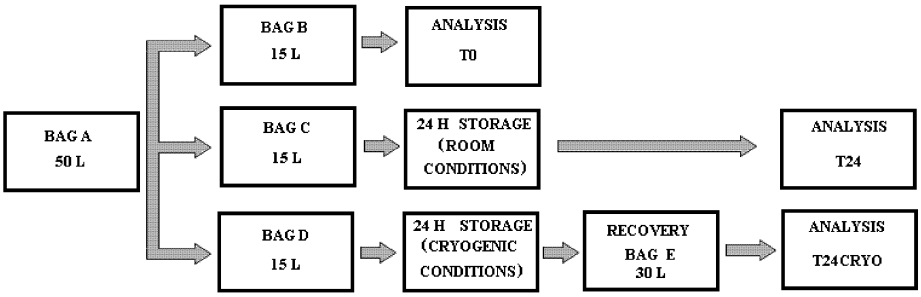

Figure 2. *Scheme of the procedure.*

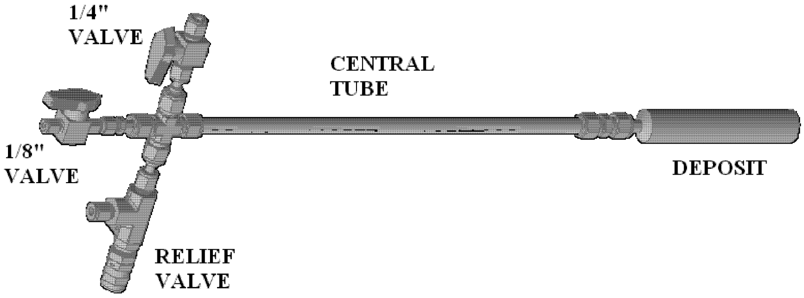

Figure 3. *Scheme of the condenser used.Inside the condenser, there is a 1/8" (diameter) tube from the 1/8" valve to the bottom part of the deposit, allowing to increase the efficiency of the recovery process.*

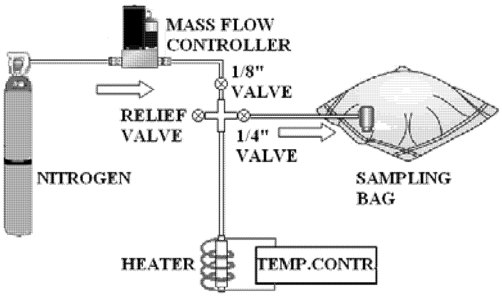

Figure 4. *Scheme of the recovery set-up.*

Recovery of cryo-condensed samples

The reconstitution of the condensed samples was carried out by using the experimental set-up shown in Fig. 4. A 30 L Nalophan bag (bag E) was connected to the outlet port of the condenser and the outlet valve was then opened. After that, the condenser was removed from the liquid nitrogen and kept at room temperature during 5 minutes to allow the condensed gas to expand into the Nalophan bag. After this, the condenser was placed into a 20ºC isothermal water bath to reach room temperature, and set up as is shown in Fig. 4. A 600 mL/min nitrogen (99.9999% purity, Air Liquide) flow rate is passed through the condenser flushing out the sample compounds remaining inside the condenser. This flow is maintained during 25 minutes. After the first 10 minutes, the heater (Electricfor, Spain) is switched on, allowing the condenser to heat up at 4ºC/min up to a temperature of 80-90 ºC. After 15 minutes, the heater is switched off and removed. At this point, the condensed sample is reconstituted and ready for analysis by Dynamic Olfactometry.

The odour concentration of the reconstituted sample must be corrected taking into account the dilution factor. In order to determine this parameter, the volume of the bags D and E was previously determined prior to their use. They were filled completely with nitrogen gas (99.9999% purity, Air Liquide, France) and, after that, the bags were completely emptied by using a flow rate calibrated pump (Apex, Casella, UK).

