



Evolution of the perceived odour intensity assessed by GC-Olfactometry of emissions from household and building products

Olivier Ramalho, Jerome Lebasnier

► To cite this version:

Olivier Ramalho, Jerome Lebasnier. Evolution of the perceived odour intensity assessed by GC-Olfactometry of emissions from household and building products. Healthy Building'2006, Jun 2006, Lisboa, Portugal. pp.35-40. hal-00688539

HAL Id: hal-00688539

<https://hal.science/hal-00688539>

Submitted on 17 Apr 2012

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Evolution of the Perceived Odour Intensity Assessed by GC-Olfactometry of Emissions from Household and Building Products

O. Ramalho¹ & J. Lebasnier¹

¹Centre Scientifique et Technique du Bâtiment, Health division, F-77447 Marne-la-Vallée Cedex2, France
email: ramalho@cstb.fr <http://www.cstb.fr>

Summary: *The purpose of this paper is to determine the evolution of the perceived odour intensity and the number of odorous compounds with the emissions of selected household and building products. Experiments were conducted in a small-scale glass chamber. Volatile organic compounds were sampled during one hour on a PDMS/Carboxen fiber by solid-phase micro-extraction (SPME). Perceived odour intensity and number of odorous compounds tend to decrease with the decrease of VOC emission whereas precise identification of odorous compounds tends to improve.*

Keywords: GC-O, SPME, odour intensity, odorous compounds.

Category: Building material emission

1 Introduction

Olfactometry associated with gas chromatography (GC-O) has proven to be a powerful tool to identify odorous compounds from building material emissions [1, 2, 3, 4, 5]. Along with chemical analysis and sensory evaluation, GC-O provides useful complementary information that allows the identification of malodorous compounds. GC-O is also a key tool for experts in the chemical formulation of new odorized or deodorized household or building products.

Karpe et al. [1] developed a GC-FID-MS-O multi-coupling device to identify odorous compounds from wall coverings. A manually operated integrator allows the recording of retention times from odorous compounds. Odour intensity was also reported for each identified compound (e.g. phenol, cyclohexanone, 1,2,4-trimethylbenzene, cymene) as low, medium or strong.

Jensen et al. [2] used a tape recorder to perform GC sniffing coupled with flame ionization detection of volatile organic compounds (VOC) in the headspace of a linoleum sample. They found that linoleum odour was mostly caused by saturated and unsaturated aldehydes, and carboxylic acids. However, coincidence with GC-FID recording seemed difficult.

Mayer et al. [3] have experimented GC-O on headspaces from different building materials. Odour detected at the GC-O outlet were associated with retention index and compared to retention index of GC-MS compounds. Several stepwise dilutions were used to identify the most important odour active compounds. Additionally, odour quality was associated to each olfactory detected compound.

Mayer & Breuer [4] further exploited GC-O to compare the formation mechanism of odorants from building materials with those known in the food industry. Identification of odorants was achieved by comparing odour quality and retention properties on two different GC capillary columns.

Clausen et al. [5] detected 139 odour active compounds from floor oil and linseed oil. From which, only 40 were detected by mass spectrometry. A microphone coupled with video recording of the chromatogram was used to collect comments from the six untrained panellists. Detection frequency among the panellists allows the selection of the major odour active compounds.

These studies underline the difficulty to coincide odour information expressed by a subject with the GC detector signal which marks the presence of a compound. Most of the studies rely on expressed opinions of the panellist that may distract subject awareness and do not deploy continuous recording of the panellist perception. Moreover, identification of odorous compounds is performed either in headspace or at one given time. Concentration of emitted volatile organic compounds varies with time and thus may impact on the number of odorous compounds detected by GC-O. An olfactory profile (olfactogram) may be obtained by monitoring quite instantaneously the odour intensity perceived by the sniffing subject. This profile provides a lot of information. Difficulty relies on how to interpret these data and extract the useful information.

The purpose of this paper is firstly to determine the evolution of the perceived odour intensity and number of odorous compounds with the emissions of selected household and building products conditioned in a small-scale chamber and secondly to extract useful information from obtained olfactograms.

