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Content

Several means exist to measure odour components (odorants) from livestock production facilities. One of the challenges is sampling of gaseous odorants with different chemical properties and at concentrations varying from sub ppb level to ppm level, often in humid conditions. This newsletter describes a relatively novel sampling and sample preparation method called Solid Phase Microextraction (SPME) to be used in sampling of odorants in livestock production facilities as well as in the field.

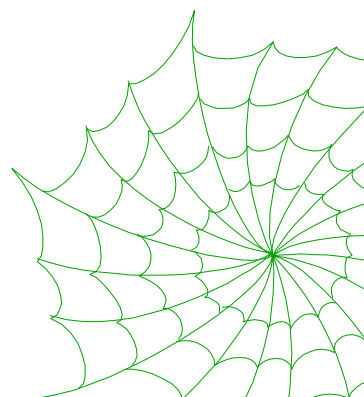


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Sampling of Odour Components from Livestock Production Facilities using Solid Phase Micro-Extraction (SPME)

Solid Phase Microextraction (SPME) is a relatively new method that combines sampling and sample preparation without the use of solvents. The method is fast and unproblematic in relation to the working environment because no organic solvents are used. Further, the initial investment is relatively small. However the labour involved in handling SPME increases the running costs of analysis and limits the number analysis pr. day. Automated SPME devices are available, but unfortunately for headspace analysis only.

Figure 1 depicts a manual SPME device manufactured by Supelco. It is basically a modified syringe with a stainless steel needle enclosing another length of stainless steel tubing fitted tightly to a short piece of solid core fused silica fibre. The bottom of the fused silica fibre is coated with a thin film of sorbent material. The needle serves to protect the fragile fibre coating during storage and use and to pierce the septum of the injection port of the gas chromatograph during analysis.



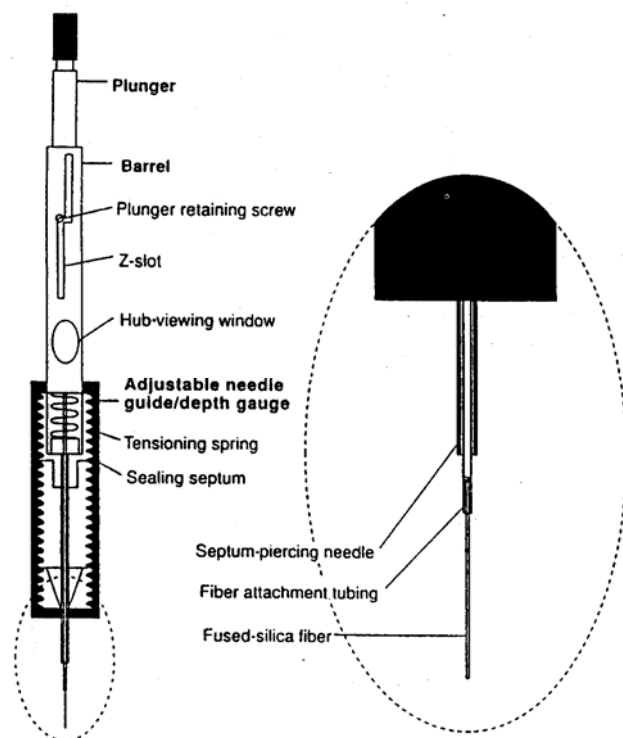
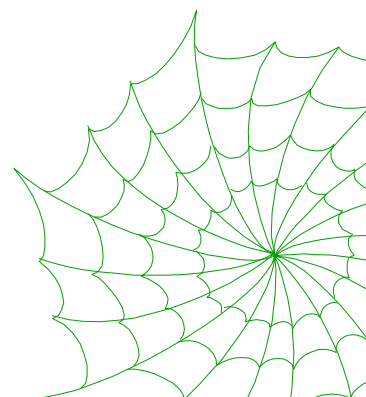


Figure 1. Graphical representation of a SPME device (Pawliszyn, 1997)

SPME is an equilibrium technique that utilizes the partitioning of organic components between a liquid or vapour phase and thin polymeric films coated onto fused silica fibres in the SPME device. The air-to-fibre partitioning is affected by various parameters including: type of fibre coating, analyte concentration in air, sample size, sampling time, air velocity, temperature, humidity, physicochemical properties of the analytes, and presence of other analytes. Thus, quantification requires that extractions are carefully controlled.

In theory, equilibrium between the analytes in the gaseous phase and the fibre coating should eventually arise (Pawliszyn, 1997). An analysis using an odorant mixture showed that equilibrium can be difficult to reach within reasonable time and that the time to reach equilibrium depends on the analyte (Figure 2). Further, positive exclusion likely occur, since the abundance of some of the analytes appears to decline following the equilibrium. A sampling time of approximately 10 minutes appears to work well from the point of view of analytical sensitivity, prevention of positive exclusion, and to reduce sampling time. Longer sampling time may be used in order to increase the sensitivity.



