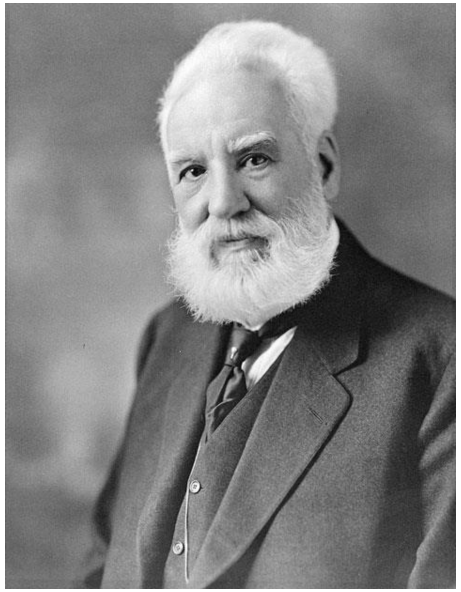
Methods for the measurement of environmental odours: state of the art and open challenges

Ing. Marzio Invernizzi

“Did you ever try to measure a smell? Can you tell whether one smell is just twice as strong as another. Can you measure the difference between one kind of smell and another. It is very obvious that we have very many different kinds of smells, all the way from the odor of violets and roses up to asafetida. But until you can measure their likenesses and differences you can have no science of odor. **If you are ambitious to found a new science, measure a smell.**”



Alexander Graham Bell, 1914

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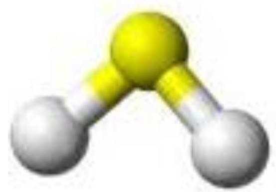
To recall: some definitions

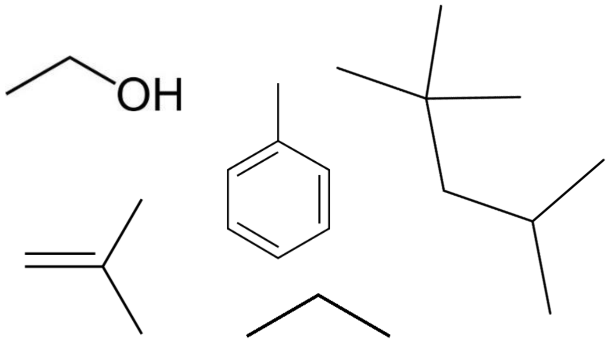
Odour: sensation perceived by means of the olfactory organ in sniffing certain volatile substances [SOURCE: EN ISO 5492:2009, 3.18]

odour does not coincide with the odorant that produces it, nor is it an intrinsic characteristic of molecules, but rather corresponds to the sensation that the substance causes after being interpreted by the olfactory system.



Odorant: substance which, when volatilised in neutral gas, has the potential to stimulate the human olfactory system so that an odour is perceived

Odorant gas: gas that contains one or more odorants



Odour nuisance scheme (van Harreveld 2001)

Odorant formation process → Transfer to air → Release to atmosphere → Dispersion

↓

Exposure
- Frequency of exposure
- Duration of exposure
- Intensity of exposure
- Quality od the odour

→ **Detection and perception**
- Time of day/activity
- Context
- Relation to source
- Association with odour

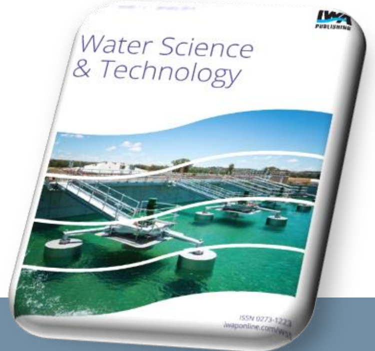
→ **Appraisal by receptor**
- Receptor characteristics perception of individual health

→ **Annoyance**
- Receptor characteristics:
- Coping strategy
- Attitude to 'status quo'
- Relation to source (economic)

↓

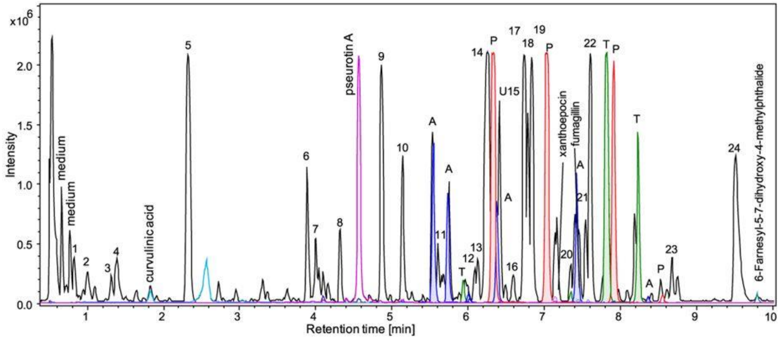
Nuisance
- Access to complaint channel
- Expected result of complaint
- Access to legal instruments

→ **Complaint action**



Why it is difficult to measure odour nuisance? (even 100 y later)

Chemical analysis is rarely a completely resolutive tool for odour analysis: the smell, in fact, is a **psychometric stimulus** that resides in the nervous system of the person who smells, **not strictly linked to the chemical** composition of the odorant mixture



Composto	CAS	mg/ m3
Methanethiol	74-93-1	0.16
Ethanol	64-17-5	9.22
Acetone	67-64-1	0.52
Dimethyl sulfide	75-18-3	0.05
2-Butanone	78-93-3	1.34
2-Butanol	78-92-2	0.38
o-Cymene	527-84-4	10.59
D-Limonene	5989-27-5	24.64
γ-Terpinene	99-85-4	0.41
Tetradecane	629-59-4	1.44

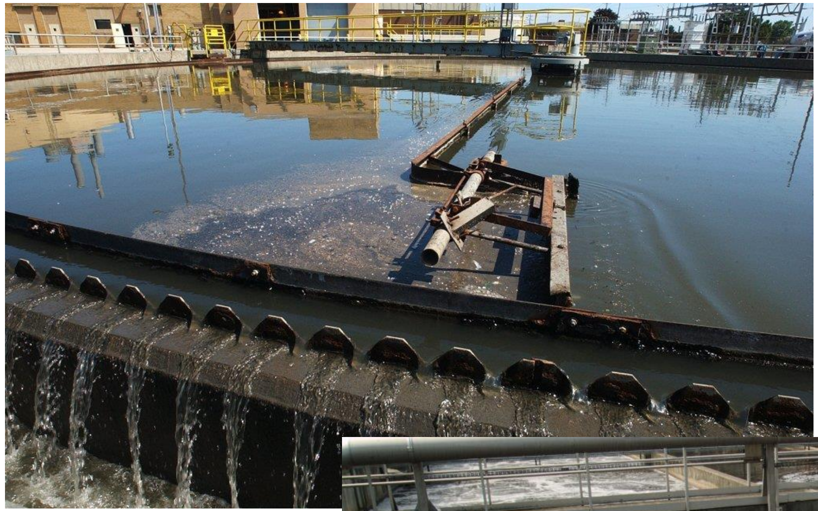
Odour = f (Chem conc)

?

