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Evaluation of Olfactory Properties of Gas Odorants

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This work describes the methodology adopted to analyse the olfactory properties of different gas odorants, with the aim of evaluating the possibility of introducing a new, sulphur-free gas odorant (Gasodor® S-Free). For this purpose, the compliance with the current regulation on the matter, i.e. the Italian Norm UNI 7133:2012 was verified, which specifies that "the odour given to the gas by means of the odorant shall be characteristic, unpleasant and of constant type at any concentration in air". Sensorial tests were run comparing the odorant S-Free with the two traditional odorants (TBM/IPM/NPM and THT) and with other "interfering" odours, in order to verify that the odour of the tested odorant is "characteristic", thereby meaning that it shouldn't be confused with other odours that might commonly be perceived in a domestic environment, in the case of an accidental gas leak. The Principal Component Analysis (PCA) applied to the results of sensorial tests shows that the odour of the S-Free is recognized as similar to the odour of the other traditional odorants, and that it is clearly discriminated from the interfering odours. These results indicate that the odour of the S-Free odorant is "characteristic", meaning that it is not confused with other interfering odours. Moreover, this study points out the effectiveness of the proposed methodology for the qualitative evaluation of the olfactory properties of gas odorants.

1. Introduction

Historically, gas for domestic use was the so called "town gas" obtained from coal. Coal is a solid fossil fuel, with heterogeneous chemical composition, variable in function of the progress of the carbonification process, generally containing non negligible amounts of sulphur (some %) (Smith and Batts, 1974), which is the origin of the town gas characteristic odour. In the handing over to natural gas, which is "cleaner" and therefore less odorous than town gas, it has become necessary to artificially odorize the gas, with the purpose of making it recognizable at low concentrations in order to avoid incidents or explosions due to accidental gas leaks (Stevens et al., 1987). Indeed, natural gas is not completely odourless as pure methane (NIOSH, 2000), because it generally contains a variable amount of impurities.
It is because of the sulphurous odour of town gas that natural gas has traditionally been odorized with sulphur-based odorants. Currently, in Italy two gas odorants are used: one consists entirely of tetrahydrotiofene ("THT"), whereas the other one is a mixture of three mercaptans, i.e. terbutyl mercaptan, isopropyl mercaptan and normalpropyl mercaptan ("TBM/IPM/NPM").
During combustion, sulphur forms sulphur dioxide (SO_2), which is a pollutant gas with negative effects on the environment and on human health both in an indirect (acid rain precursor) and direct manner (toxic). The Threshold Limit Value (TLV) of SO_2 expressed as Time-Weighted Average (TWA) is 2 ppm (NIOSH, 2006). For this reason, in the last years, the use of fuels with low sulphur contents is being encouraged. As a consequence, there are high investments for desulphurization of fossil fuels, and "light" fuels (which generally have lower sulphur contents) are being preferred to "heavy" fuels (e.g., methane has almost completely been substituted to gasoil for domestic heating). Considering this trend to reduce or even eliminate sulphur from fuels, the intentional subsequent addition of sulphur compounds to a low sulphur containing, and therefore valuable, fuel as methane, seems contradictory.
As an indication, the quantity of odorants added to natural gas, despite being in the order of magnitude of some mg/m^3, is not negligible if compared to the TLV of SO_2. More in detail, the minimum concentrations

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of TBM/IPM/NPM and THT in the distributed Italian gas are equal to 8 mg/m^3 (TBM/IPM/NPM) and 32 mg/m^3 (THT), corresponding to 2.3 ppm and 8.9 ppm, respectively.
These considerations highlight the reasons why, in recent years, the possibility to introduce alternative, sulphur-free odorants is being studied (Hennings and Reimert, 2007; Ruzsanyi et al., 2007).
This work describes the methodology adopted to analyse the olfactory properties of different gas odorants, with the aim of evaluating the possibility of introducing a new, sulphur-free gas odorant (Gasodor® S-Free) (Graf et al., 2007). For this purpose, the compliance with the current regulation on the matter, i.e. the Italian Norm UNI 7133:2012, was verified.
The proposed methodology involves a set of sensorial tests comparing the odorant S-Free with the two traditional odorants (TBM/IPM/NPM and THT) and with other “interfering” odours, in order to verify that the odour of the tested odorant is “characteristic”, thereby meaning that it shouldn’t be confused with other odours that might be perceived in a domestic environment in the case of an accidental gas leak.

