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Toward an Objective Odor Characterization of Compounds Emitted in Industrial Zones: the "Langage Des Nez®" as an Efficient Tool

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When studying odour nuisance, sensory analyses show many advantages making these approaches essential along with chemical analyses. However, sensory analyses face the problem of subjectivity related to the panel. This subjectivity, even if it may be cured when assessing the odour intensity, is still an obstacle when describing the odour profile. One method offers a solution: The Langage des Nez®. This is an approach that uses definite chemical referents as odour descriptors. The aim of this work is to experiment the efficiency of this method when analysing the odour of incidentally emitted compounds in industrial zones.
The odour of 44 chemical compound that can be released incidentally in the industrial zone of the city of Le Havre, France, was described using the Langage des Nez®. A trained panel was asked to describe the odour of each compound using one, two or three referents from the Langage des Nez® and attributing a score over 9 for the chosen referents as a degree of representativity. Based on the frequency of citation of each referent and the attributed scores, one two or three referents were chosen as odour descriptors. The obtained results reveal that no correlation can be clearly established between the chemical structure of the compound and its odour descriptor(s). The difference between odour profiles obtained using conventional methods from the literature and the ones using Langage des Nez® revealed that the later offers a more objective and precise lexicon. This work shows that the sensory approaches are indispensable when assessing odour nuisance. The use of Langage des Nez® upgrades these analyses to an objective and reliable tool to anticipate potentially emitted odours during industrial incidents in any industrial city.

1. Introduction

Odour annoyance is the leading cause of complaints regarding environmental issues (Hayes et al., 2014). Surrounding population of industrial areas, landfills, waste management sites, water treatment plants, livestock farming, etc. may be exposed to odorous compounds and subsequently to odours. Odour annoyance may imply several negative impacts on health and economy (Blanes-Vidal et al., 2012).
Odour annoyance can be defined as a mismatch between the odorous reality and the expectations. It is the result of several factors linked to the odour itself, the context and the impacted populations (Jaubert, 2010).When studying odour nuisance, five factors are usually considered: Frequency, Intensity, Duration, Odour offensiveness (hedonic tone) and Location. They are known as the FIDOL factors(Nicell, 2009). Since the description of the odour's nature often results in non-consensual information due to its high degree of subjectivity, This approach prefers taking into account the hedonic tone of odour avoiding non-consensual characterization coming from the high degree of subjectivity of the assessment of the odour quality.
Odours are mainly caused by the interaction of the olfactory system with volatile organic compounds (VOCs). Therefore, when studying odour impact, two approaches may be used: physico-chemical analyses and/or olfactory analyses. Physico-chemical approaches may be used to identify the potentially odorous compounds and quantify their respective concentrations (Zhu et al., 2016). It is thus supposed to provide more reliable and

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objective results than using conventional olfactory analyses with human panels. However, chemical analyses do not give sensory information besides several obstacles may be encountered e.g. odour perception threshold below the detection limit of the instrument or the reactivity of the odorants in the atmosphere. Thus, olfactory analyses are still a preferred solution. They allow the quantification (by assessing intensity and odor concentration) and qualification of perceptions by using a human panel (Sucker et al., 2008). Sensory analyses may offer a simpler, cheaper and more sensitive approach.

Having mentioned that, it should not be forgotten to mention that olfactory analyses still lead to subjectivity and non-repeatability issues. This may be due to the difference of odour perception and sensitivity toward some odorous compounds from a person to another. Intensity assessment can be objectified by the use of an odour intensity reference scale (OIRS) (Henry et al., 2011) and panel selection (EN13725, 2003). Odour nature description methods still rely on conventional and obsolete methodologies that use descriptors based on evocations (e.g. lemony, oily, musty, etc.) (Fisher et al., 2018). These methods are considered subjective because the descriptors used may vary from a person to another due to the intervention of emotions, behaviour and other past experiences when conveying sensorial information on a certain odour (Jaubert, 1990). A method called, “The Field of Odours” was developed to assess the odour quality limiting subjectivity and improving repeatability and agreement within a trained panel (Jaubert et al., 1995). It was used to survey odour quality in the Normandy region by a web of assessors deployed all over the area(Leger, 2016).