“sensation of the olfactory organ”

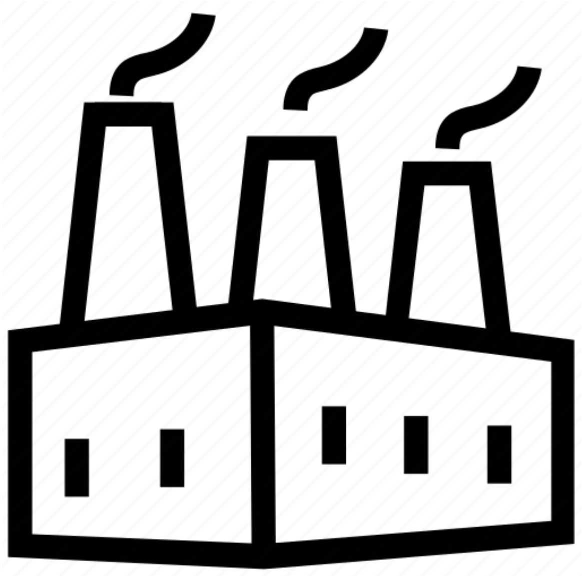
Why it is difficult to measure odour nuisance? (even 100 y later)

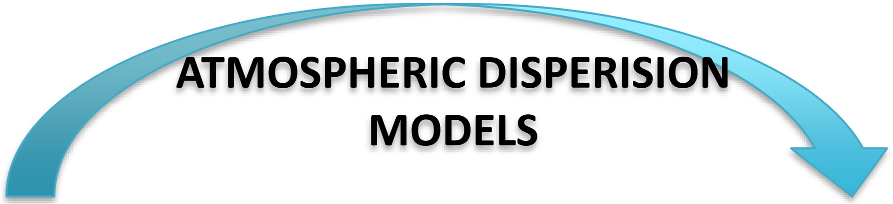
Odorous emissions often come from **sources** that we could define as **complex**, whose quantification is not trivial. Example of complex sources are diffuse emission from a wastewater treatment basins, piles or storage tanks.



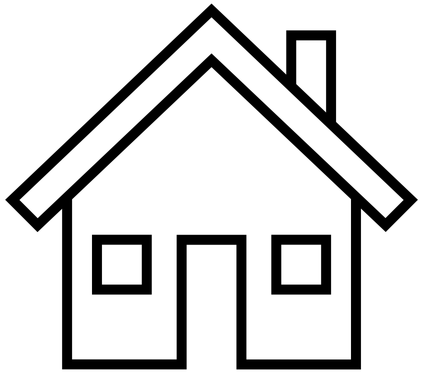
Why it is difficult to measure odour nuisance? (even 100 y later)

Olfactory impact is different from those of macro-pollutants because the impact is quantifiable as “***How much the receptor perceives***”, **not “*What does the plant emit*”.**





Model ≠ reality



Olfactory impact assessment approaches

Humans

- Dynamic Olfactometry (EN 13725)
- Field Inspection (EN 16841)
- Citizen reports

Tools

- Chemical analysis with single compound qualification
- Non-specific chemical analysis
- Single gas analysis (i.e. H_2S, NH_3)
- IOMS

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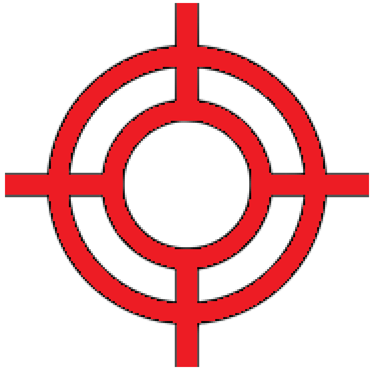
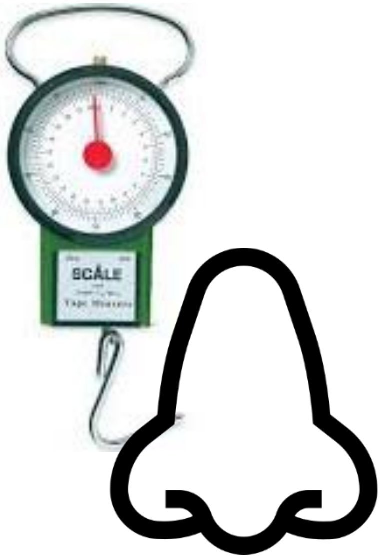
Dynamic Olfactometry (EN 13725)

It is a <u>sensory technique</u>, which uses a dilution instrument (olfactometer) to present an odorant gas, at different concentration levels, in a controlled manner to a group of selected evaluators.

Dynamic olfactometry makes it possible to determine the <u>odour concentration</u> of an odorous air sample relative to the sensation caused by the sample directly on a panel of suitably selected people.



