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Analytical challenges in odour measurement: linking human nose with advanced analytical techniques

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Today, still a lot of effort is done in studying, developing and optimising electronic noses. Compared with man-made sensors for vision and hearing, our ability to mimic the chemical senses, smell and taste, is still relatively primitive. Our understanding of the physics behind smell is incomplete. Since no odour measurement technique is able to characterize the odour with a similar sensitivity as the human nose, GC-MS-Sniffing (GC-MS-O) is discussed briefly as a tool with high potential to develop new noses. GC-MS-Sniffing makes it possible to identify the volatiles with high odour relevance. Next, research has been done to link mass spectrometric and olfactometric results. The goal of this research is to generate a general formula that makes it possible to predict the odour concentration.

1. E-noses: critical approach

Despite the success of electronic noses in some areas, the efforts to develop a universal device that enables us to make a fine discrimination of flavours, perfumes, and smells and eventually replace the human nose, are disappointing. The initial hope was to approach the ability of human odour sensing by increasing the number of individual sensors. However, the reason for the nose's unequalled performance has turned out to be not only the high number of different human receptor cells, but their selectivity and their unsurpassed sensitivity for some odorants. Therefore, instead of creating redundant information by adding more similar sensors, current research efforts are targeting both these directions. Sensors with new sensitive layers are under development. Khamis et al. (2009) tested arrays of chemical sensors based on homo-oligomer single-stranded DNA to detect several gaseous analytes. This biosensors

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(DNA, imprinted molecules, or even immobilized natural sensors) seem to be promising developments that are likely to increase the sensitivity and importantly selectivity.
Initially, electronic noses were introduced to move away from sophisticated analytical instruments to a simple and straightforward device. However, recent developments and publications show that the newest generation of e-nose technology is complex and has a limited working range. The main part of electronic noses have to be trained specifically for a certain scope. The necessary study work, preconcentration, specific design and follow-up by highly experienced consultants, often result in high costs. Röck et al. (2008) concluded that the established all-around electronic nose systems produced by different companies prove their use in basic research and for some particular applications. However, in practice the VOC composition resulting in odour, is different from situation to situation. This is why the application of electronic noses is not always straightforward, and hence there is a need for more non-selective odour detection tools. It has to be highlighted that despite the disadvantages (selectivity, sensitivity, etc.) e-noses can supplement advanced analytical techniques or odour panels. In particular some assets such as mobility, ease of use, compatibility with on-line measurement, etc. reflect the potential of e-nose technology. Indeed, for some applications e-noses are already very compatible. Van den Velde et al. (2008) proved that screening breath odour makes it possible to discriminate patients with hepatic pathologies. Cajka et al. (2010) collected fingerprints (GC profiles) of 265 speciality beer samples and were able to separate high quality Belgium Trappist beers from others.

2. GC-MS-Sniffing as interesting tool for the development of new generation e-noses

The authors of this manuscript would like to state that efforts in odour research (e-nose technology) should not only be given to discriminant analyses (grouping applications) or specific black-box devices (specific training). There is a need for development, and an important potential and market-demand for technology that predicts the odour concentration. Typically, odour measurement techniques can be done using sensory measurements or by means of analytical techniques. For a lot of complex problems however, only the human nose in combination with chemical analysis is capable making a fine discrimination of flavours, perfumes, and smells. Experience has proven that the use of human receptors is superior and more cost-effective than applying electronic noses which are on the market today. Therefore, Odournet has invested in equipment that makes it possible to perform GC-MS-Sniffing analyses. A GC-MS-sniffing analysis includes that the individual compounds are simultaneously screened by two different detectors: a mass spectrometer and a conditioned (temperature and humidity) 'sniffing port'. During a GC-MS-sniffing analysis a trained and qualified employee of Odournet is smelling at the 'sniffing port'. Using this methodology not only qualitative and quantitative information of the volatiles (mass spectrometry), but also sensory information (human nose) can be collected for each volatile organic compound in the investigated sample. Using GC-MS-sniffing, the most relevant odour compounds can be selected. The goal of GC-MS-sniffing is to generate a list of compounds with significant contribution to the total odour character of a sample (both odour type as odour intensity). It is noteworthy to mention that to our knowledge no standard methods for these types of analyses have been published yet. Therefore it is important that next to development of new odour detection tools, equal attention is given to the optimization of GC-MS-sniffing methodology and publication of a standard method. Standardisation is critical to guarantee a more frequent application of GC-MS-Sniffing as a powerful tool in environmental odour research.