The aim of this work is to experiment this methodology and characterize its performance to describe objectively the odour quality of several volatile compounds from industrial origin that can be released incidentally and may cause odour annoyance in order to anticipate them. The context of the city of Le Havre was chosen as a model to apply this new and objective odour monitoring method. The city of Le Havre in France has an active industry (and a large harbour. The city has known odorous emissions from different industrial plants (Quéré et al., 1994) and underwent several odorous incidents. Over the years, many campaigns were organized in order to characterize the air odour quality in the city.

2. Material and methods

2.1 Selection of 44 compounds potentially emitted in the Le Havre industrial zone

A list of 68 stocked compounds, reaction by-products and previously released by incident compounds was acquired from the industrials thanks to “*France Chimie en Normandie”* and “*Atmo Normandie”*, respectively the professional organization dedicated to the Chemical companies and the air quality monitoring network in Normandy, France.

Table 1: List and characteristics of the 44 selected odorous compounds: mass concentration in triacetin (in w/w %) and evocative odour description from the literature(NIOSH, 2010; Ruth, 1986).

Odorant	w/w%	Evocation description	Odorant	w/w%	Evocation description
1,2-dimethylaniline	2	Amine	Diphenylamine	100	Pleasant, floral
1-butanethiol	2×10^{-4}	Cabbage, sulphurous	Ethylbenzene	1	Aromatic
1-pentanol	1	Sweet, alcohol	Heptane	15	Essence
1-propanol	20	Alcohol like	Hexone	1	Pleasant
2,2'-iminodiethanol	100	Ammonia	Indene	0.25	Glue, mothballs
2-butanol	5	Pleasant	Isopropyl acetate	5	Fruity
2-diethylaminoethanol	1	Amine	Isopropylamine	1	Acrid, ammonia
4-methylpentane-2-ol	0.5	Sweet, sweat	Methyl acrylate	0.05	Acrid
Acetic anhydride	10	Acid, sharp	Mesitylene	1	Aromatic
Acrylic acid	1	Rancid, sweet	Methyl methacrylate	0.5	Arid, fruity, sulfidic
Butylamine	1	Ammonia	Methyl tert-butyl ether	1	Terpene like
Caprolactam	100	Unpleasant	Morpholine	0.5	Ammonia
Chlorobenzene	1	Almonds, sweet	m-Xylene	1	Sweet, aromatic
Cyclohexanol	0.5	Camphor	n-butyl acetate	0.5	Fruity
Cyclohexene	0.5	Sweet	n-butyl acrylate	0.5	Musty
Diethyl ether	1	Sweet, acrid	Nitromethane	100	Sweet, fruity
Diethylamine	0.5	Fishy, ammonia	o-Dichlorobenzene	1	Aromatic, pleasing
Diisopropylamine	0.5	Fishy, amine	o-Xylene	1	Aromatic
Diisopropyle ether	1	Sharp, sweet, ether	Phosphorus pentasulphide	0.005	Rotten egg
Dimethyl sulphide	0.01	Cooked cabbage	p-Xylene	1	Sweet, aromatic
Dimethylamine	0.5	Fishy, ammonia	Pyridine	0.5	Fishy
Diphenyl ether	1	Geranium like	Triethylamine	0.25	Ammonia

From this list were removed carcinogenic, mutagenic or toxic to reproduction compounds (CMR) based on The French National Research and Safety Institute (INRS) data. Considering these requirements, 44 compounds were studied; they are named “odorants” within this paper (Table 1).

2.2 The Langage des Nez® (LdN)

The Langage des Nez® is a sensory method that uses a well-defined collection of chemical odorants as referents to describe an odour quality (Figure 1).