2 Methods

Three different odorous materials have been tested sequentially in small glass chambers (Climpaq): an air freshener (orange-jasmin), a linoleum flooring and a gloss white alkyd paint. The paint was applied on a polyester sheet with an automated Erichsen applicator (initial thickness 100 μm). Paint samples were left drying during 68 hours before introduction in the test chamber. These sides of the linoleum samples were covered by an aluminium adhesive that prevent emission of VOC from the side or bottom of the flooring. Environmental conditions were maintained throughout all experiments at 23 °C and 50% relative humidity. Specific ventilation rates were close to those found indoors, e.g. 0.124 $\text{m}^3\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ (air freshener), 0.5 $\text{m}^3\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ (alkyd paint, wall scenario), and 1.25 $\text{m}^3\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ (linoleum flooring).

Emissions have been monitored at selected intervals (4, 24, 48 and 72 hours) during 4 days. Sampling was realized by solid phase microextraction (SPME) on an 85 μm stableflex carboxen / polydimethylsiloxane fiber (Supelco) during 1 hour. Sampling was duplicated each time using two PDMS/Carboxen fibers. SPME [6] was used as the sampling technique as it allows direct injection of sampled compounds in the gas chromatogram without use of intermediate steps (thermodesorption, cryotrap, transfer line) that may affect some delicate odorous compounds.

A sampling time of 1 hour was found to be appropriate to reach gas-fiber equilibrium. The SPME fiber was exposed with varying durations to a mixture of 12 VOCs in headspace (Fig. 1). Competition was observed among adsorbed VOCs. An exposure of 1 hour increases sensitivity to most compounds and equilibrium is achieved. On the counterpart, 1 hour exposure does not allow quantification as response curves are not linear.

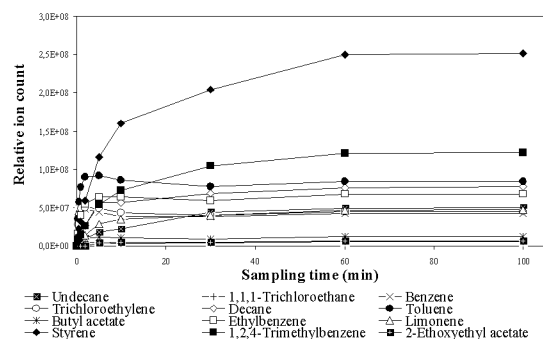


Fig. 1: The effect of exposure time on amount of VOC collected (expressed by RIC) with a PDMS/Carboxen fiber.

After sampling, the SPME fiber was then immediately injected in splitless mode on a HP5890 series II GC equipped with a polar capillary column (Solgel Wax 60m, 0.25 mm id, 0.25 μm ; SGE). The choice of a polar column is also focused on odorous compound detection. Absorbed and adsorbed VOC are totally extracted from the fiber at 300°C during 3 min. Helium was used as carrier gas with a flowrate of 1.4 mL/min. Oven temperature was initially maintained at 30 °C during 3 min then increased at 3.5 °C/min until final temperature of 200 °C is reached. Maximum temperature is hold during 10 min. Double detection was provided with a HP 5790 MSD mass spectrometer operating in 70 eV EI scanning mode (35-300 m/z) and an olfactometry sniffing port (ODO II, SGE). Humidified air at 10.4 mL/min charged with the part of the capillary column outlet was continuously provided to the nose. The MS transfer line was kept at 280 °C. The double detection (GC-MS-O) allows the immediate identification of odorous compounds. However, several column configuration were tested before reaching optimal adequation between MS peak and odorous event as a delay from either side may be observed. This delay also change with oven temperature. So peak concordance was tested with a mix of reference odorous compounds (same as Fig.1) spanning the entire chromatogram.

Monitoring of perceived odour intensity of the sniffing subject was achieved with a portable linear potentiometer (6 cm long scaling from 0 to 10 V) associated with a pocket data acquisition system working at 5 Hz frequency (TAUPE-M, MIS France). This high frequency was used to match the sampling frequency of the gas chromatograph. With this method, the subject translates his perception of odour intensity by moving the potentiometer with his hand. This method is somehow related to the fingerspan technique developed by some authors [7]. The subject has been trained with reference compounds at varying dilution before performing the experiments.

SPME sampling is reproducible as shown by duplicate sampling using two PDMS/Carboxen fibers (Fig. 2). In the first run, the sniffing subject focused on odour intensity perception, whereas in the second run, he defines the odour quality (from own experience) and hedonics (pleasant or unpleasant) for each odorous event.

