

On the importance of odour threshold to identify molecules responsible for the odour of a material

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Abstract

In the industrial environment, materials with unpleasant smell are a major problem. Indeed, the odour is one of the most important criteria in the selection, the purchase and the use of a material. An unpleasant odour can cause the rejection of the material by the consumer. Odour control is therefore an important industrial and economic issue. The difficulty is to combine physico-chemical and olfactometric data to identify chemical compounds responsible for the odour. Nowadays, the relationship between these two kinds of data is realized by an expert with his own knowledge.

The identification efficiency of the concerned compounds depends on the expertise level. So, to decrease the result interpretation uncertainty, the aim of this project is to develop a protocol allowing to identify compounds of interest in the entire physico-chemical analysis results. This protocol will be developed in the form of an automated toolbox which combines statistical techniques. This identification should be as exhaustive as possible to identify compounds responsible for odour concentration and/or acceptability and/or quality. This tool will allow enhancing the reliability of the odorous compounds identification, realised by expert to this day.

Keywords: Odour, materials, data mining, modelling

1. Introduction

All materials emit compounds in the air. Sometimes, the mix of compounds or just one of these compounds is responsible for an unpleasant odour associated to these materials [(NESA *et al.*, 2004), (WYPYCH, 2013); (ROGNON and POURTIER, 2014)].

This unpleasant odour could be linked to different dimensions of the odour as odour concentration, acceptability and/or quality [(AFNOR, 1996); (GOURONNEC, 2000); (AFNOR, 2003); (GOURONNEC, 2004)].

However, people use to associate an unpleasant odour with a health hazard but this is not justified. Indeed, many compounds are odorless at their concentration in the air (particularly indoor air) but are not insignificant for the health and vice versa (PIERUCCI *et al.*, 2005).

Despite that, an unpleasant odour implies a rejection of a material and then economic issues. This rejection can also be due to a disgust feeling.

Given the negative impact of the unpleasant odour of a material on people, there is a need of control and work on this odour. To solve this problem the key step is the identification of the compounds responsible for the odour (MEIERHENRICH *et al.*, 2005).

Currently, this work is realized by an expert. The expert in charge of the compounds identification might be an odour expert or the most appropriate person in a firm to deal with this issue (chemist). So with his knowledge, each expert develops his own approach (SEZILLE *et al.*, 2014).

A frequent approach applied is a Gas Chromatography simultaneously associated with an olfactometry analyses (GC-O) (FERNANDEZ *et al.*, 2009). And, others approaches realized by odour expert consist in dealing with a lot of different kinds of data (by their nature, size, source and precision). So, the main difficulty is to manage to match up these data in the most pertinent and exhaustive way.

In this way, all of these approaches present some drawbacks, which are sources of the identification result (CHOLLET and VALENTIN, 2000). Some drawbacks are linked to the expert and some of them are linked to the data.

Indeed, about the expert, the variability is linked to the fact that there is a disparity in skills from one expert to another (CHOLLET and VALENTIN, 2000). Furthermore, at equal competences, the analysis sharpness of the physico-chemical spectra could be a source of variability too. In addition, this approach is a time-consuming analysis and

creates a dependency of the manufacturer on the expert about this issue.

The aim of the ongoing project is to develop an automated methodology to remedy the expert work heterogeneity. The assets of this methodology are data treatment standardization, time saving and independence of the company.

As the data used and crossed by the expert are the pillars of the work of identification, it's necessary to ensure their completeness, accuracy and reliability.

In this paper the methodology implemented in the project and the importance of data treatment (especially odour detection threshold bibliographic data) are described.

2. Methodology

2.1. Data collected and used by the expert

In response to odour issue, the expert has to manage several data sources.

When an unpleasant odour is detected, the compounds emitted are sampled and analyzed.

Firstly, the air sample is analyzed by GC-MS to identify its composition: the nature and the concentration of each compound. Then the expert collects physico-chemical data.

Secondly, the air sample is analyzed by olfactometry to characterize the odour by its dimensions. Then, the expert collects olfactometric data.

Thirdly, the expert has to use bibliographic data to use parameters of compounds.

The expert will then juggle with all that flow of information to identify, in the most exhaustive way, compounds responsible for the odour.