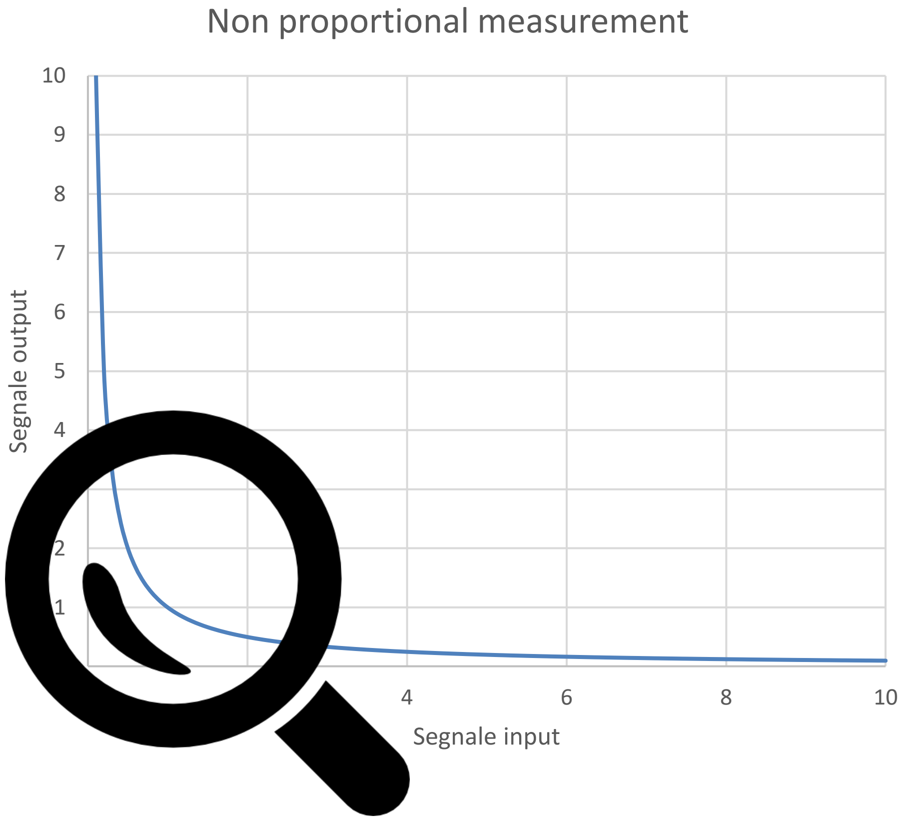
ENDPOINT SOLUTION

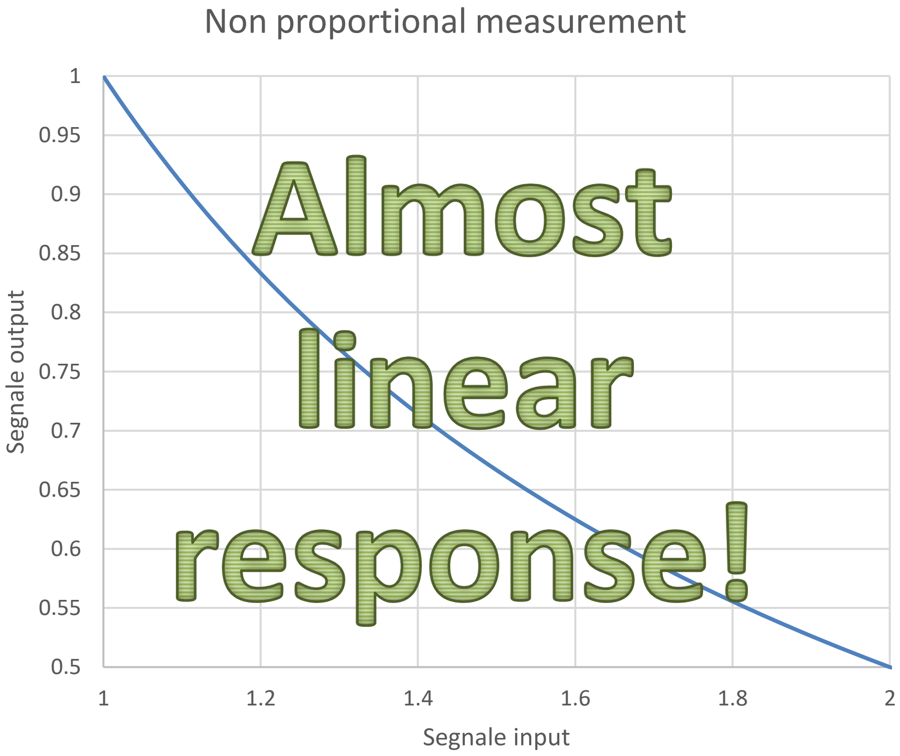


Dilution measurement method

If a strongly non-linear sensor is available, a measurement can be carried out according to the controlled dilution technique.

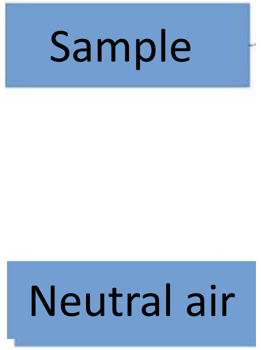
Dilution methods





Dilution measurement method

If a strongly non-linear sensor is available, a measurement can be carried out according to the controlled dilution technique.



The odour concentration is expressed in European odour units per cubic metre **(ou_E/m^3)** and represents the number of dilutions with neutral air required to bring the sample concentration to the odour detection threshold concentration.

$$\frac{ou_E}{m^3} =$$

No. of dilutions required to bring an air sample to the perception threshold limit