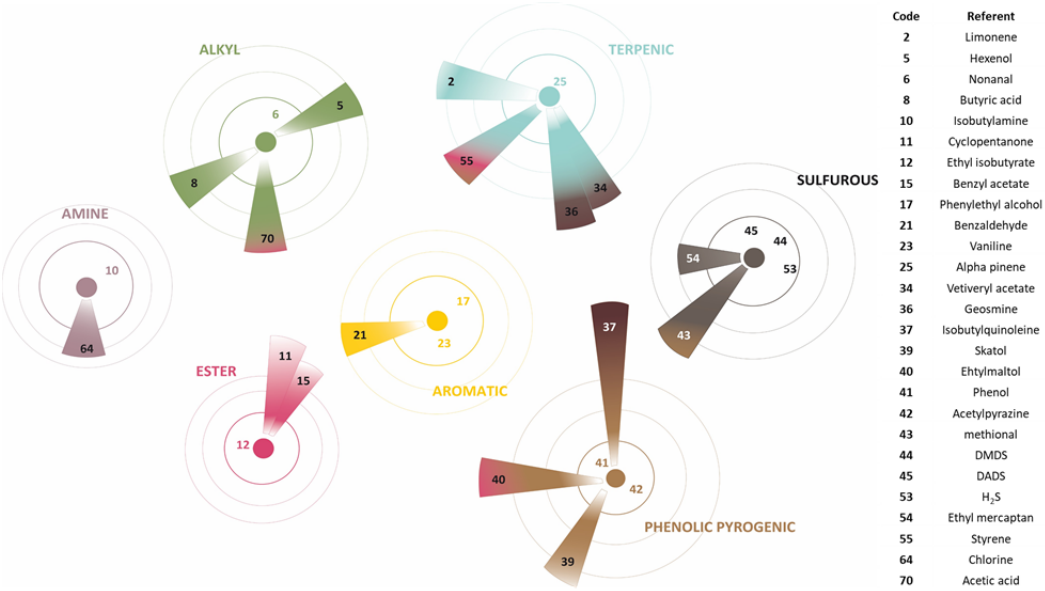

Figure 1: the Langage des Nez® basic collection, made up of 27 odour referents located in a space around nucleus with marked odour characteristics (DMDS: dimethyl disulphide, DADS: diallyl disulphide).

The 27 referents constitute a basic collection distributed in seven poles based on their similarities (Figure 1). Each referent corresponds to a chemical compound, diluted into an inodorous solvent at a concentration inducing a medium intensity odour i.e. an odour that can be perceived under a natural breathing without sniffing. The 7 poles are: terpenic, alkyl like, esteric, amine like, phenolic/pyrogenic, sulphurous and aromatic. Referents close to the nuclei are considered representatives of the pole. The further the referent from the pole, the less similar it is (Figure 1).
LdN® requires a specially trained panel that memorizes the odour of each referent. When characterizing an “unknown” odour, the panel describes the scented odour by comparing it to the less different referent in terms of odour nature. This approach is supposed to provide objective and repeatable results over time and assessors.

2.3 Olfactory test sessions

Odorants to be characterized, selected for this study, listed in Table 1, were prepared in triacetin (glycerine triacetate, Alfa Aesar, 98%) an odourless solvent from commercial standards provided with the highest purity available. Only heptane was prepared in isohexadecane for solubility reasons (isohexadecane is odourless). The concentrations (in w/w %) were adapted so that the odorant may have a similar medium intensity to the referents Table 1. In each analysis session, the odour was evaluated, using odourless sniffing paper sticks. For each evaluation, the paper stick is dipped on 1 cm in the solution, and used immediately.
The jury consisted in 67 panellists (40 women and 27 men) aged from 22 to 82. They were students, residents from Le Havre (France) and employees from the surrounding industrial sites. All assessors were well trained to use the LdN® method.
Olfactory test sessions are organized in two phases of analysis:

- Phase 1- First analysis: the odorants are scented and described using the LdN® by a minimum of 18 assessors.

Panellists were demanded to choose within the referents of the basic collection of LdN® one, two or three referent(s) to describe the odour of the selected compound. For each referent chosen, a value is given, ranking over 9, according to its degree of representativity relative to this unknown odour. The sum of the

values given in case of using two or three referents must be 9. In case of choosing one referent, the score will automatically 9. The scale was chosen in order to force the panellists to choose the more representative referent and to avoid the choice of two equal referents.