2. Materials and methods

2.1 The Italian Norm UNI 7133:2012

The Italian Norm UNI 7133:2012 “Odorization of gas for domestic or similar uses” has the aim to fix the physical and chemical properties of odorants, their concentration and the ways for dosing and controlling them.
More in detail, Part 4 of the Norm “Definition of odorant requirements”, point 5.4 “Type of odour”, specifies that “the odour given to the gas by means of the odorant shall be characteristic, unpleasant and constant at any concentration in air.” The Norm indicates that this verification shall be performed by sensorial tests, using a panel of at least 4 examiners, who shall smell 3 odorant samples corresponding to 3 different concentrations, with the specific to assess that the odour may be defined as “characteristic”, or however “well identifiable” by the users.

2.2 Design of the experiment

In order to verify the compliance of the Gasodor® S-Free (S-Free) odorant to the Norm, it was decided to set up a test procedure aiming to verify that the odour of the odorant is “characteristic”, thereby meaning that it shouldn’t be confused with other odours that might commonly be perceived in a domestic environment, in the case of an accidental gas leak.
For this purpose, a set of tests were run in order to compare the olfactory properties of the new odorant with respect to the traditional odorants (TBM/IPM/NPM and THT), and to other “interfering” odours, i.e. typical kitchen odours and other domestic odours.
A first phase of the study involved the use of an electronic nose, whose functioning is based on the principle that similar odours generate similar olfactory patterns, and vice versa. These preliminary tests highlighted that the three odorants (including the S-Free) are recognized as similar to each other, and that they are effectively discriminated from the interfering odours tested.
The second phase of the study, which is described more in detail in this paper, was based on sensorial tests, which involved a suitable number of examiners and the elaboration of their responses by statistical analysis. In this case the 3 odorants were compared to each other and to interfering odours. The interfering kitchen odours were onion and fish odours, which in the first phase of the study by means of electronic noses turned out to be the odours, among the ones being tested, to be closest, and therefore most similar, to the gas odorants. Other odours tested were an acrylic varnish and a sulphur compound, which, due to their chemical nature, might present some similarity to the S-Free the first, and to the sulphur-based traditional odorants the latter. Moreover, some samples of natural gas (pure and diluted) were tested, in order to compare the olfactory properties of odorized gas to those of non-odorized gas.

2.3 Tested odours

Three gas odorants were tested: the S- Free, and the traditional odorants TBM/IPM/NPM and THT (Table 1). The odorants were provided in bottles, having the same concentrations at which they are normally distributed, i.e. 8 mg/m^3 for the TBM/IPM/NPM and 32 mg/m^3 for the THT. The concentration of the S-Free bottle was chosen in order to represent a possible distribution concentration, i.e. 27 mg/m^3. Samples were prepared by filling Nalophan^{TM} bags (Capelli et al., 2013) directly from the bottles. The samples were analysed by dynamic olfactometry in order to determine their odour concentration. Dynamic olfactometry is a sensorial technique (standardized by the European Norm EN 13725:32003) that allows the determination of odour concentration, expressed in odour units per cubic metre (ou$_E$/m^3), which represents the number of dilutions with neutral air required in order to bring an odorous sample to its odour threshold concentration.

Table 1: Composition of the 3 gas odorants

Odorant	Components	Formula	%	PM (g/mol)
S-Free	Methylmetacrylate	$C_5H_8O_2$	80	100
	Ethylacrylate	$C_5H_8O_2$	20	
TBM/IPM/NPM	Terbutyl mercaptan	$C_4H_{10}S$	75	86
	Isopropyl mercaptan	C_3H_8S	16	
	Normalpropyl mercaptan	C_3H_8S	9	
THT	Tetrahydrotiophene	C_4H_8S	100	88

