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Odor Concentration Prediction by Gas Chromatography and Mass Spectrometry (GC-MS): Importance of VOCs Quantification and Odor Detection Threshold Accuracy

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Odor annoyance is the second most important nuisance in Europe. So, the knowledge of the odor concentration is very important to assess the odor impact on the environment. In Europe, EN 13725 regulates the method to measure the odor concentration. If olfactometry is the only normalized method to measure odor concentration, it is nevertheless often interesting to be able to assess it on the basis of a physico-chemical analysis. To reach this goal, the odor concentration can be obtained by the following equation:

$$Odor\ Concentration = \sum_{i=1}^{n} OAV_i = \sum_{i=1}^{n} \frac{C_i}{ODT_i}$$

In this equation, OAV_i is the odor activity value that corresponds to the ratio of the chemical concentration to the odor detection threshold of compound i. C_i corresponds to the concentration of compound i in the gaseous mixture and ODT_i to the odor detection threshold of this compound. These two parameters affect odor activity value and therefore odor concentration assessment accuracy.
In this context, the main goal of our experiment was to determine what conditions are suitable to obtain the most precise prediction.
Our study consisted in the first step to generate a calibrated gaseous mixture of odorous compounds and to analyze it by GC-MS and olfactometry (EN 13725). The reproducibility of the gaseous mixture generation was tested. Physico-chemical results were analyzed using a global quantification (mg/m^3 toluene eq.) on one side and individual quantification of each compound on the other side.
In the same way, we used odor detection thresholds from the literature on one side and odor detection thresholds measured in our lab, according to EN 13725, on the other side.
This study allowed us to emphasize the weight of quantification and odor thresholds accuracies on odor concentration prediction.

1. Introduction

Odors became an important industrial and societal concern because "environmental stress" perceived in residential areas creates a sense of insecurity and a negative perception of the quality of life. Exposure to odor causes in some people mental disorders (depression, aggression) and somatic disorders (dry throat, immuno-depression, and nausea) identical to those observed under stress (Schlegelmilch et al., 2005, Gostelow et al., 2001, Renault et al., 2006). Although air quality has improved over the last thirty years, the odor nuisances are regularly presented in France as the second reason for complaints after those related to noise pollution. In Europe, around 20% of the population undergoes olfactory discomfort (Bokowa, 2010).

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Persistent odors are usually the most poorly tolerated (Day et al. 1998, Van Durme et al. 1992, Schlegelmilch et al., 2005). In this context, the importance of knowing the odor concentration is obvious. Indeed, this parameter directly represents the sensitivity of the odor to the dilution, i.e. its persistence.
The odor concentration is obtained by the olfactometric measure in accordance with the standard EN13725. However, depending on the context, this method can be expensive and difficult to implement. Sometimes, access to an olfactometer may be impossible. A cost-effective strategy to circumvent this problem may be to identify the major contributing odorants compounds in the gaseous mixture and to correlate the chemical composition and its odor concentration.
This approach is based on the evaluation of odorous potential of each compound in the gaseous mixture. To do that, the concept of odor activity value (OAV) defined as the ratio of the chemical concentration to the odor detection threshold has been introduced and widely used (Friedrich and Acree 1998; Kim and Park 2008; Parker et al. 2010; Parker et al. 2012; Trabue et al., 2006).

$$OAV_i = \frac{C_i}{ODT_i}$$

OAV_i : Odor Activity Value of compound *i* (dimensionless)
C_i : Chemical concentration of compound *i* (mg.m^{-3})
ODT_i : Odor Detection Threshold of compound *i* (mg.m^{-3})

The odor concentration may then be correlated to the odor activity value by adding the OAV of all individual compounds in the mixture (Gallego et al., 2012, Wu et al. 2016).

$$Odor\ Concentration = \sum_{i=1}^{n} OAV_i$$

The objective of this study was to estimate the influence of the uncertainty related to the quantification of the components of the mixture and that associated with odor detection thresholds on the quality of the prediction of the odor concentration. For this, a mixture of six compounds was made and analyzed by GC-MS, and by olfactometry. The odor detection threshold of each compound was also measured.

2. Materials and methods

2.1 Selected odorous compounds

A mixture of six different odorous compounds was realized for this study. These compounds are presented in table 1, along with their CAS number (Chemical Abstracts Service) and their odor detection thresholds (ODT) obtained in literature (Van Gemert, 2011). As several odor detection thresholds were frequently available for a single compound, and the order of magnitude could be considerably different, a geometric mean was used in order to obtain an average value ($\boldsymbol{ODT_i^{lit}}$), in line with common practice (Parker et al. 2012).