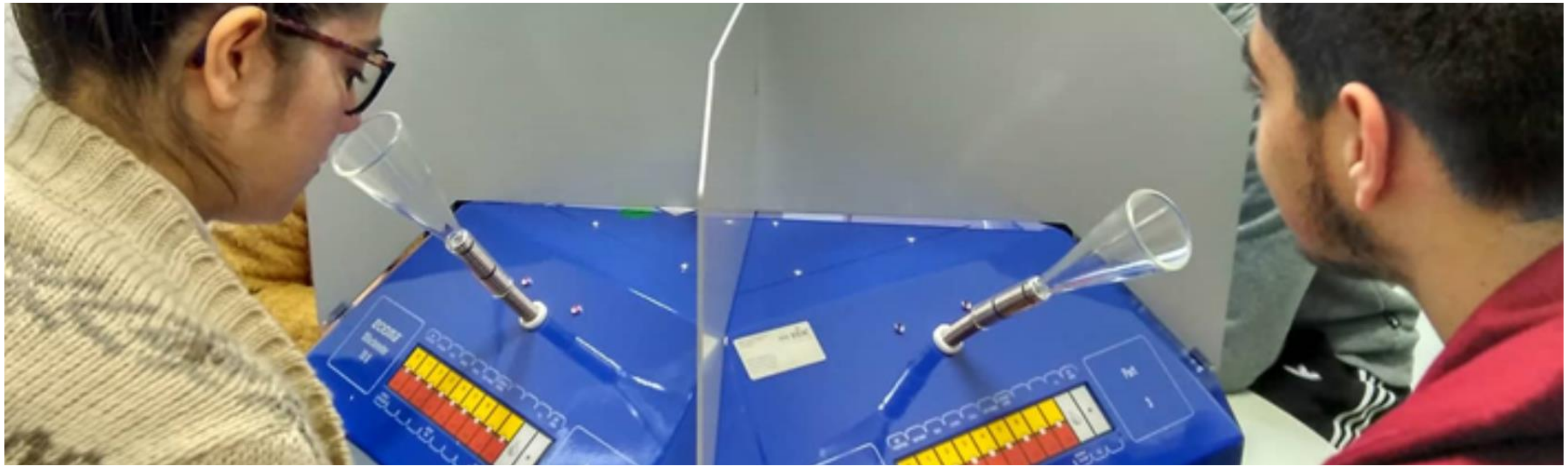
$$100\,\frac{ou_E}{m^3} =$$

I have to dilute the sample 100 times with neutral air to bring it to the (statistical) threshold value of perception

Odour concentration according to EN 13725

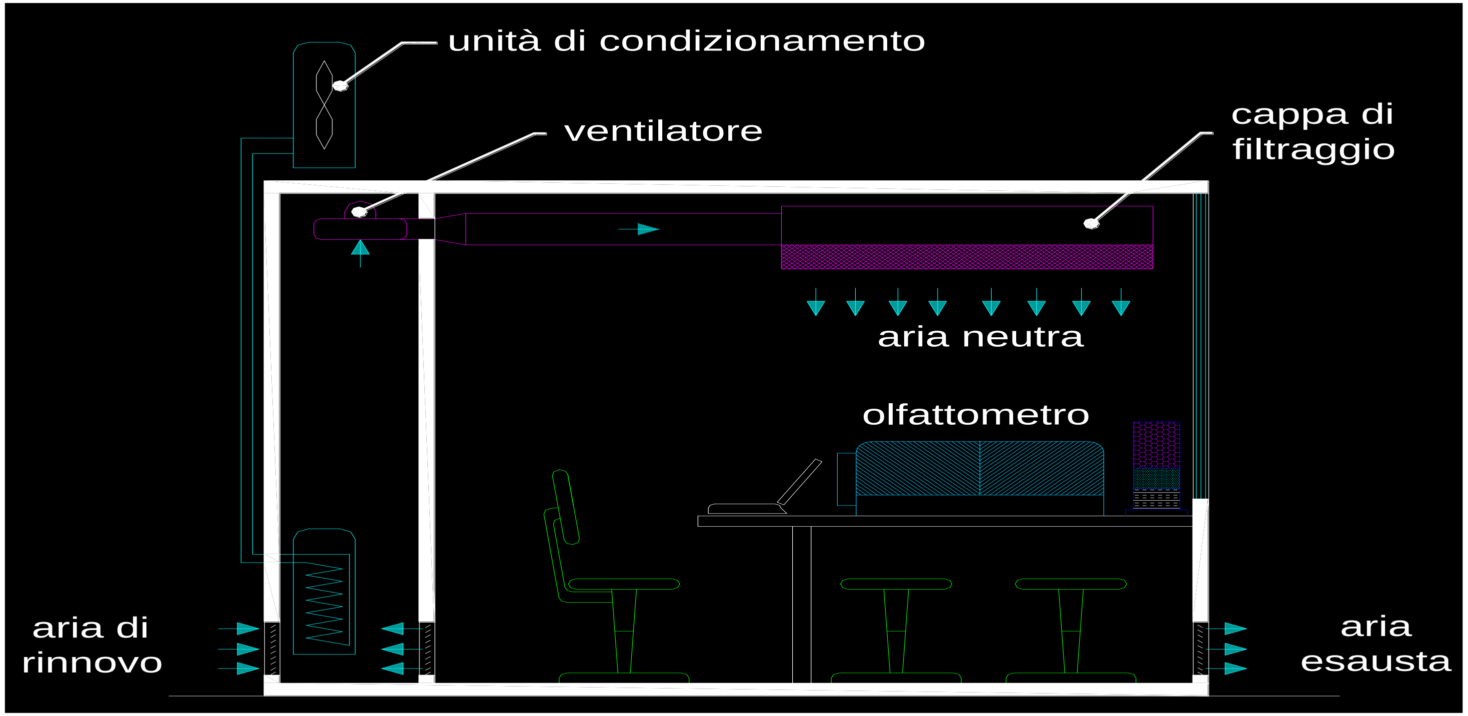
The analysis is carried out by presenting the sample to the panel at increasing concentrations using an olfactometer, until the panel members begin to perceive a different odour from the neutral reference air.

The osmogenic sample is alternated with neutral air to clean the 'sensor' and sometimes replaced with ('blanks') to check the panel's reliability



Olfactometric Chamber

The olfactometer chamber must be ventilated to maintain an odourless environment and provide fresh air to the test group in the olfactometer chamber (CO_2 < 0.15%).
The air must be filtered through activated charcoal before entering the chamber.



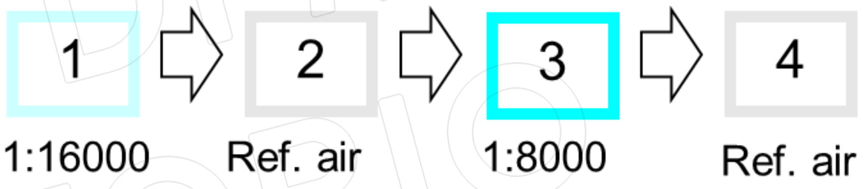
Dynamic Olfactometry (EN 13725)

Former Rector!