Importance was given to breathing frequency as it may influence odour detection probability (especially with concentration near threshold value) and also odour intensity rating [8]. The subject was therefore assigned to breathe evenly and regularly.

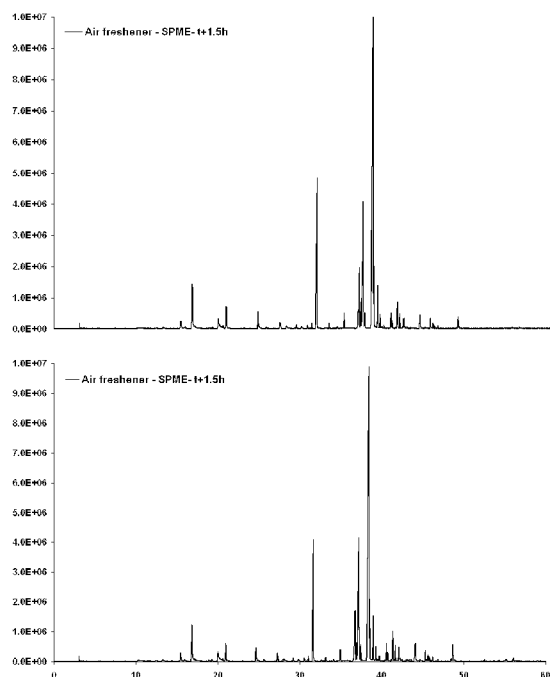


Fig. 2: RIC chromatogram of air freshener emission. Reproducibility of two PDMS/Carboxen fiber sampling.

3 Results

Analyses of the emission of tested products result in an olfactogram and a chromatogram for each sample. The evolution between the first and the last sample (typically three days later) is presented for the alkyd paint (Fig. 3), the air freshener (Fig. 4) and the linoleum (Fig. 5). Chromatogram and olfactogram (reversed) have been superposed to enhance peak matching.

The major odorous compounds emitted by the alkyd paint were carboxylic acids (hexanoic, pentanoic, propanoic acids) characterized by a rancid odour note and aldehydes (trans-2-octenal, trans-2-heptenal, octanal, hexanal, pentanal) characterized by woody or fruity notes. Almost all odorous compounds were judged as unpleasant especially hexanoic acid exhibiting a tenacious and long lasting odour. Octanal (fruity note) was the unique compound judged as olfactory pleasant.

The number of detected odorous events vary from 72 (after 3 h) to 59 (after 74 h), a 18% decrease. From these only 28 are identified by MS spectra. Some compounds remain below the detection limit and others are difficult to identify on their mass spectra alone. Total RIC area from GC-MS decrease by 19%. This small decrease matches the observed difference in number of odorants.

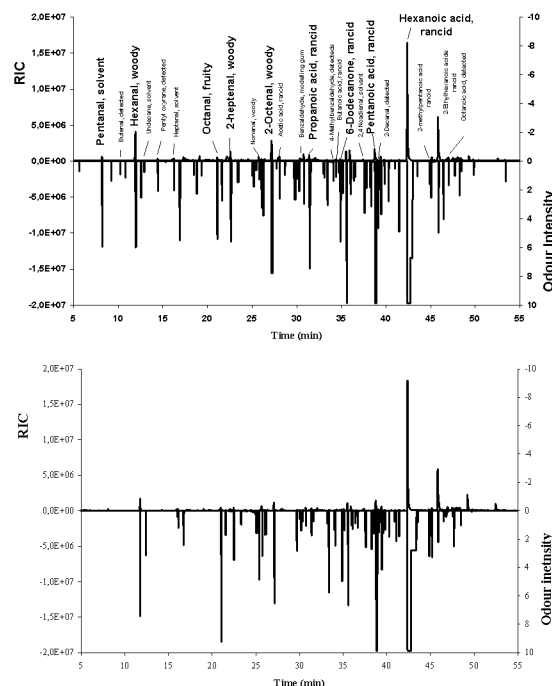


Fig. 3: Evolution of VOC and odorous events from alkyd paint emission after 3 h (top) and 74 h (bottom).