- Phase 2- If conditions of consensus, detailed in part 2.6, were not matched, the olfactory analysis was remade. Based on the results of the first phase, and for each odorant, referents having a total relative contribution (Eq 2- detailed in part 2.6) greater than 10% where chosen as phase 2 descriptors. This limited the choice of descriptors for the assessors. Odorants that needed a phase 2 analysis, had their odours described using the list of limited descriptors.

2.4 Data Analysis

Two metrics were taken into consideration: the frequency of citation of a referent and the value given to it. For each tested odorant and each referent cited was calculated (i) the frequency of citation *f* and (ii) the total relative contribution N_{ic} as:

$$f = \frac{number\ of\ times\ the\ referent\ was\ cited}{number\ of\ panelists} \times 100 \quad \text{(Eq1)}$$

and $$N_{ic} = \frac{\sum values\ given\ to\ a\ reference\ i}{\sum all\ the\ values\ given\ for\ all\ references} \times 100 \quad \text{(Eq 2)}$$

For each odorant, one to three referents had to have a frequency of citation greater than 30% and a N_{ic} ≤10% to consider that a consensus was obtained. These referents are selected as odour descriptors. If not, the odorant was reanalysed in the phase 2.

After the odour referents get selected, an odour score, OS_i, is calculated for each referent, based on the following equation:

$$OS_i = \frac{N_{ic,i}}{\sum N_{ic}\ of\ chosen\ referents} \times 9 \quad \text{(Eq 3)}$$

3. Results and discussion

3.1 Panel's consensus

Around 80 % of odorants did not have to get a phase 2 analysis. This shows a good consensus of the panel. Phase 2 analysis concerned the following odorants: o-dichlorobenzene, 1-butanethiol, methyl isobutyl ketone, caprolactam, cyclohexene, methyl tert-butyl ether, phenyl ether, o-xylene and dimethyl sulphide. This is not linked to a specific chemical category, but it was observed that the bad quality of consensus is often due to the scattering of responses from assessors within close referents from a same pole e.g. methyl isobutyl ketone was described by assessors using styrene (f=39%, Nic=19%), cyclopentanone (f=39%, Nic=16%), ethyl isobutyrate (f=50%, Nic=24%) and benzyl acetate (f=50%, Nic=21%) with three of them close referents from the "ester pole".

3.2 Olfactory analysis results

Table 2 gathers the odour description for the 44 odorants considered in this study: it gives the cited referents, the OS_i over 9 calculated from Equation 3 and the number of assessors who participated to the analysis

For 16 of the 44 targeted odorants, they are described using only one referent. Among them, we mainly found amines (2-diethylaminoethanol, diethylamine, diisopropylamine, isopropylamine, morpholine and triethylamine) which are effectively described by the amine-like odour referent which is "Isobutylamine". However, 2,2'-iminodiethanol and diphenylamine which also are characterized by an amine function are described by a distant referent, respectively "Acetylpyrazine" and "Limonene".

For 11 of the 44 targeted odorants, they are described by two referents. These referents could belong to the same pole, as it is the case for the odorant 4-methylpentane-2-ol described by the referents "Pinene" and "Vetiveryl acetate". Here the use of two close referents suggests the strict affiliation of this odorant to the terpenic pole and illustrating a specific note of this pole. On the contrary, a referent can be described by two distant referents as the odorant pyridine described by the referents "DADS" and "Isobutylmamine". In this case, two odorous facets are expressed and perceived by the human brain. The same type of observation can be done concerning dimethylamine. Moreover, in this group of odorants it can be noticed that the presence of an acrylate function (methyl acrylate, methyl methacrylate and butyl acrylate) is correlated with the referent "DADS" from the sulphurous pole. It is quite surprising taking into correlation the absence of sulphur atom in the structure of these molecules.

Finally, for 17 odorants of 44, they are described using three referents. For the main cases, these referents are coming from different poles and suggest an odour nature with several facets. In this group, it is interesting to compare the description of two odorants with close chemical structures: propanol and pentanol. For the first

one, it is described using referents from the aromatic and alkyl like poles; for the second one using referents from the pole esteric, terpenic and phenolic/pyrogenic. So, in spite of similar chemical structure, no odorous similarities can be noticed.
This analysis clearly exhibits the fact that no prediction can be done in terms of odour description considering its main chemical function or chemical similarities with another odorous compound.