Yes/no method

Sampled osmogenic air passes through predilution units and is mixed with neutral air (with 2n exponential trend)

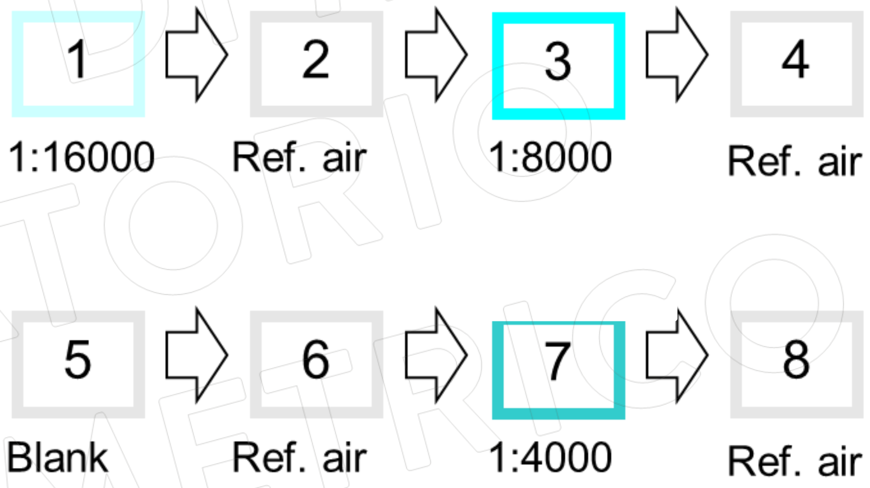
Initial dilution high enough to ensure initial non-detectability of the sample



Yes/no method

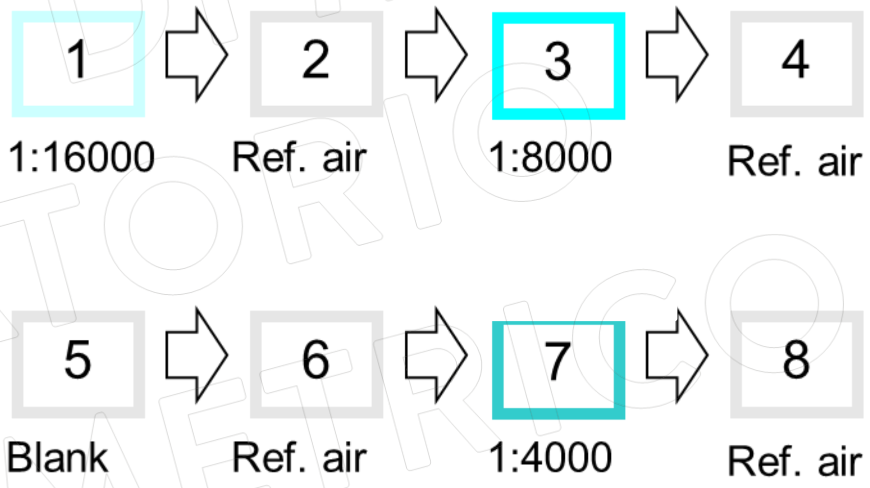
Sampled osmogenic air passes through predilution units and is mixed with neutral air (with 2n exponential trend)

With each round, the dilution of the sample decreases by increasing the concentration of the mixture



Yes/no method

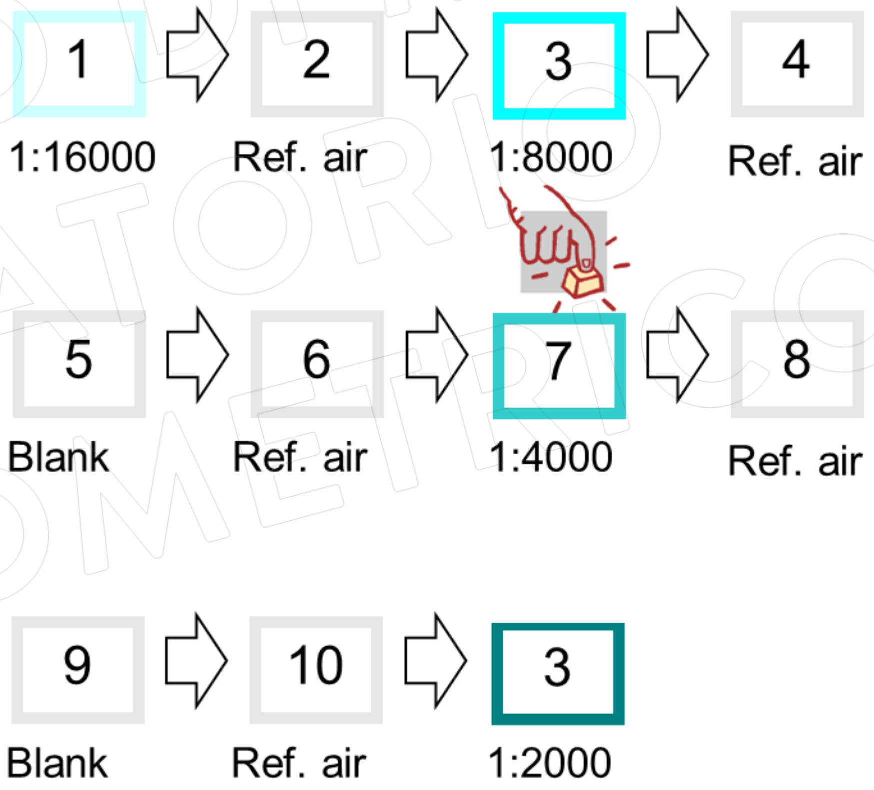
Sampled osmogenic air passes through predilution units and is mixed with neutral air (with 2n exponential trend)



When a panellist perceives something other than neutral air, they press their button

Yes/no method

Sampled osmogenic air passes through predilution units and is mixed with neutral air (with 2n exponential trend)



Each panel member has to confirm their opinion at the next round (higher concentration)

Dynamic Olfactometry (EN 13725)

The odour concentration is then calculated as the geometric mean of at least 12 odour detection threshold values multiplied by a factor depending on the olfactometer dilution factor (2).

	Threshold Round		
Panelist	**1**	**2**	**3**
1	4000	8000	16000
2	8000	8000	16000
3	8000	8000	4000
4	4000	8000	16000
5	1000	1000	2000
6	16000	8000	8000
7	16000	16000	16000
8	8000	8000	8000

But the real threshold was between the step of selection and the previous one!

$$C_{od,panelist} = \sqrt{C_{od,threshold} \cdot C_{od,upper\ threshold}}$$

$$C_{od,panelist} = C_{od,threshold} \cdot \sqrt{2}$$

Dynamic Olfactometry (EN 13725)

The odour concentration is then calculated as the geometric mean of at least 12 odour detection threshold values multiplied by a factor depending on the olfactometer dilution factor (2).