The determination of the odour concentration of the odorant samples is necessary in order to verify that a dilution 1:100 of the distribution concentration, which is conventionally assumed to be the concentration that may be perceived inside a domestic environment (alarm concentration defined by the UNI 7133:2012 – 2), is suitable for sensorial analysis, i.e. sufficient in order to allow the examiners to express a qualitative judgment on the perceived odour.
As far as the interfering odours samples are concerned, they were all obtained using the headspace technique, by inserting the chosen odorant inside a 6 L Nalophan^{TM} sampling bag, and then by filling the bag with neutral air. Fish odour was simulated using trimethylammine (TMA). "Varnish" odour was obtained using an acrylic water varnish produced by MisterColor S.p.A. (safety sheet: http://www.mistercolor.it/media/upl/85_smalto-lucido-ecolabel.pdf), and the tested sulphur compound was Dimethyldisulphide (DMDS). Also these samples were analysed by dynamic olfactometry in order to evaluate the necessity of diluting them as to obtain samples having comparable odour concentrations, suitable for sensorial analysis. Non-odorized gas was obtained from a natural gas bottle. It is important to highlight that the natural gas bottle doesn't contain 100% pure methane, but natural gas containing small and not identifiable quantities of impurities, which make the gas not completely odourless. Natural gas samples were prepared both pure and diluted (1:100), in analogy with the odorant samples. The detail of all the samples used, their preparation, dilution and final odour concentration are reported in Table 2.

Table 2: Sample preparation and odour concentration

Odour	Origin	Dilution ratio	c_{od} (ou/m^3)
TBM/IPM/NPM	Bottle 8 mg/m^3	1:128	1400
THT	Bottle 32 mg/m^3	1:64	720
S-Free	Bottle 27 mg/m^3	1:128	1200
Fish	0.5 µl TMA in 6 L air	1:1	1100
Varnish	150 cm^2 of paper immersed in acrylic varnish in 6 L air	1:4	850
Onion	1 peeled and cut onion in 6 L air	1:4	825
DMDS	0.5 µl DMDS in 6 L air	1:1	n.d.
NG (pure)	Natural gas bottle	1:1	n.d.
NG (diluted)	Natural gas bottle	1:64	n.d.

2.4 Method for the evaluation of odour quality

In order to evaluate odour quality, a sensorial test method based on the use of "descriptors" (e.g., Suffet et al., 2004; VDI, 1994) was specifically designed. This method requires the identification of a reduced set of qualitative descriptors that allows to characterize the quality of the tested odours.
The principle of the test method is to ask the examiners to attribute a numeric value comprised between 0 and 6 to each descriptors, using a similar scale to the one used for the evaluation of odour intensity (VDI 1992); where 0 corresponds to an intensity level of "non-perceptible" and 6 to "extremely strong".
In this specific case, seven descriptors were identified in order to characterize the odour quality: 1) strong/intense, 2) unpleasant, 3) sulphuric, 4) pungent/irritating, 5) chemical, 6) rancid/mouldy 7) sweet/sweetish. Once a value between 0 and 6 is attributed to each of the 7 descriptors, the arithmetic means of the responses of the examiners can be visualized on "radar" graphs that allow to realize an

"olfactory pattern" for each of the odours tested. The olfactory patterns may then be compared by means of specific techniques of multivariate statistical analysis, e.g. Principal Component Analysis (PCA) (Pardo et al., 2000; Sironi et al., 2007).

Besides using the descriptors, the examiners were also asked to describe the odour character with own words, and whether the perceived odour could be associated with gas odour.

The tests for the evaluation of the S-Free odour quality at different concentrations involved the analysis of 5 S-Free samples at 5 different concentrations by 20 expert examiners, selected according to the criteria of the European Norm on dynamic olfactometry EN 13725:2003. The 5 concentrations to be tested were chosen around the reference dilution of 1:100 of the distribution concentration (Table 3).

Table 3: Concentrations of the tested S-Free samples

Dilution ratio	Concentration (μg/m^3)	Concentration (ppb)
1:512	53	13
1:256	110	27
1:128	210	51
1:64	420	103
1:32	840	206

The tests for the comparative evaluation of the odour quality relevant to odorants, interfering odours and non-odorized gas, given the higher subjectivity associated with this kind of evaluation, required the use of a larger panel, in this case consisting of 120 examiners, both "experts", i.e. selected according to the EN 13725:2003 (38 out of 120 examiners), and non-experts (82 out of 120 examiners), aging from 20 to 75.

3. Results and discussion

3.1 Evaluation of the olfactory quality of the S-Free odorant at different concentrations

The arithmetic means of the panel responses for each descriptor were reported in a radar graph (Figure 1a).