The most odour active compounds identified from the air freshener were typical compounds from the aroma industry : phenylmethyl acetate, linalool, lilial, cis- and trans-citral, neryl nitrile, geranyl nitrile, octanal, phenylethanol, alpha-ionone, alpha-terpineol. Odour notes vary from floral, fruity and sweet. Apart from a few exceptions (phenylethanol, wineplug odour; acetic acid: vinegar, geranyl nitrile, irritating odour), all compounds were judged as pleasant to the nose.

Three days later, the number of odorous events has dramatically decreased from 46 to 14 (-70%). MS identification covers only 24 compounds as most of them are under analytical detection limit. Total RIC area has also decreased (71%).

The linoleum flooring tested yields very low emission, even in the first hours (Fig. 5). Major odour active compounds were aldehydes (octanal and hexanal) with fruity and woody notes, and pentanoic acid with a rancid odour quality. A large majority of odorous compounds were judged unpleasant, except octanal and nonanal.

The number of odorous events was initially 42 to finally reach 20 (52% decrease). Fourteen substances have been identified. The others were below detection limit. The variation in total RIC area was only 13%. This large difference may be explained by the fact that VOCs were emitted at concentrations close to odour thresholds. A small change in concentration may drastically decrease the number of odorous events detected.

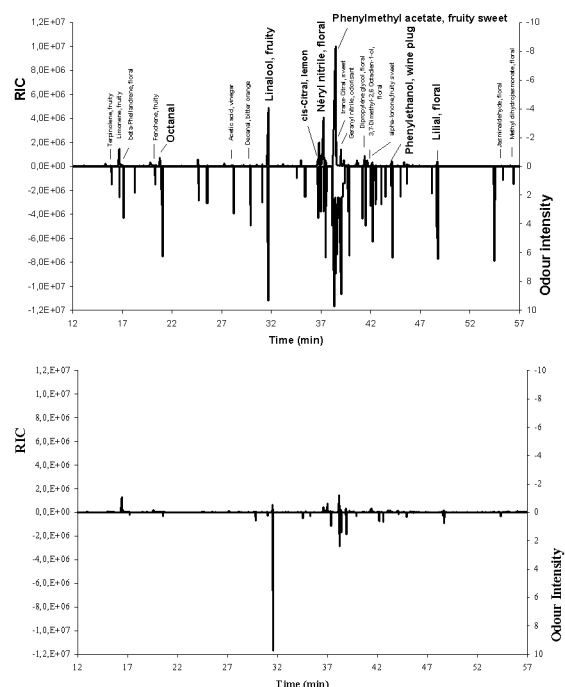


Fig. 4: Evolution of VOC and odorous events from air freshener emission after 1.5 h (top) and 74 h (bottom).

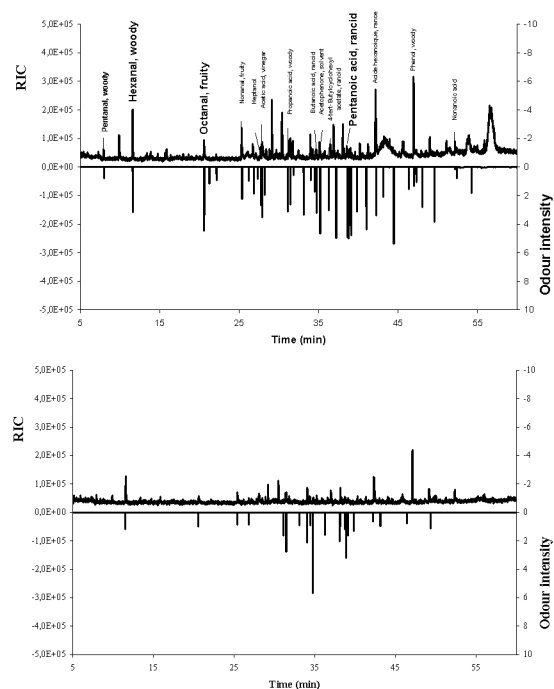


Fig. 5: Evolution of VOC and odorous events from linoleum emission after 1 h (top) and 74 h (bottom).