But the issue is the fact that, beside the variability of the identification due to the expert, there is a variability linked to the data source.

Indeed, the quality of physico-chemical data by GC-MS, depends on the quality of separation, quantification and identification of the compounds. Concerning olfactometric data, the variability is due to the subjectivity of the sensorial analysis. The other source of variability is linked to the lack of homogeneity and completeness of bibliographic data and more particularly odour detection threshold (ODT) data. This last parameter is the identification key of compounds responsible for the odour. Indeed, it's the minimal concentration that is required to detect the odour of a compound. Bibliographic data of ODT presents a low reliability, when data are available.

It is difficult to work on the variability due to physico-chemical or olfactometric analysis but it's possible to work on the variability and completeness of bibliographic data all the more that this is the key of the identification.

2.2. Software of treatment

The ODT values of literature are collected on the Excel software and the improvement work of the reliability and the completeness of bibliographic data is realized on the R software (version 3.3.1 - 64-bit).

3. Bibliographic data treatment

3.1. Improvement of reliability of available bibliographic data

As it's explained below, the ODT value available in the literature are marred by a high variability. To illustrate this variability, the case example of the butyl acetate compound is presented in the Table 1 (VAN GEMERT, 2011).

Table 1 : Butyl acetate ODT values in the literature (Van GEMERT, 2011)

Authors	Butyl Acetate ODT values (mg/m ³)
Jung-1936	0.044
May-1966	35.000
Köster-1971	480.000
Hellmann&Small-1973-1974	0.030
Dravnieks-1974	3.000
Anon-1980	0.320
Naus-1982	0.700
Nagy-1991	1.000
Patterson&al-1993	7.700
CM&C et CM -1994	11.500
Zimer&al-2000	0.061
Nagata-2003	0.077
CM&al-2004	0.015
Cain&Schmidt-2009	0.010

The sources of variability can be explained by a lot of parameters as authors 'nationalities or the country normalization. More specifically, variability could be linked to the olfactometric analysis type because of the expected answer type (DRAVNIKS and PROKOP, 1975), the dilution rate direction [(FALCY and MALARD, 2005); (UENO *et al.*, 2009)], the panel recognition rate (LEONARDOS *et al.*, 1969). The variability could also be linked to the sample quality (FALCY and MALARD, 2005), the chosen compounds to the panel selection : one compound in Europe (AFNOR, 2003) and five compounds in Japan (UENO *et al.*, 2009), the panel subjectivity [(DRAVNIKS and PROKOP, 1975); (FALCY and MALARD, 2005); (LEONARDOS *et al.*, 1969)], the environmental conditions or the panel applied correction : Odour intensity correction (UENO *et al.*, 2009) or the retrospectively sorting (AFNOR, 2003).

Once available data is cleaned, the second step of work on bibliographic data is the completeness of ODT values for compounds with any ODT values.

3.2. Completeness of bibliographic data

In the literature, some authors have studied just one compounds whereas others have studied a lot of compounds. Furthermore, some compounds are solely informed by one authors whereas others compounds are informed a lot of time. The ODT database total missing value proportion is 99% (on 1238 compounds) and the proportion of compounds informed at least by one author is 53%. This proportion encourages to use predictive modelling to complete the bibliographic database.

To apply this modelling, the first constraint is finding dimensions which have a potential impact on the odour of compounds and more particularly on their ODT values. Some dimensions are identified as molecular weight, vapor pressure, lipophilicity or polarity (MEIERHENRICH *et al.*, 2005) but these dimensions are, along with ODT, marred with an important amount of incompleteness and, sometimes, variability.

That's why, the most appropriate solution found is to use QSAR/QSPR (Quantitative Structure-Activity Relationship/Quantitative/Structure-Property Relationship) approach. Indeed, this approach allows to predict physical dimensions (property, activity) from structural index (ROY *et al.*, 2015). Using this approach allows working with a complete base of prediction.

This approach is used in many different domains and in many different applications as the mosquito repellent potency of a compound [(MA *et al.*, 1999); (NATARAJAN *et al.*, 2005); (BASAK *et al.*, 2007)], the hydrocarbon compounds dipole moment study (NESTEROV *et al.*, 2004), the ketones acidity study (YUAN *et al.*, 2012), the alkanes boiling point (RAWAT and SATI, 2013) or to the new medicinal compounds making (GOULON-SIGWALT-ABRAM, 2008)].

