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Development and Technology Assessment of the Analytical Performance of an Eight Position Dynamic Olfactometer

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The European technical standard “Air Quality—Determination of Odour Concentration by Dynamic Olfactometry” adopts dynamic olfactometry, a sensorial methodology based on the employment of a panel of human assessors, as the official methodology for the measurement of odour concentration in gas samples. The olfactometer is the device, useful to dilute the odor sample with neutral air, according to precise ratios and to present it to the panel for the analysis. The present paper describes the development of an Italian olfactometer, able to host eight assessors, designed to improve the instrumental performance of the devices actually present on the market, and to increase the accuracy and repeatability of the olfactometric measurement. In particular, in the paper the principal features of the instrumental device and the results of calibrations of dilution valves will be shown.

1. Introduction

The odour emission monitoring involves different analytical approaches to the odour annoyance evaluation and its characterization (Brattoli et al., 2011). Among them, the sensorial approach, employing human assessors, has been chosen as the international standard methodology by the scientific community, due to its effectiveness to evaluate the effect of the whole odour mixture on olfactory human apparatus. Moreover, this approach is preferred to the conventional analytical instrumentations, able to provide information about the chemical composition of the mixture, because human nose is the best odour detector, much more sensitive than them to a wide range of different chemicals at very low concentrations.
The European technical law EN 13725/2003 standardizes the dynamic olfactometry, a sensorial methodology, to the determination of odour concentration in gas samples. It is based on the use of a dilution apparatus, called olfactometer, which presents the odour samples diluted with odour free air, at precise ratios, to a panel of human assessors, selected according to a reference gas (n-butanol) (EN 13725, 2003). The technical law admits two standardized methods for the presentation of odour sample to the panel: forced choice and yes/no method. In the first method, two or more sniffing ports are used where the odour sample is presented at one port and neutral air at the other port(s). The examiners have to choose the port from which odour exits. In the yes/no methods each examiner sniffs from a single port and communicates if the odour is detected or not.
The EN 13725/2003 provides all of the standard procedures to the odour air sampling, to the determination of odour concentrations expressed in odour units (numerically equal to the dilution factor necessary to reach the odour threshold, that is the minimum concentration perceived by the 50% of population), to the panel selection and to the olfactometer calibration. Moreover, it gives indications about the appropriate materials to be used in olfactometry, the required technical features that dilution apparatus have to respect and the quality procedures to obtain valid data.
To assert that an olfactometer measurement is valid and reliable, a minimum number of four panellists should be employed and their responses should be in conformity to the following criteria:

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- The assessors cannot commit mistakes of more than 20% for the detection of neutral air, presented randomly in a sequence of dilution; if this criterion is not satisfied for one or more panellists, he or they have to be eliminated by the measurement.
- Retrospective screening. This criterion verifies the coherence of panel results, basing on the evaluation of ΔZ parameter, calculated for each individual panel response as the ratio between the individual threshold value and the geometric mean of all individual threshold values. This parameter must satisfy the following relation: $-5 \leq \Delta Z \leq 5$. If one or more individual threshold values do not satisfy this criterion, then all responses given by the panel member with an inadequate ΔZ must be eliminated by the final result and the procedure is repeated until all data provided by panel member are consistent with the criterion.

So that, the number of panellists, who give valid responses, affects the repeatability of the measurement results and the olfactometric data quality. For this reason, it is an advantage if olfactometric measurements are executed by employing more than four panellists, in order to ensure the control procedures conformity.

The present paper describes the development and the technology assessment of an olfactometer, designed to host eight examiners, completely made by an Italian team. The project was part of a public funding on the establishment of public research laboratories in Regione Puglia received by the Chemistry Department of University of Bari, called VOC and ODOR. The technical development of the instrumentation was conducted by ARCO SolutionS srl, spin off company of the Chemical and Pharmaceutical Sciences Department of University of Trieste. VOC and ODOR permitted to develop a highly specialized laboratory, equipped with fixed and mobile systems for monitoring chemical, sensory and instrumental for the VOCs analysis. It was set up also a mobile laboratory, that, among the other instrumentations, contains an olfactometric laboratory able to perform the direct transfer of the gaseous mixture to the olfactometer, in order to limit the effects of potential contamination and modifications in the samples. To this purpose, it was necessary to develop a portable olfactometer, equipped with eight positions in order to increase the accuracy and repeatability of the olfactometric measurement and to respond more adequately to EN 13725/2004.