4 Discussion

The number of odorous events tend to decrease with time but odorous compounds are more easily identified after 28 hours (correspondance with identified VOC compounds is easier), as resolution is improving in the analytical column. One other aspect that may affect identification is odour

adaptation. In Fig. 6, the evolution of a detailed portion of the olfactogram is presented. A good resolution is not achieved after 4 or 28 hours. However, the effective analytical resolution appears to be quite good (Fig. 7) : phenylmethyl acetate ($rt = 38.4$ min), trans-citral ($rt = 38.6$ min), geranyl nitrile ($rt = 39$ min). Therefore, it is likely that odour adaptation occurs in the first hours of emission, and hinders the precise identification of odorous compounds.

Another factor that may interfere with detection of odorous events is the breath frequency [8]. Measurements conducted on a subject performing normal and regular breath show that breathing events (inspiration and expiration) occur every 3 seconds with a breath duration of about 2.4 seconds (Fig. 8). Thus, during one MS peak of 30 seconds duration, about 6 breathing cycles can be observed. It is therefore obvious that breath frequency affect odour adaptation, but how it does affect it remains unclear.

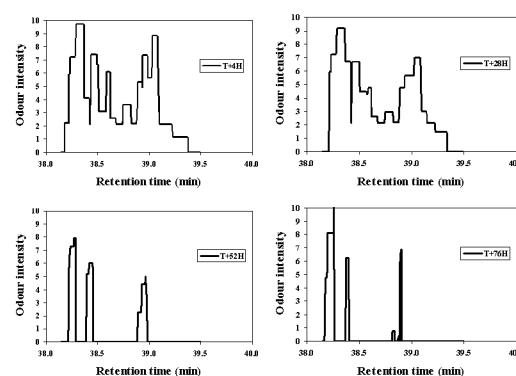


Fig. 6: Evolution of perceived odour intensity of emissions of an air freshener by GC-MS-O, after 4, 28, 52 and 76 hours in a small-scale chamber.(2 min detail).

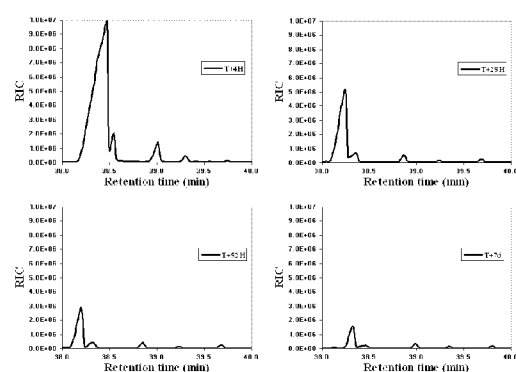


Fig. 7: Evolution of VOC emissions of an air freshener by GC-MS-O, after 4, 28, 52 and 76 hours in a small-scale chamber.(2 min detail).

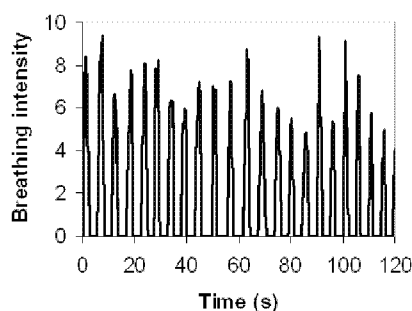


Fig. 8: Breath frequency as a function of time. Intensity is in arbitrary units.

The so-called olfactogram provides also useful information, i.e. odour intensity for each detected compound. It can be expressed either by peak area or peak height. The latter parameter was used by Bernet et al. [9] to discriminate wines from their odour. One main advantage is that peak height does not take into account possible adaptation. This advantage is a drawback too as a tailing peak is caused by odour adaptation but also by odour persistence which represents a valuable information. For example, hexanoic and pentanoic acids were both rated at the maximum height. However, hexanoic acid odour is so persistent that the odour intensity remains maximum over several tens of seconds. This is reflected by a higher peak area (see Fig. 3). But in other cases, the peak area is not appropriate as discussed earlier (e.g. phenylmethyl acetate, Fig. 6 in the first hours).

In this experiment, the maximum intensity is the subject representation of an overwhelming odour. Bernet et al. [9] consider that even untrained assessors manage to achieve self calibration with the finger span technique from odour intensities without use of a reference. This is the case in our experiment, as the subject after some training managed to create his own odour intensity scale with the potentiometer. However, the use of an internal odorous standard may consolidate the calibration and enhance inter-laboratory comparisons.