3. Linking chemical analysis to olfactometric analyses

Odournet R&D efforts are mainly focused on finding correlations between mass spectrometric analyses and olfactometric measurements according to EN 17325. This kind of information is essential to further optimise e-nose technology. Similar, Blanes-Vidal et al. (2009) determined the major airborne chemical compounds that are responsible for the unpleasant odour perceived in swine facilities. Applying a multivariate data analysis strategy involving principal components analysis and multiple linear regression the relationship was analysed between concentrations of 35 gases and the odour concentration. From this study it was concluded that by measuring sulphur containing compounds (hydrogen sulphide, dimethyl sulphide, dimethyl disulphide, dimethyl trisulphide) a relative satisfactory prediction can be made of the odour concentration. For the mushroom producing sector Noble et al. (2001) have developed a very cheap method for measuring the odour concentration. By means of very simple, low-cost analytical tools (colorimetric tubes) only the concentration of hydrogen sulphide and dimethyl sulphide has to be measured and inserted in equation [1] and Figure 1:

$$\ln (ou/m^3) = 7.601 + 0.934 \ln (H_2S + DMS + 0,375) \quad (r=0,948, P < 0.001) \qquad (1)$$

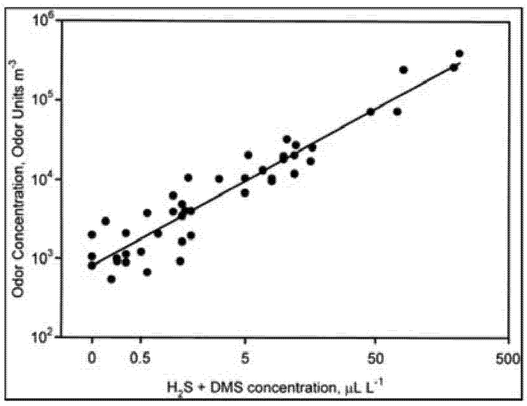

Figure 1. Correlation between odour concentration (ou/m³) and corresponding concentrations of hydrogen sulphide and DMS

Defoer et al. (2002) found a good linear relationship of the odour concentration with the TVOC concentration (R^2=0.9, n=19). For biofilter emissions in the animal rendering sector a good correlation was found between organic sulphur containing compounds and the corresponding odour concentration (R^2=0.94, n=8). Odournet has also proved that H_2S is a very good indicator to predict the odour concentration in wastewater treatment plants. Not only for malodours correlations are found between chemical and sensoric data. Berna et al. (2009) proved using linear discriminant analysis (LDA) that wines with different aromas (odours) can be discriminated based on a GC-MS analysis.

Odournet's ambition is to correlate mass spectrometric screening results with olfactometric results on both a sector as universal level. The ultimate goal is to generate models that are able to predict odour concentrations without specific training. Therefore a large sampling dataset has been collected containing mass spectrometric profiles and corresponding odour concentrations. To make the system more sensitive and not solely dependent on the direct vapor partitioning, a preconcentration step has been introduced. Therefore a fixed gas volume is preconcentrated on Tenax tubes which are thermally desorbed in the GC-MS. Gas samples are collected from different sectors ranging from wastewater treatment plants, rendering activities, paper mills, manure processing to fragrance emissions. The goal was to find not only for each individual sector, but also an universal formula to predict the odour concentration of a gas matrix. Figure 2 proves that the first results are promising.

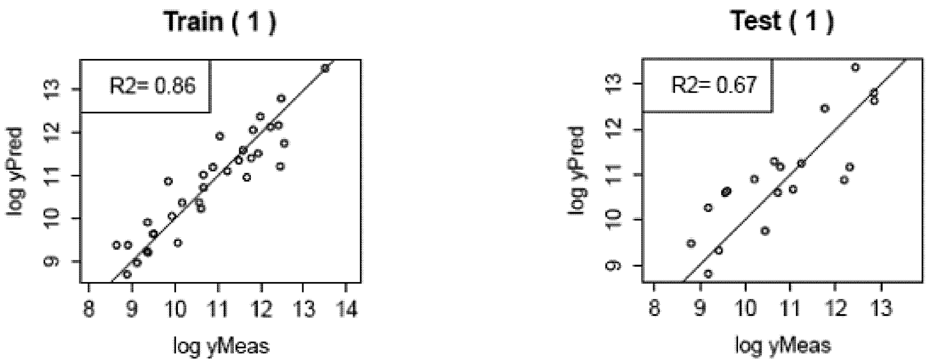

Figure 2. Representation of training set used to generate a universal odour predicting equation which is tested on random selected gas samples (right graphic). yPred = predicted odour concentration (Odournet Model), yMeas = measured odour concentration (olfactometry EN13725).

From Figure 2 it can be seen that inserting concentrations of several selected volatile organic compounds in a logarithmic model enables us to predict the odour concentration with a quite good correlation. The universal odour predicting equation was used on a test set containing gas samples from different sectors and with odour concentrations ranging between 5000 and 500 000 ou/m³. The correlation of 67% on the test set is mainly due to a relatively high measurement uncertainty on the corresponding odour concentrations that are allowed by the olfactometric analyses according to ISO13725. Secondly, the training set proved to be characterized by an unequal data distribution over the different sectors. This means that the model is mainly fitted for the dominant sector, leading to overfitting and less good prediction for the minor sectors. At this moment Odournet is collecting more data from a wide range of sectors in order to reduce this overfitting problem and improve the performance of the odour predicting model.

The development of a general odour prediction model might be the base of a new type of MS-based electronic nose that is non-selective and highly sensitive.

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