Table 2: Odour analysis of the 44 selected compounds: cited referents using their codes (refer to figure 1), OS between brackets and number of assessors who participated to the analysis

Odorants	Panel	odour referents			Odorants	Panel	odour referents		
		1	2	3			1	2	3
1,2-Dimethylaniline	51	39(4)	41(3)	64(2)	Diphenylamine	21	2(6)	55(3)	
1-Butanethiol	20	45(9)			Ethylbenzene	34	55(9)		
1-Pentanol	50	8(5)	21(3)	6(1)	Heptane	25	55(3)	11(3)	15(3)
1-Propanol	18	11(5)	41(2)	55(2)	Hexone	20	12(5)	11(4)	
2,2'-Iminodiethanol	23	42(9)			Indene	18	55(9)		
2-Butanol	37	11(9)			Isopropyl acetate	32	11(6)	12(2)	55(1)
2-Diethylaminoethanol	32	10(9)			Isopropylamine	31	10(9)		
4-Methylpentane-2-ol	50	25(7)	34(2)		Mesitylene	40	36(5)	25(3)	55(1)
Acetic anhydride	49	70(9)			Methyl acrylate	49	45(7)	55(2)	
Acrylic acid	34	70(9)			Methyl metacrylate	47	45(5)	55(4)	
Butylamine	34	10(6)	6(3)		Methyl tert-butyl ether	20	25(3)	15(3)	11(3)
Caprolactam	20	21(4)	64(3)	11(2)	Morpholine	63	10(9)		
Chlorobenzene	56	55(5)	11(2)	21(2)	m-Xylene	35	55(9)		
Cyclohexanol	52	41(6)	55(2)	11(1)	n-Butyl acetate	51	15(7)	11(1)	12(1)
Cyclohexene	20	55(3)	11(3)	45(3)	n-Butyl acrylate	33	45(6)	15(3)	
Diethylamine	34	10(9)			Nitromethane	20	11(7)	12(2)	
Diethyle ether	47	11(5)	55(3)	15(1)	o-Dichlorobenzene	20	55(4)	21(3)	64(2)
Diisopropylamine	37	10(9)			o-Xylene	20	55(5)	25(4)	
Diisopropyle ether	33	55(4)	11(3)	12(2)	Phosphorus pentasulphide	34	53(9)		
Dimethyl Sulphide	20	44(5)	54(4)		p-Xylenes	50	55(4)	17(3)	41(2)
Dimethylamine	48	10(7)	42(2)		Pyridine	31	45(5)	10(4)	
Dephenylether	20	2(3)	6(3)	25(3)	Triethylamine	20	10(9)		

For each of the 44 odorants, evocations (as reported in the literature) are given in Table 1. The words used are usually not precise and ambiguous (as example "fruity" could refer to many odorants), subjective ("pleasant"). These evocations prove the key strengths of the LdN® method: (i) The LdN® method permits to highlight multifaceted odorants as methyl methacrylate, described in the literature as sharp, fruity and sweet (NIOSH, 2010) while the LdN® description evidences a sulphurous facet. (ii) The LdN® method provides differentiated description for 1,3,5-trimethylbenzene, ethylbenzene and o-xylene whereas they are usually gathered under the same descriptor “aromatic odour”. (iii) Finally hedonic description are avoided while they are usually reported in the literature, as for caprolactam (NIOSH, 2010). When comparing evocative lexicons reported by the literature and the description provided by this study, improvements are indisputable and will clearly help to interpret odour alerts.