2. Material and methods

2.1 Wolf: general description

Figure 1 shows a picture of the new eight position olfactometer, named Wolf.

Figure 1: A picture of the eight position dynamic olfactometer (Wolf)

The olfactometric apparatus is composed by:

- a mechanical section constituted by a central unit and the user's position;
- a pneumatic section including the diluter and the air distributor;
- the electric and electronic section for all the connections;
- the software.

Wolf has a dual pneumatic circuit for compressed air, one for the reference air and the other for the Venturi dilution system. The pneumatic section represents the core of the system; it is composed by a dosage, a dilution and a distribution group. The dosage unit is responsible to adjust the gas sample flow according to the concentrations required by the operator. It is equipped with two collectors, C1 and C2, with the gas flow control valves (VFLUX) and with electrovalves (VDIL). The valves are equal to 15, corresponding to dilutions that the instrument can perform. The collector C1 is constituted by 15 outputs to needle type flow control valves, connected with the two-way on/off type electrovalves, whose outputs are then connected to the collector C2. It presents an output to an ejector, able to mix the sample with pure air and two outputs connected to two specific valves to perform its cleaning (VCLNIN and VCLNOUT).

The dilution group is mainly constituted by the ejector. It generates the vacuum level, sufficient to suck the gas to be analyzed from C2 and then mix it with the pure air through the valve Vmix. The ejector presents three-way connection: an input for the pure air, one for the sample suction and an outlet of the mixture to the collector C3. The distribution group uses the collector C3 to distribute the mixture from the dilution group to the eight positions and the collector C4 for the distribution of the pure air. Each collector consists of an input port and eight output ports, each of them connected to eight electrovalves (VUSR). Figure 2 shows a diagram of operation of the pneumatic section, in which the different parts are displayed.

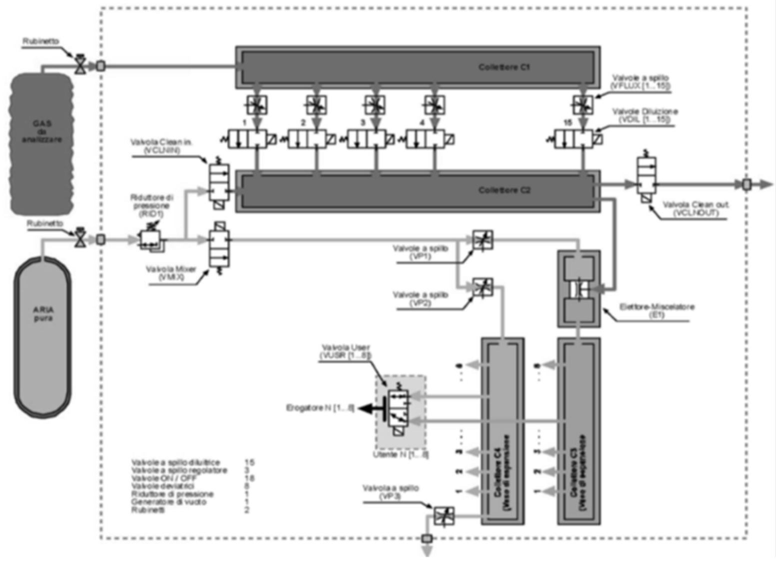

Figure 2: Scheme of the pneumatic section

Wolf adopts the yes/no method for the presentation of odour samples and the dilution steps are produced automatically. The range of dynamic dilutions goes from the maximum dilution equal to 2^{16} to the minimum one less than 2^2 (corresponding to 3.5 value).

The materials used for the apparatus and for the interface nose/olfactometer are in compliance with the specific requests of the European technical law (Teflon for the connection tubes, glass for the masks, stainless steel for the other components). A constant flow of neutral air streams through the eight positions in order to clean continuously the lines by residual odours.