Table1: Selected odorous compounds – Odor detection thresholds from literature

Molecule	CAS number	$\boldsymbol{ODT}$ (min-max)	Number of values	$\boldsymbol{ODT_i^{lit}}$
		(mg /m^3)		(mg/m^3)
n-butanol	71-36-3	0.01-42	38	0.668
Methyl butanoate	623-42-7	0.03-0.077	3	0.056
Triethylamine	121-44-8	0.022-1	3	0.206
R-Limonene	5989-27-5	0.045-55	3	0.517
Cyclopentanone	120-92-3	31	1	31
Butyl acetate	123-86-4	0.01-480	14	0.654

2.2 Generation of reference gaseous mixture

A liquid mixture was done by injection of a well-known volume of each VOC (micropipette) and weighing of the solution after each introduction in the glass vessel. Then, 50µL of the mixture was introduced in the injection port of a chromatograph heated at 250°C to volatize the liquid. The gaseous phase was then diluted with 40 L of clean air to obtain the required concentration in a Nalophan® bag.

2.3 Analyses

2.3.1. GC-MS analyses

Physico-chemical analyses were performed by a TD-GC-MS method (Turbomatrix from Perkin Elmer followed by a Thermo Scientific Trace gas chromatograph coupled with a Thermo Scientific DSQ mass detector). The analytical column was an Optima 5-ms Accent 60 m x 0.25 mm x 1 µm. Helium was used as carrier gas at 1.5 mL/min in constant flow mode. The GC oven temperature program was set as followed: 9 min at 40°C, a ramp at 15°C/min until 90°C, 4 min at 90°C then a ramp at 10°C/min until 250°C and finally 5 min at 250°C. The ionization of compounds was made by electronic impact at 70 eV. The full scan mode was used to analyze fragments from 20 to 250 amu (atomic mass unit). Compounds identification was led by comparison of our spectra with those referenced in the NIST library. The system was calibrated with toluene.

2.3.2. Olfactometric analyses

The odor concentration was measured according EN 13725 standards using a dynamic dilution olfactometer ODILE (Odotech Inc., Canada). Six panellists were selected for each olfactometric session. Three different evaluations were done on the same sample to evaluate the dispersion of olfactometric measurements.

3. Results and discussion

3.1 Olfactometric analyses

Three gaseous samples were constituted according to the protocol described in section 2.2 and analysed according to EN 13725 standards. The results are given in table 2.

Table 2: Reference mixture – Odor concentration

	Odor concentration (OU_E/m^3)
Sample 1	14133
Sample 2	11506
Sample 3	10543
Mean	**12061**
Standard deviation	1517

The average odor concentration is 12000 UO_E/m^3 with a standard deviation of 1500, representing a good repeatability of gaseous mixture generation and olfactometric analysis.

3.2 Importance of VOCs quantification

Table 3 shows the odor activity value ($\boldsymbol{OAV_i}$) of each compound and the global predicted odor concentration of the mixture obtained on the basis of measured concentrations ($\boldsymbol{C_i^{meas}}$), calculated concentrations ($\boldsymbol{C_i^{calc}}$) and odor detection thresholds from literature ($\boldsymbol{ODT_i^{lit}}$) as presented in table 1. $\boldsymbol{C_i^{meas}}$ corresponds to the concentration measured by TD-GC-MS and expressed in mg/m^3 toluene equivalent as usually observed in literature. $\boldsymbol{C_i^{calc}}$ corresponds to the concentration calculated on the basis of the mass of liquid mixture volatilized in the sample.

Table 3: Predicted odor concentrations calculated with $\boldsymbol{ODT_i^{lit}}$

Molecule	CAS number	C_i^{meas}	C_i^{calc}	ODT_i^{lit}	$OAV_i = \frac{C_i^{meas}}{ODT_i^{lit}}$	$OAV_i = \frac{C_i^{calc}}{ODT_i^{lit}}$
		(mg toluene eq./m^3)	(mg/m^3)	(mg/m^3)		
n-butanol	71-36-3	72.7	163.7	0.668	109	245
Methyl butanoate	623-42-7	99.9	189.4	0.056	1 777	3 367
Triethylamine	121-44-8	5.1	149.4	0.206	25	724
R-Limonene	5989-27-5	29.1	183.3	0.517	56	354
Cyclopentanone	120-92-3	57.2	198.0	31	2	6
Butyl acetate	123-86-4	59.2	186.3	0.654	91	285
$\boldsymbol{Predicted\ odor\ concentration} = \sum_{i=1}^{n} \frac{C_i}{ODT_i}$					**2059**	**4981**

The results show that none of the predicted odor concentrations is close to the value measured by olfactometry (12000 OU_E/m^3). However, the use of the exact concentrations provides a significant gain in the evaluation.