3 Results and discussion

In Figure 5, the representation of T0, T24 and TCRYO is shown. The two plots compare the difference in results between the odour sample analyzed at time zero and the same sample analyzed after 24 hour of storage, being T24 stored under room conditions and, T24CRYO under cryogenic conditions. Therefore, a new method for storing odour samples is compared to the classical EN-13725 method (whose repeatability and accuracy, calculated according to the requirements of EN-13725, are 0.294 and 0.209 respectively). Offset lines (± 35%) were established on the basis of the uncertainty (k=2) for Dynamic Olfactometry (and storage) standard method, calculated according to the ISO GUIDE 98:1995 “Guide to the expression of uncertainty in measurement (GUM)”. Each analysis (given by the geometrical mean of three rounds) was done once, and each point of the plot corresponds to a different sample, prepared or collected the day of the T0 analysis. Therefore, the comparison between the two methods was carried out once for each individual sample, but repeated for many samples (some of them similar). Under the circumstances showed above, it can be clearly observed an improvement on the consistence of the method, being the accuracy better. Considering the x=y line as the target value, the area determined by the ± 35% uncertainty offset lines as acceptable, and a 35% uncertainty (in the x and y axis direction) for each point, 5 out of the 35 points should be discarded (the five points at the bottom of the left plot) in the T24 graph. Meanwhile, no data points in the right plot would be out of the “acceptable area”. Additionally, the average deviation for T24 measurements compared to T0 (target value) is 41%. On the contrary, the average deviation for T24CRYO measurements is 12%. Although a more exhaustive statistical analysis should be done, these results are in good agreement with scientific literature, and are found to support the VDI 3880 proposal, thus it is open to question the suitability of the 30 h maximum storage period established by the EN-13725. According to the results obtained in this study, the cryocondensation technique appears to be a promising strategy to overcome this problem.

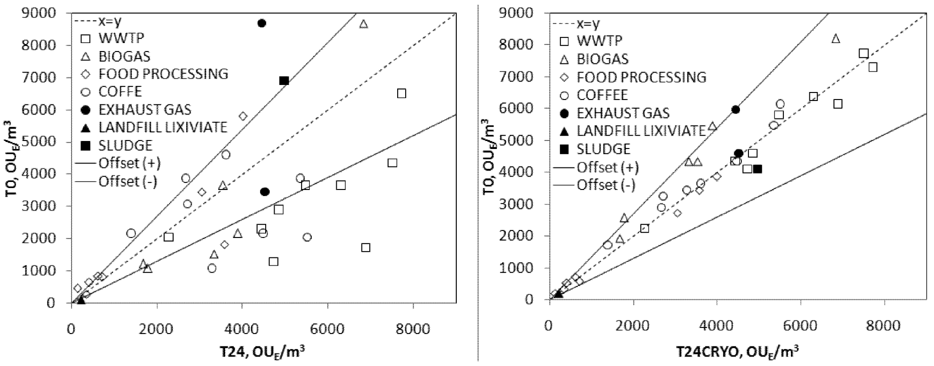

Figure 5. *Odour concentration results. Comparison between T0 the reference (sample measured at time zero) and (left): T24 (same sample measured after 24h storage at room temperature), and (right): T24CRYO (same sample measured after 24h storage under cryogenic conditions). Offset lines (35%) were established on the basis of the uncertainty (k=2) calculated according to the ISO GUIDE 98:1995; Guide to the expression of uncertainty in measurement (GUM)*

4 Conclusions

It is established by EN-13725 that an odour sample cannot be stored for more than 30 hours after its sampling. However, depending on the type of sample, the stability (or representativeness compared to time zero) of the sample even within this period can be seriously compromised. The storage method using the cryocondensation technique proposed in this study allows an improvement of the stability of the samples after 24 h storage. Although more types of samples need to be evaluated and a more exhaustive statistical analysis needs to be done, this method presents a very promising methodology for sampling and storing odours, that will be able to fulfil the requirements not only of current standards such as EN-13725, but also future ones which will be more restrictive such as VDI-3880.

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