	First screening					
	Threshold Round			Threshold = Zite Round		
Panelist	**1**	**2**	**3**	**1**	**2**	**3**
1	4000	8000	16000	5657	11314	22627
2	8000	8000	16000	11314	11314	22627
3	8000	8000	4000	11314	11314	5657
4	4000	8000	16000	5657	11314	22627
5	1000	1000	2000	1414	1414	2828
6	16000	8000	8000	22627	11314	11314
7	16000	16000	16000	22627	22627	22627
8	8000	8000	8000	11314	11314	11314
					Geo average	

Dynamic Olfactometry (EN 13725)

The odour concentration is then calculated as the geometric mean of at least 12 odour detection threshold values multiplied by a factor depending on the olfactometer dilution factor (2).

	First screening								
	Threshold Round			Threshold = Zite Round			DeltaZ Round		
Panelist	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
1	4000	8000	16000	5657	11314	22627	-1.78	1.12	2.24
2	8000	8000	16000	11314	11314	22627	1.12	1.12	2.24
3	8000	8000	4000	11314	11314	5657	1.12	1.12	-1.78
4	4000	8000	16000	5657	11314	22627	-1.78	1.12	2.24
5	1000	1000	2000	1414	1414	2828	-7.13	-7.13	-3.56
6	16000	8000	8000	22627	11314	11314	2.24	1.12	1.12
7	16000	16000	16000	22627	22627	22627	2.24	2.24	2.24
8	8000	8000	8000	11314	11314	11314	1.12	1.12	1.12
					Geo average	**10079**			

ΔZ : how much the individual data varies from the average

-5 ≤ ΔZ ≤ 5

(panels that have an aberrant response are eliminated)

Dynamic Olfactometry (EN 13725)

The odour concentration is then calculated as the geometric mean of at least 12 odour detection threshold values multiplied by a factor depending on the olfactometer dilution factor (2).

	First screening								
	Threshold Round			Threshold = Zite Round			DeltaZ Round		
Panelist	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
1	4000	8000	16000	5657	11314	22627	-1.78	1.12	2.24
2	8000	8000	16000	11314	11314	22627	1.12	1.12	2.24
3	8000	8000	4000	11314	11314	5657	1.12	1.12	-1.78
4	4000	8000	16000	5657	11314	22627	-1.78	1.12	2.24
5	1000	1000	2000	1414	1414	2828	-7.13	-7.13	-3.56
6	16000	8000	8000	22627	11314	11314	2.24	1.12	1.12
7	16000	16000	16000	22627	22627	22627	2.24	2.24	2.24
8	8000	8000	8000	11314	11314	11314	1.12	1.12	1.12
					Geo average	**10079**			

Dynamic Olfactometry (EN 13725)

The odour concentration is then calculated as the geometric mean of at least 12 odour detection threshold values multiplied by a factor depending on the olfactometer dilution factor (2).

	First screening									Second screening		
	Threshold Round			Threshold = Zite Round			DeltaZ Round			Threshold = Zite Round		
Panelist	1	2	3	1	2	3	1	2	3	1	2	3
1	4000	8000	16000	5657	11314	22627	-1.78	1.12	2.24	5657	11314	22627
2	8000	8000	16000	11314	11314	22627	1.12	1.12	2.24	11314	11314	22627
3	8000	8000	4000	11314	11314	5657	1.12	1.12	-1.78	11314	11314	5657
4	4000	8000	16000	5657	11314	22627	-1.78	1.12	2.24	5657	11314	22627
5	1000	1000	2000	1414	1414	2828	-7.13	-7.13	-3.56			
6	16000	8000	8000	22627	11314	11314	2.24	1.12	1.12	22627	11314	11314
7	16000	16000	16000	22627	22627	22627	2.24	2.24	2.24	22627	22627	22627
8	8000	8000	8000	11314	11314	11314	1.12	1.12	1.12	11314	11314	11314
					Geo average	**10079**					Geo average	

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The odour concentration is then calculated as the geometric mean of <u>at least 12 odour detection threshold</u> values multiplied by a factor depending on the olfactometer dilution factor (2).

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	Threshold Round			Threshold = Zite Round			DeltaZ Round			Threshold = Zite Round			DeltaZ Round		
Panelist	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
1	4000	8000	16000	5657	11314	22627	-1.78	1.12	2.24	5657	11314	22627	-1.78	1.12	2.24
2	8000	8000	16000	11314	11314	22627	1.12	1.12	2.24	11314	11314	22627	1.12	1.12	2.24
3	8000	8000	4000	11314	11314	5657	1.12	1.12	-1.78	11314	11314	5657	1.12	1.12	-1.78
4	4000	8000	16000	5657	11314	22627	-1.78	1.12	2.24	5657	11314	22627	-1.78	1.12	2.24
5	1000	1000	2000	1414	1414	2828	-7.13	-7.13	-3.56						
6	16000	8000	8000	22627	11314	11314	2.24	1.12	1.12	22627	11314	11314	2.24	1.12	1.12
7	16000	16000	16000	22627	22627	22627	2.24	2.24	2.24	22627	22627	22627	2.24	2.24	2.24
8	8000	8000	8000	11314	11314	11314	1.12	1.12	1.12	11314	11314	11314	1.12	1.12	1.12
					Geo average	10079					Geo average	12911			

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	First screening									Second screening					
	Threshold Round			Threshold = Zite Round			DeltaZ Round			Threshold = Zite Round			DeltaZ Round		
Panelist	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
1	4000	8000	16000	5657	11314	22627	-1.78	1.12	2.24	5657	11314	22627	-1.78	1.12	2.24
2	8000	8000	16000	11314	11314	22627	1.12	1.12	2.24	11314	11314	22627	1.12	1.12	2.24
3	8000	8000	4000	11314	11314	5657	1.12	1.12	-1.78	11314	11314	5657	1.12	1.12	-1.78
4	4000	8000	16000	5657	11314	22627	-1.78	1.12	2.24	5657	11314	22627	-1.78	1.12	2.24
5	1000	1000	2000	1414	1414	2828	-7.13	-7.13	-3.56						
6	16000	8000	8000	22627	11314	11314	2.24	1.12	1.12	22627	11314	11314	2.24	1.12	1.12
7	16000	16000	16000	22627	22627	22627	2.24	2.24	2.24	22627	22627	22627	2.24	2.24	2.24
8	8000	8000	8000	11314	11314	11314	1.12	1.12	1.12	11314	11314	11314	1.12	1.12	1.12
					Geo average	**10079**					Geo average	**12911**			