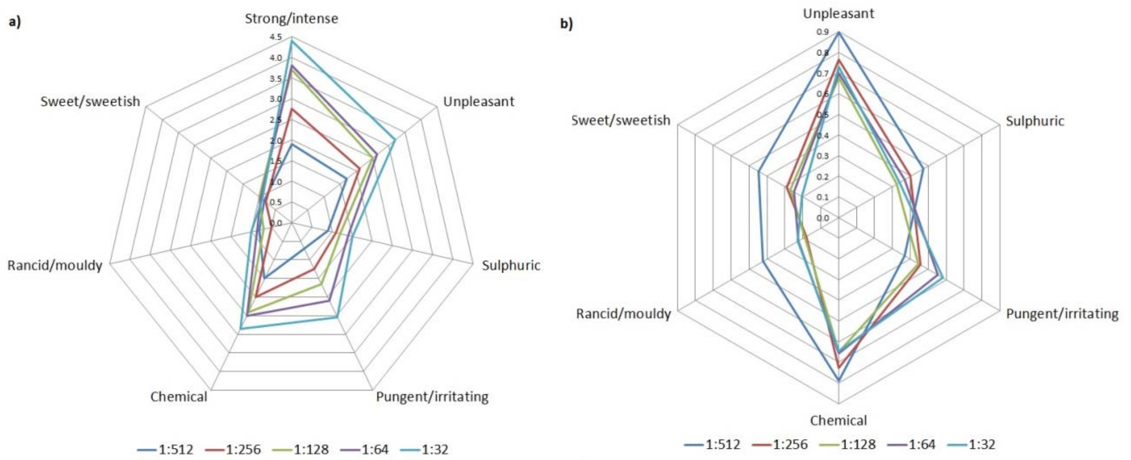

Figure 1: a) Radar graph without normalization, b) normalized radar graph

The shapes of the different curves turned out to be similar, thus proving that the odour quality is similar for all the concentrations tested.

It is possible to give a better representation of the results by normalizing them with respect to the odour intensity, i.e. by dividing the results relevant to each descriptor by the value attributed to the intensity descriptor. Based on the normalized radar graphs (Figure 1b) obtained by representing the results of the evaluations of the 20 assessors interviewed, it is possible to observe that the curves relevant to the S-Free samples at the different concentrations tested do almost overlap, thus proving that the odour properties of the odorant are not altered by its dilution in air.

3.2 Comparative evaluation of the olfactory quality of gas odorants, interfering odours, and non-odorized gas

Also in this case, the results of the tests were processed by calculating the arithmetic means of the values between 0 and 6 attributed to the descriptors by the 120 examiners, and then reporting them in two radar graphs: one non-normalized (Figure 2a), and the second one normalized with respect to odour intensity (Figure 2b).

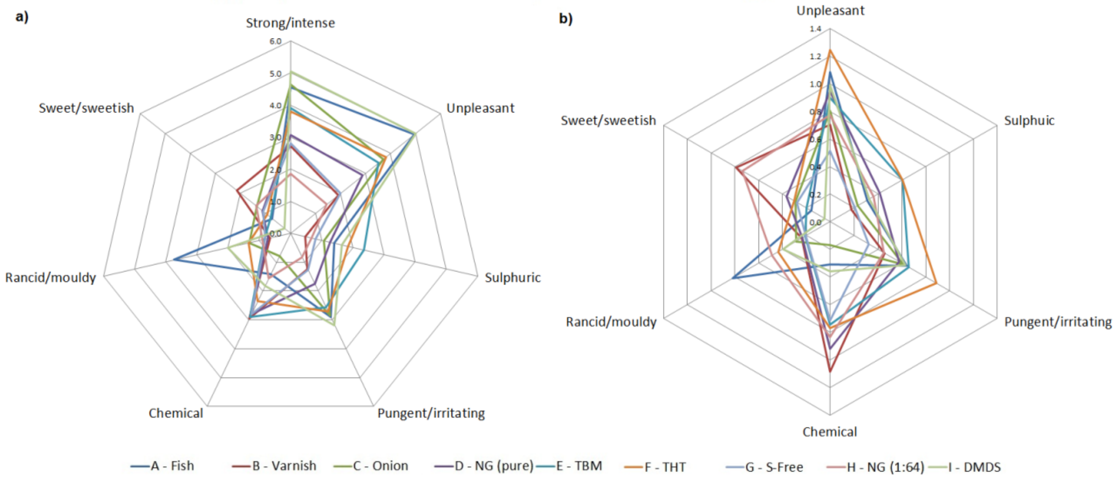

Figure 2: a) Radar graph without normalization, b) normalized radar graph

As expected, due to the higher number of samples tested (9 instead of 5) and to their different qualities, the radar graphs are hardly interpretable. Nonetheless, some interesting considerations can be done.