2.2 The software

The software has been designed to set the different operational parameters related to the breathing time, the flushing time between rounds, the flushing time after sample, the percentage of blank samples in the dilution sequence, the order of presentations of the different step of dilution, the number of panel members participating to the analysis. In general, the software is able to manage the olfactometric tests, the panel database, the data storage and the elaboration of results, as well as to control manually the different dilution valves. As example, in Figure 3 two software screenshots are shown.

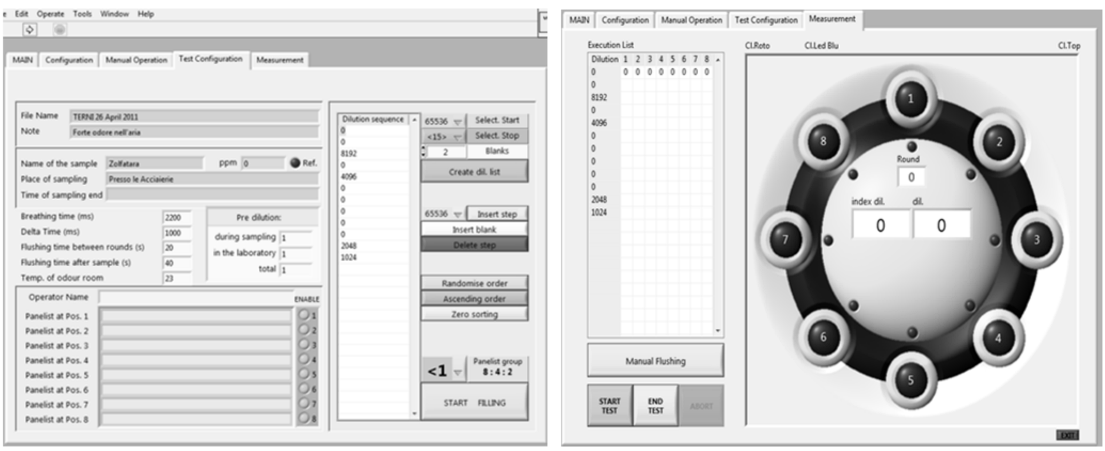

Figure 3: Screenshots of the Wolf software

2.2 Technological assessment

The design of the interface nose/olfactometer has been developed, taking into account the prescriptions, described in the EN 13725/2003. In fact, this interface allows operators to sniff comfortably without distractions during the odour evaluation. The conical shape of the masks permits to measure an air velocity through them in the range of 0,2 m/s - 0,5 m/s, as required by the technical law. It has been verified with a multi-functional measuring instrument “Testo 400”, equipped with a hot bulb probe.
Moreover, the air flow, streaming through each port, is greater than 20 l/min, tested with a Primary Air Flow Calibrator “Gilian Gilibrator-2” equipped with a high flow cell (2 to 30 LPM).

2.3 Calibration of the dilution valves

The EN 13725 prescribes a methodology to verify the correct operation of the olfactometer and in particular, of the dilution valves, evaluating two parameters: the accuracy (A_d) and the instability (I_d).
The method uses a tracer gas and an opportune analyser; the most frequently used is the propane with a FID (Flame Ionization Detector). It is necessary to collect at least five test results for each dilution. Each test result, indicated with y_{id}, is calculated as average values among ten observations o_j, measured every five seconds one from each other.
The accuracy (A_d) is calculated, according to the Eq. (1)

$$A_d = \frac{|d_{w,d}| + (A_{w,d} + r_d)}{\mu_d} \leq 0.20 \quad (1)$$

where:
$d_{w,d}$ represents the precision due to the systematic error, as Eq. (2)

$$d_{w,d} = y_{w,d} - \mu_d \quad (2)$$

$y_{w,d}$= average value of the test results
μ_d = expected concentration of the tracer gas
$A_{w,d}$ is a statistical parameter, calculated as Eq. (3)