3.3 Importance of odor detection thresholds

The values of odor detection thresholds, if available in the literature, are often dispersed (Table 1). This is due to the wide variety of authors who have made measurements using different techniques at very different times. Making the choice of the most relevant values requires either to clean these databases with complex algorithms, or to realize its own measures. It is this second solution that was chosen in this study. The minimum and the maximum values of the odor detection thresholds measured for the six molecules of the mixture ($\boldsymbol{ODT_i^{lab}}$) are given in Table 4. The number of determinations of each odor detection threshold measured also figures in this table. The $\boldsymbol{ODT_i^{lab}}$ is the geometric mean of all the values measured for each individual component.

Table 4: Selected odorous compounds – Odor detection thresholds measured in our lab.

Molecule	CAS number	Number of determinations	ODT (min-max)	ODT_i^{lab}	Standard deviation
			(mg /m^3)	(mg/m^3)	
n-butanol	71-36-3	11	0.040-0.210	0.088	0.067
Methyl butanoate	623-42-7	4	0.024-0.033	0.029	0.004
Triethylamine	121-44-8	8	0.019-0.045	0.033	0.009
R-Limonene	5989-27-5	7	0.055-0.118	0.083	0.019
Cyclopentanone	120-92-3	5	0.731-1.389	0.933	0.255
Butyl acetate	123-86-4	9	0.046-0.100	0.061	0.024

It may be noted that except for cyclopentanone for which only one value was available, the odor detection thresholds measured in our laboratory ($\boldsymbol{ODT_i^{lab}}$) are in the lower range of those found in the literature (Table 1).

Table 5 illustrates the results obtained with this new data, using measured concentrations and calculated ones.

Table 5: Predicted odor concentrations calculated with $\boldsymbol{ODT_i^{lab}}$

Molecule	CAS number	C_i^{meas} (mg toluene eq./m^3)	C_i^{calc} (mg/m^3)	ODT_i^{lab} (mg/m^3)	$OAV_i = \frac{C_i^{meas}}{ODT_i^{lab}}$	$OAV_i = \frac{C_i^{calc}}{ODT_i^{lab}}$
n-butanol	71-36-3	72.7	163.7	0.088	823	1854
Methyl butanoate	623-42-7	99.9	189.4	0.029	3445	6530
Triethylamine	121-44-8	5.1	149.4	0.033	154	4513
R-Limonene	5989-27-5	29.1	183.3	0.083	351	2213
Cyclopentanone	120-92-3	57.2	198.0	0.933	61	212
Butyl acetate	123-86-4	59.2	186.3	0.061	969	3046
$\boldsymbol{Predicted\ odor\ concentration} = \sum_{i=1}^{n} \frac{C_i}{ODT_i}$					**5804**	**18368**

The results obtained using the odor detection thresholds measured in our lab are globally higher and closer to the measured value (12000 OU_E/m^3) than those obtained previously with the literature values.
To summarize and compare all these results, table 6 gives the relative errors on odor concentration ($\boldsymbol{\delta_{OC}}$) obtained using measured ($\boldsymbol{C_i^{meas}}$) or calculated chemical concentrations ($\boldsymbol{C_i^{calc}}$) and odor detection thresholds from literature ($\boldsymbol{ODT_i^{lit}}$) or measured in our laboratory ($\boldsymbol{ODT_i^{lab}}$). Relative error is defined as the quotient of the absolute error (difference between the approximate value and the actual value) and the absolute value of the actual value:

$$\delta_{OC} = \frac{(approximate\ value - actual\ value)}{|actual\ value|}$$

It is an algebraic relative error: if positive, it means that the approximate value is greater than the actual value (overestimation) and if it is negative that it is lower (underestimation).

Table 6: Relative error on odor concentration prediction

	C_i^{meas}	C_i^{calc}
ODT_i^{lit}	- 0.829	- 0.587
ODT_i^{lab}	- 0.519	+ 0.523

Examination of this table shows that the most distant results of the value measured by olfactometry are those obtained with the geometric mean of odor detection thresholds from literature and the values of the chemical concentrations evaluated on the basis of GC / MS analysis (underestimation of 83%). Using the exact concentrations and the geometric mean of odor detection thresholds from literature, or concentrations evaluated on the basis of the GC / MS analysis and odor detection thresholds measured in the laboratory lead to substantially the same underestimation of the odor concentration (respectively 52 and 59%). Only the use of the exact concentrations and odor detection thresholds measured in our laboratory value leads to an odor concentration overestimated by 52%.

4. Conclusion

The objective of this work was to assess the influence of the uncertainty related to the components quantification of a gaseous mixture and that associated with odor detection thresholds on the quality of the odor concentration prediction as measured by olfactometry. For this, a mixture of six compounds was constituted.

The first results highlight the influence of the two parameters studied (quantification of mixture components and odor perception thresholds) on the prediction of the odor concentration. Improving the precision of data, logically, results in an improvement of the prediction. Controlling the uncertainty of these data, especially that related to odor detection thresholds, appears to be crucial in view of developing a model integrating the interaction effects (synergy / inhibition) between the odorous compounds.

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