The sample of diluted (1:64) non-odorized natural gas presents mean values relevant to the different descriptors that are significantly lower with respect to the other samples. This result proves that if the natural gas is not artificially odorized, it is almost odourless. This is also confirmed by the fact that over 16% of the interviewed assessors answered negatively to the question "do you perceive any odour?" in the tested sample. Another important result concerns the low percentage of assessors, equal to 9%, which have answered positively to the question asking if the odour of the non-odorized natural gas could be associated to the odour of kitchen gas.

The non-diluted non-odorized natural gas is, as expected, more odorous than the diluted natural gas. The odour of natural gas is due to the presence of low quantities of impurities that are hardly identifiable or reproducible, giving that, without artificial odorization, natural gas odour wouldn't be recognizable in case of accidental leaks. This result is supported by the percentage of assessors that answered positively to the question relevant to the associability of the pure natural gas odour to the kitchen gas odour, which turned out to be just 35%.

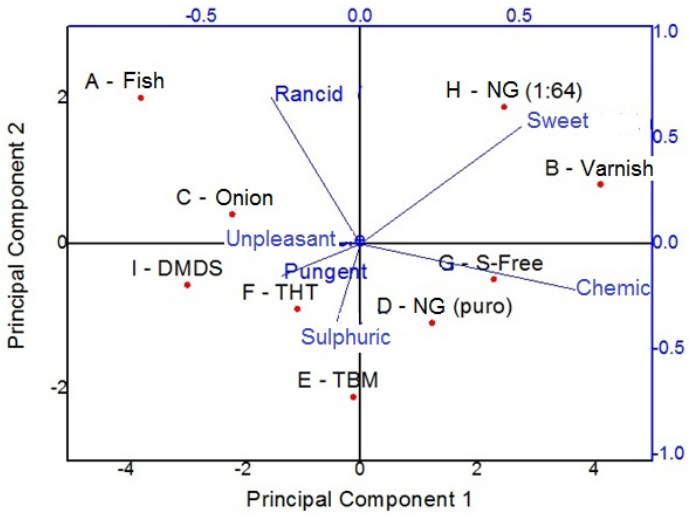

Figure 3: PCA of the mean values attributed to the descriptors normalized by the odour intensity

This proves that what people tend to recognize as gas odour is not the odour of the gas itself, but rather the odour of the odorant, and more specifically the odour of the odorant they are used to. This consideration is clearly supported by the answers obtained to the question regarding the associability to the kitchen gas odour relevant to the odorants samples. For instance, considering only the answers of the assessors living in the municipalities where the odorant TBM/IPM/NPM is distributed (108 out of the 120 assessors interviewed), a very interesting result is observed: 83% stated that the odour of the TBM/IPM/NPM could be associated to the kitchen gas odour, whereas this percentage decreases dramatically to 44% if referred to the odour of THT.

Finally, the PCA obtained from the results of the tests for the evaluation of the olfactory quality of odorants, interfering odours and non-odorized gas (Figure 3) clearly shows that the proximity of the points relevant to the 3 odorants indicates a similarity of their odours. This similarity is highlighted by the position of the points relevant to the interfering odours, especially the “domestic” ones of fish and onion, which are located totally elsewhere. More in detail, the point relevant to the S-Free is located close to the other odorants and to the pure natural gas, and far from the points relevant to the considered interfering odours, thereby including the point relevant to the varnish odour, which, due to its chemical nature, should have a greater similarity to the S-free odorant.

4. Conclusions

This study evaluates the possibility of introducing a new, sulphur-free gas odorant (Gasodor® S-Free), by evaluating its olfactory properties, which are fundamental for its safety use. The discussed results prove that the S-Free odour can be defined as “characteristic”, meaning that it is not confused with other interfering odours, and unpleasant. Both these attributes are important in order to guarantee that people associate the odour of the odorant to a danger situation, and thereby to avoid incidents or explosions due to accidental gas leaks.

Moreover, this study points out the effectiveness of the proposed methodology, which is based on sensorial tests involving the use of qualitative descriptors and an appropriate panel selection for the qualitative evaluation of the olfactory properties of gas odorants.

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