$$A_{w,d} = \sqrt{\frac{1}{2n}} \quad (3)$$

n= number of test results
r_d = repeatability, calculated as Eq. (4)

$$r = t \cdot \sqrt{2} \cdot s_{r,d} \quad (4)$$

$s_{r,d}$ = standard deviation (Eq. (5))

$$s_{r,d} = \sqrt{\frac{\Sigma\,(y_{i,d} - y_{m,d})^2}{(n-1)}} \quad (5)$$

The instability is calculated, according to the Eq. (6)

$$I_d = \frac{1.96 \cdot s_{i,d}}{y_{i,d}} \times 100 \leq 5\% \quad (6)$$

where $s_{i,d}$ is the standard deviation calculated for the ten observations.

3. Results and discussion

The calibration of the dilution valves has been made using propane as tracer gas and a FID as analyzer. To cover the whole range of dilutions, three propane cylinders of different concentrations, respectively 200,000 ppm, 10,000 ppm and 1,000 ppm purchased from Air Liquide Italia Service s.r.l. whit an expanded uncertainty of ±2%, have been used. Regarding the verification of the valves conformity, analysis have been acquired with a flame ionization detector Eco Control model ER600.
In Table 1 the results of the instability and accuracy, calculated for each dilution step, are shown.

Table 1: Instability and accuracy values for dilution steps

Propane concentration (ppm)	Dilution step	Instability I (%)	Accuracy (A_d)
200,000	65,536	1	0.004
200,000	32,768	0.5	0.007
200,000	16,384	1.5	0.025
200,000	8,192	0,5	0.127
200,000	4,096	1.1	0.011
200,000	2,048	2.7	0.098
10,000	1,024	2	0.090
10,000	512	0.9	0.034
10,000	256	0.6	0.020
10,000	128	2.7	0.052
10,000	64	1.8	0.007
10,000	32	0.8	0.013
1,000	16	1.3	0.016
1,000	8	3.1	0.021
1,000	4	2.2	0.003
1,000	3,5	4.6	0.038

As indicated in table 1, the instability and the accuracy values are in compliance with the prescribed limits, requested by the EN 13725/2003.
In order to compare the analytical responses given by Wolf with those obtained by using a commercial olfactometer, samples of the standard, n-buthanol, have been analysed. In particular, samples of n-buthanol at a concentration of 60,7 ppm were analysed by using Wolf and Ecoma series TO8 employing the same members of panel. In Table 2 some examples of the olfactometric results on n-buthanol are reported, showing that the panel responses are comparable:

Table 2: Olfactometric results of n-buthanol samples (Wolf and Ecoma TO8)

N-buthanol concentration (ppm)	C_{od} (ou_E/m^3) TO8 ($Z_{LL} – Z_{UL}$)	C_{od} (ou_E/m^3) Wolf ($Z_{LL} – Z_{UL}$)
60,7	**1149** (457-2892)	**1218** (589-2399)
60,7	**1085** (719-1637)	**1086** (576-2044)

The odour concentration values are presented, taking into account the uncertainty (upper and lower limits of the 95 % confidence interval) (VDI guideline 3881,1986).
Other tests on gas standard and real samples will be executed in order to obtain important feedback in order to emphasize the advantages of the new olfactometer.

4. Conclusions

The need to increase the accuracy and repeatability of the olfactometric measurement, had led to the development of a new device, completely performed by an Italian team. It is able to host eight assessors at the same time, and it was designed to improve the instrumental performance of the devices actually present on the market. The contemporaneous employment of more than four panellists (up to eight) allows to ensure the control procedures conformity, that exclude invalid responses. The different parts of the instrumentation (mechanic, pneumatic, electric parts) have been studied and realized, considering the EN 13725 requests. Moreover, great attention is paid to the software, from the graphical interface to the operational features. The most important tests have been dealt with the technological assessment, regarding the verification of the air flow through the different port, the air velocity through the masks and the calibration of the dilution valves. The parameters requested by the technical law result perfectly satisfied. The next step of the research will be the testing using gas standard samples and real ones and the comparison of the Wolf olfactometric results with them obtained by other olfactometers, already present on the market.

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