Dynamic Olfactometry (EN 13725)

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	First screening									Second screening					
	Threshold Round			Threshold = Zite Round			DeltaZ Round			Threshold = Zite Round			DeltaZ Round		
Panelist	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
1	4000	8000	16000	5657	11314	22627	-1.78	1.12	2.24	5657	11314	22627	-1.78	1.12	2.24
2	8000	8000	16000	11314	11314	22627	1.12	1.12	2.24	11314	11314	22627	1.12	1.12	2.24
3	8000	8000	4000	11314	11314	5657	1.12	1.12	-1.78	11314	11314	5657	1.12	1.12	-1.78
4	4000	8000	16000	5657	11314	22627	-1.78	1.12	2.24	5657	11314	22627	-1.78	1.12	2.24
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6	16000	8000	8000	22627	11314	11314	2.24	1.12	1.12	22627	11314	11314	2.24	1.12	1.12
7	16000	16000	16000	22627	22627	22627	2.24	2.24	2.24	22627	22627	22627	2.24	2.24	2.24
8	8000	8000	8000	11314	11314	11314	1.12	1.12	1.12	11314	11314	11314	1.12	1.12	1.12
					Geo average	10079					Geo average	12911			

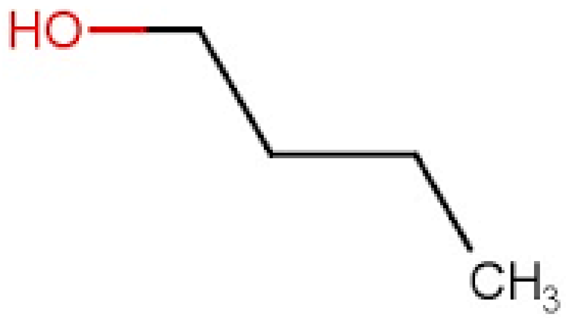
Odour concentration $^{ou_E}/_{m^3}$

Since there are huge differences in olfactory sensitivity among the population, a 'standard sensitivity' to a particular odorant is defined.

This is achieved by defining for n-butanol in nitrogen at a given concentration a conventional olfactory perception threshold (EROM): 123 ug of n-butanol in 1 cubic metre of nitrogen (= 40 ppb).

This standard simple mixture has an odour concentration (by definition) of 1 ouE/m3

Human noses calibration with n-butanol!



Measurement limits of dynamic olfactometry

In the dynamic olfactometry method, the gaseous sample, in order to be subjected to olfactometric measurement, must be diluted to the perception threshold.

Then samples with a low 'starting' concentration (slightly above the olfactory threshold) cannot be measured at all.

More precisely, the detection limit of the method is approximately 10÷100 ou_E/m^3. Samples with concentrations below these values are not reliably measurable

In the revision of the standard, mentioning the field blank, it is stated that 'they are in the range of 15 to 30 ou_E/m^3, with peaks up to 100 ou_E/m^3'.

$$\nexists\, C_{od} = 0$$

Panel selection and measurement uncertanty

EN 13725 allows individual perception thresholds of panel members to be within a factor of two (20÷80 ppb) of the reference threshold (40 ppb)

The measurement uncertainty component associated with the 'calibration' of the panel and the dilution step of the olfactometer (2):

is of the same order of magnitude!

Uncertanty

Each laboratory should therefore estimate its own measurement uncertainty based on its own repeatability and reproducibility data.

For an odour concentration result of **1000 ou_E/m^3**, a confidence interval like this:

$$500\ ou_E/m^3 < C_{od} < 2000\ ou_E/m^3$$

is reasonable!

Measurement to be made at emission source !

BS EN 13725:2022

Stationary source emissions. Determination of odour concentration by dynamic olfactometry and odour emission rate

bsi.knowledge

Overview

This document specifies an objective method for the determination of the odour concentration of a gaseous sample using dynamic olfactometry with human assessors. The document also specifies a method for the determination of the odour emission rate from stationary sources, in particular:

a. a) point sources (conveyed or ducted emissions);
b. b) active area sources (e.g. biofilters).

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

The field of application of this European Standard
does not include:

- […]