Another difficulty lies on the duration of a chromatogram, about 2 hours for each run in this experiment. This requires a complete and steady attention of the sniffing subject which is difficult to maintain for an individual. Furthermore, chromatographs are typically located in laboratories where background noise is usually high. Thus, temporary lacks of attention may arise throughout the olfactogram and affect odorous events detection. Obviously, highly intense odorous events are not affected as they can awaken a distracted assessor. Slightly intense odorous events eluting in the second half of the chromatogram are likely to be affected. This can not be predicted

Most importantly, sample representativity must be preserved in order to further exploit odour intensity information. As discussed earlier in the methods chapter, 1-hour sampling by SPME does not allow quantification. This means that proportion of individual VOCs in the original gas phase is not respected and thus GC-MS-O information may not reflect reality. Further work is needed to use SPME in the linear range yet not sensitive enough. Adsorbents like Tenax TA are useful but thermodesorption may affect stability of some odorous compounds. Representativity is also needed at the GC-O outlet, in the glass cone where the effective concentration of eluted compounds are difficult to determine. This implies that the GC-O experiment may (or may not) provide false identification of odorous compounds that do not normally contribute to the odour of the real gas mixture. This may arise with peri-threshold concentrations.

Conclusion

GC-MS-O is a simple and powerful technique that can provide a lot of valuable information. Real-time perception monitoring allows the construction of an olfactogram based on odour intensity. Correspondence between MS peaks and odorous events is achieved by superposition of both chromatogram and olfactogram. Multiple runs may be used to provide more information like odor quality or hedonic assessment. However, data interpretation must be cautiously made as multiple factors may affect the olfactogram, i.e. analytical resolution, odour persistence, odour adaptation, breath frequency, assessor's attention. Sample representativity is the key factor of data interpretation. Both sampling technique and GC-O outlet may affect representativity.

SPME simplifies sample preparation and reduces loss of odour active compounds. But the technique lacks sensitivity and thus cannot yet be used in the linear response range with shorter sampling times.

Despite all drawbacks, GC-MS-O can be successfully used to identify major odor active compounds emitted by household or building products and their evolution with time. How they affect overall odour remains still difficult to predict. But first, further research is needed for GC-MS-O to be a standardized technique providing the same results whatever the laboratory, i.e. the quantification of the odour attribute of a given compound.

References

- [1] P Karpe, S Kirchner & P Rouxel. Thermal desorption-gas chromatography-mass spectrometry-flame ionization detection-sniffer multi-coupling: A device for the determination of odorous volatile organic compounds in air. *J. Chrom. A*, 708(1995), 105-114.
- [2] B Jensen, P Wolkoff & CK Wilkins. Characterization of linoleum. Part 2: Preliminary odor evaluation, *Indoor Air*, 5(1995), 44-49.
- [3] F Mayer, K Breuer & E Mayer. Determination of Odoractive Volatiles Emitted by Building Materials by a New Method using Gas Chromatography-Olfactometry. *Proc. Healthy Buildings 2000*, August 6-10th, 2000, Espoo, Finland, pp 119-124.
- [4] F Mayer & K Breuer. Material odor – odoractive compounds identified in different materials – The surprising similarities with certain foods, possible sources and hypotheses on their formation. *Proc. Indoor Air'2005*, September 4-9th, 2005, Beijing, China, pp 2024-2029.
- [5] PA Clausen, HN Knudsen, K Larsen, V Kofoed-Sørensen, P Wolkoff & CK Wilkins. Use of gas chromatography olfactometry (GC-O) to detect unknown emissions from building products containing linseed oil. *Proc. Indoor Air'2005*, September 4-9th, 2005, Beijing, China, pp 2053-2058.
- [6] J Pawliszyn. Solid phase microextraction – Theory and practice. 1997. Wiley-Vch Ed. 247 p.
- [7] B Berglund, U Berglund & T Lindvall. On the principle of odour interaction. *Acta Psychologica*, 35(1971), 255-268.
- [8] K Hanaoka, N Vallet, P Giampaoli, B Heyd & P MacLeod. Possible influence of breathing on detection frequency and intensity rating in gas chromatography-olfactometry. *Food Chem.*, 72(2001), 97-103.
- [9] C Bernet, N Dirniger, P Claudel, P Etiévant and A Schaeffer. Application of finger span cross modality matching (FSCM) by naive assessors for olfactometric discrimination of Gewürtzaminer wines.