The reason why this approach is selected is the fact that the odour encoding reside in the recognition substrate/receptor (DE MARCH, 2015) and that the molecular complexity would determine the acceptability and the olfactory notes quantity (KERMEN *et al.*, 2011). Some authors have already worked on the subject [(DEMOLE and STOLL, 1964); (ZARZO, 2012)] and tried to model the ODT values from QSAR/QSPR approach [(CZERNY *et al.*, 2011); (XU *et al.*, 2012); (PAL *et al.*, 2014); (TOROPOV *et al.*, 2016)]. However, in these studies, the number of compounds is low and specific compounds are often chosen. In the present project, the aim is to generate the approach for whatever compounds.

Then, a predictive modelling will be applied according to a QSAR/QSPR approach with the best statistical methodology. Some statistical treatments can be identified as potential solution as Partial least square regression, Support Vector Matrice or Neural Network. Furthermore, a sorting of index can also be applied in parallel.

Thus, at this step, the obtention of a reliable and complete ODT database will improve the expert work, but its own variability has to be resolved by other tools. The aim for the future step is to automate the work of the expert.

4. Automation of the work of expert

This automation is realized with a toolbox which allows weighting the concentrations of each compound from the physico-chemical data by its own ODT value (the ODT values are now available for all compounds with varying degrees of accuracy thanks to the previous steps). Then, the obtained data is combined to olfactometric data to identify a bouquet of compounds for each odour dimension.

This toolbox will be developed on a synthetic gaseous mixture of about 50 compounds. This mixture will be used to eliminate physico-chemical data uncertainty. Indeed, the nature and the chemical concentration of each compound are well-controlled. Furthermore, the toolbox efficiency could be tested.

The result of the automated approach will be then compared to the expert approach to judge the accordance between the two approaches and validate the toolbox efficiency.

5. Evaluation of needed precision on olfactometric and physico-chemical data by materials application

The aim of this part is evaluating the precision of physico-chemical and olfactometric data required to have a good result on materials samples.

Indeed, for physico-chemical data, the purpose is to evaluate the improvement of the separation, the quantification and the footprint qualities on the identification result, with different techniques: TD-GC-MS, TD-GC2D-MS and PTR-MS (Figure 1).

For the olfactometric data, the purpose is to evaluate the potential precision gain with an increase of the jury size (6, 12 and 18).

This approach will allow to rule the analysis quality on the final result about the identification of the potential compounds responsible for the materials odour.

6. Conclusion

To conclude, the methodology is structured into four steps:

- A work of ODT database implementation and reliability,
- A complementary work of this ODT database improvement and completeness,
- The development of an automatic method based on statistical toolbox to link odour characteristics to compound or group of compounds responsible of odour,
- An evaluation of the required physico-chemical and olfactometric analyses accuracies on the identification work.

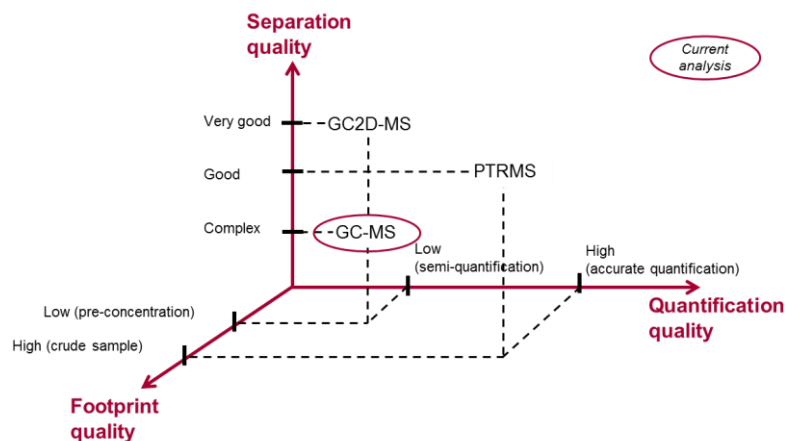


Figure 1 : Precision of physico-chemical data analysis

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