4. Conclusion

This article presents a research study using an original methodology, the Langage des Nez®, to analyse environmental odours. In this work, 44 odorants that may be emitted incidentally in industrial cities had their odour nature described using this objective method based on chemical referents, which creates a lexicon that does not change from an assessor to another. This characterization showed that it was independent of the chemical structure and thus displays the sensory analysis as an essential analysis along with chemical approaches. This will definitely help to provide a rapid alert of authorities in charge of industrial risk assessment, thanks to suitably-located trained residents and almost real-time monitoring, an alert system that cannot be obtained from more classical physico-chemical analysis systems. This work may be done in other cities that may be exposed to the risk of odorous incidents in order to anticipate them or have an idea of the

odorants in case of similar incidents. The objective analysis of odorants is an essential step regarding environmental issues to a monitoring over time and the assessment of the impact of corrective actions.

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References

Blanes-Vidal, V., Suh, H., Nadimi, E.S., Løfstrøm, P., Ellermann, T., Andersen, H.V., Schwartz, J., 2012. Residential exposure to outdoor air pollution from livestock operations and perceived annoyance among citizens. Environment International 40, 44–50. https://doi.org/10.1016/j.envint.2011.11.010.

EN13725, 2003. EN13725, Air quality—Determination of odour concentration by dynamic olfactometry.

Fisher, R.M., Barczak, R.J., Suffet, I.H. "Mel," Hayes, J.E., Stuetz, R.M., 2018. Framework for the use of odour wheels to manage odours throughout wastewater biosolids processing. Science of The Total Environment 634, 214–223. https://doi.org/10.1016/j.scitotenv.2018.03.352.

Hayes, J.E., Stevenson, R.J., Stuetz, R.M., 2014. The impact of malodour on communities: A review of assessment techniques. Science of The Total Environment 500–501, 395–407. https://doi.org/10.1016/j.scitotenv.2014.09.003.

Henry, C.G., Schulte, D.D., Hoff, S.J., Jacobson, L.D., Parkhurst, A.M., 2011. Comparison of Ambient Odor Assessment Techniques in a Controlled Environment. Transactions of the ASABE 54, 865–1872.

Jaubert, j, 2010. La gêne olfactive : composantes – moyens d'appréciation. Pollution Atmosphérique. https://doi.org/10.4267/pollution-atmospherique.91.

Jaubert, J.N., 1990. Des éléments de la construction de notre référentiel olfactif. Parfums, cosmétiques, arômes 87–94.

Jaubert, J.-N., Tapiero, C., Dore, J.-C., 1995. The field of odors: toward a universal language for odor relationships. Perfumer & flavorist 20, 1–16.

Leger, C., 2016. Odour pollution tracking : the interest to use a framework and to set up olfactory signatures. The experience of Air Normand, air quality monitoring in UpperNormandy. Presented at the Atmos'Fair, Paris, France.

Nicell, J.A., 2009. Assessment and regulation of odour impacts. Atmospheric Environment 43, 196–206. https://doi.org/10.1016/j.atmosenv.2008.09.033.

NIOSH, 2010. NIOSH Pocket Guide to Chemical Hazards. Department of Health & Human Services, Centers for Disease Control & Prevention. National Institute for Occupational Safety & Health. DHHS (NIOSH).

Quéré, S., Perrin, M.L., Huchet, N., Delmas, V., Ledenvic, P., 1994. Odour Annoyance in Industrial Zones of the River Seine Estuary, in: Studies in Environmental Science. Elsevier, pp. 127–136. https://doi.org/10.1016/S0166-1116(08)72049-1.

Ruth, J.H., 1986. Odor Thresholds and Irritation Levels of Several Chemical Substances: A Review. American Industrial Hygiene Association Journal 47, A-142-A-151. https://doi.org/10.1080/15298668691389595.

Sucker, K., Both, R., Bischoff, M., Guski, R., Winneke, G., 2008. Odor frequency and odor annoyance. Part I: assessment of frequency, intensity and hedonic tone of environmental odors in the field. International Archives of Occupational and Environmental Health 81, 671–682. https://doi.org/10.1007/s00420-007-0259-z.

Zhu, Y., Zheng, G., Gao, D., Chen, T., Wu, F., Niu, M., Zou, K., 2016. Odor composition analysis and odor indicator selection during sewage sludge composting. Journal of the Air & Waste Management Association 66, 930–940. https://doi.org/10.1080/10962247.2016.1188865.