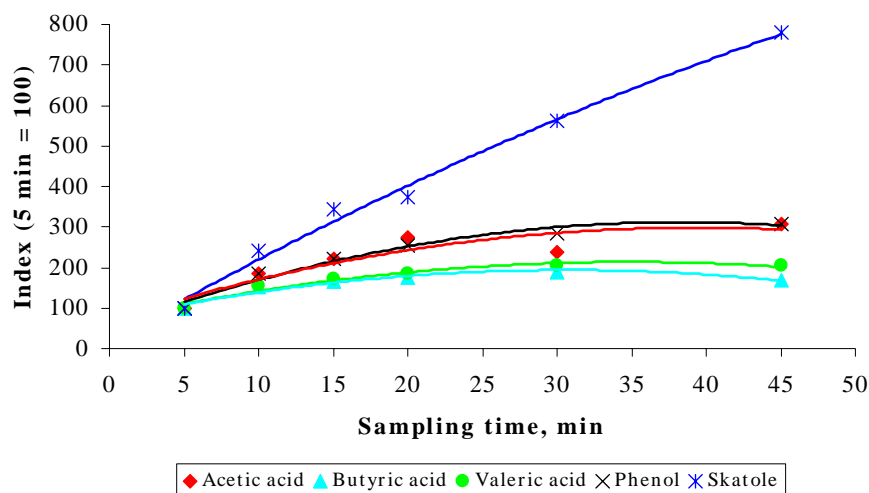


Figure 2. Relative abundance of selected odorants as affected by sampling time using divinyl benzene/Carboxen/polydimethylsiloxane coated SPME fibres (Kai, 2005)

The mass transfer of analytes between the air and the fibre coating is related to the thickness of the boundary layer surrounding the fibre (Pawliszyn, 1997). It has been demonstrated that the mass transfer is best at air velocities exceeding 0.1 m/s around the fibre (Augusto et al., 2001). This means that odorants in pig houses can be sampled simply by exposing the SPME fibre in the exhaust air stream, or in the field by exposing the fibre to the atmosphere. However, in order to observe controllable sampling conditions it is recommended to use a sampling device.

Because the extraction efficiency is affected by the boundary layer thickness, static sampling using e.g. a vial, sampling bulb or a teflon bag to contain the sample, will produce different results than dynamic sampling where the SPME fibre is exposed to an air flow. Pig houses are continuously ventilated, thus, sampling is by definition dynamic and calibration must be performed accordingly. For that purpose a setup has been constructed to deliver standard series of analyte necessary for calibration (Figure 3). The gas standard generator consists of a syringe pump equipped with a 500 μl syringe. The syringe pump injects the liquid analyte standard mixture into a dry helium gas flow passing through a glass sampling bulb. Humidified gas can be delivered by bobbling a secondary dry helium flow through an impinger containing distilled water. The dry gas flow and the humidified gas flow are joined following the sampling bulb. The flows are controlled using two mass flow controllers. To obtain identical conditions comparable with the practical sampling situation a subset of the standard gas is pulled through a septum injector by means of a diaphragm pump. The flow is controlled by a mass flow controller. Surplus gas standard is vented to a hood. All tubing is made of teflon.

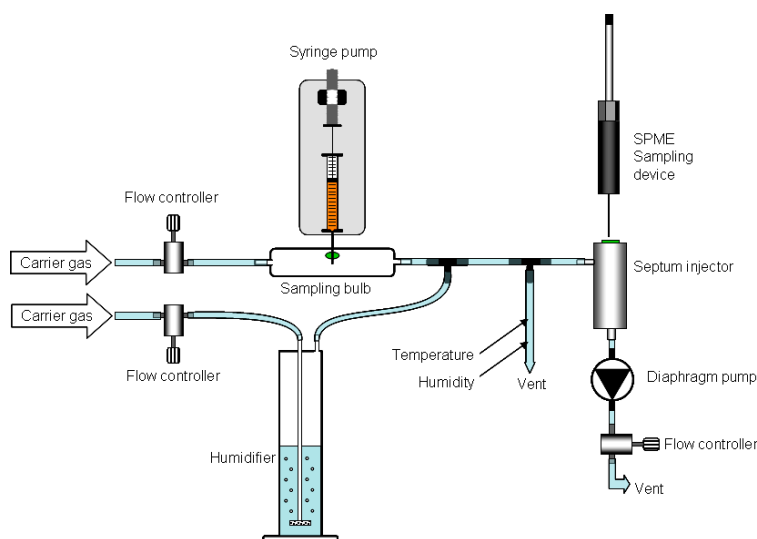


Figure 3. Design of a gas standard generator (Kai, 2005)

Quantification has been performed for a range of odorants using the gas standard generator. Calibration of highly volatile odorants such as trimethyl amine and dimethyl sulphide, however, was unsuccessful due of their highly volatile nature. The gas standard generator may be constructed to inject gaseous neat standards instead of liquid ones. By doing that a wider range of odorants may be quantified.

Other applications

Field sampling of odorants using SPME may be used in connection with the IT-based automatic sampler for agricultural odours described in the DaNet NewsLetter May 2006. With this setup SPME could be used for simultaneous sampling in grids with the purpose of e.g. validating odour dispersion models.

The slurry is the main source of odorants in pig houses, manure storages, and during and following the spreading of manure in the field. SPME also has the potential to sample odorants in liquid matrices such as pig slurry.

References

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