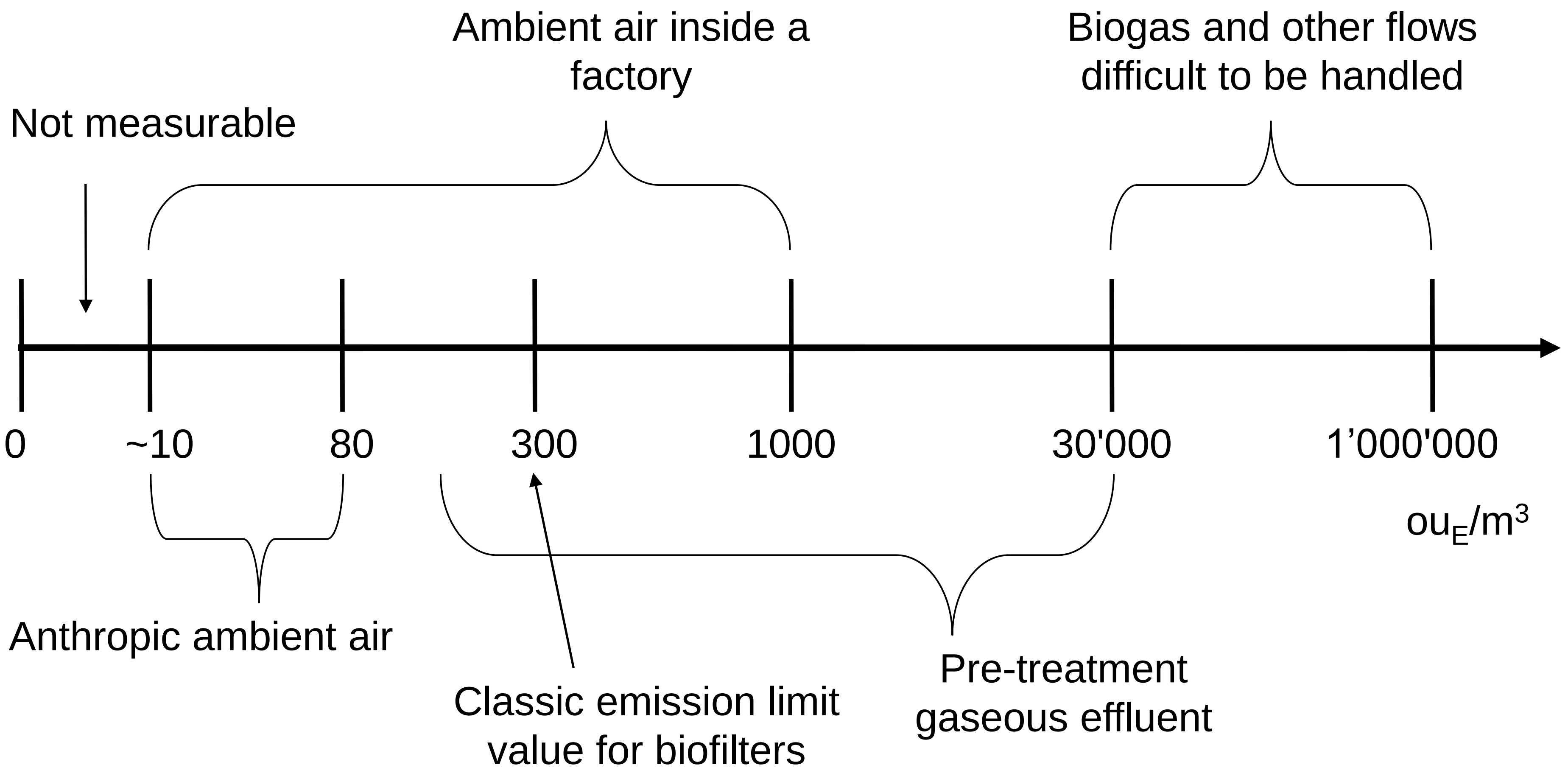
- **direct measurement of odour exposure in ambient air**. For this measurement purpose field panel methods exist which are the subject of EN 16841-1 Ambient Air – Determination of odour in ambient air by using field inspection, Grid Method;

Ambient air measurement

- Not included in EN 13725:2003 (nor in EN13725:2022)
- In various foreign legislation, too, it is only provided for in one, highly objectionable case (upwind-downwind).
- For monitoring olfactory exposure there are other techniques (IOMS, field inspection, recording of complaints, telephone surveys, etc.).
- Olfactometric monitoring of outdoor ambient air gives information in one direction only: if the concentration is high (say > 120 ou_E/m^3) I have evidence of olfactory pollution (the origin of which, however, may not be certain); if it is low I cannot draw any conclusions
- Monitoring at the receptor is generally inconclusive as to the presence or absence of odour pollution

If dynamic olfactometry had been useful in ambient air measurements, none other technique would be needed!

Rules of thumb od odour concentration (ou_E/m^3)



Odour concentration ≠ odour emission rate

In odour impact assessment, odour concentration alone is not sufficient:

the air flow associated with the monitored odour source must be taken into account, as in most cases these parameters are interrelated.

$$OER = Q_{AIR} \cdot C_{OD}$$

The basic parameter is the odour emission flux (OER), which is expressed in odour units per second (ou_E/s), and is obtained as the product of the odour concentration and airflow associated with the source.

EN 13725 states that the volumetric air flow must be evaluated under normal conditions for olfactometry:

20 °C e 101,3 kPa, wet flow, as it is

$C_{od} \neq OER$

Intensive dimension, Non-isotropic

Extensive size, Responsible for impact

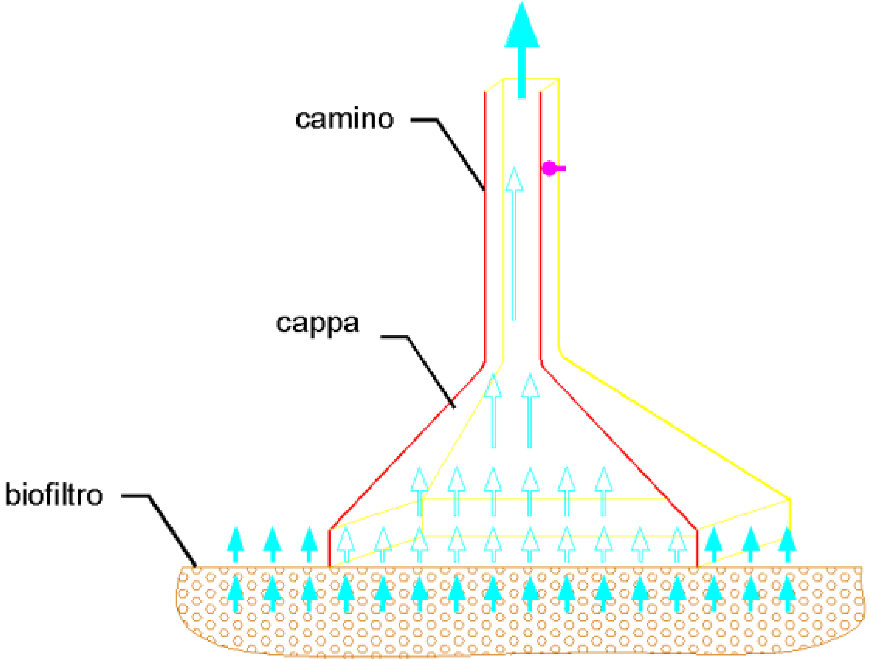
Point sources

$$\mathbf{OER} = Q_{20°C} \cdot C_{od} = \left[\frac{ou_E}{s}\right]$$

Normalized conditions for Dynamic Olfactometry

- Temperature = 20°C
- Pressure = 1 atm
- Wet flux
- As it is (no O_2 normalization)

Vair BF > 8 mm/s



Passive area sources

All hood devices are based on the same principle:

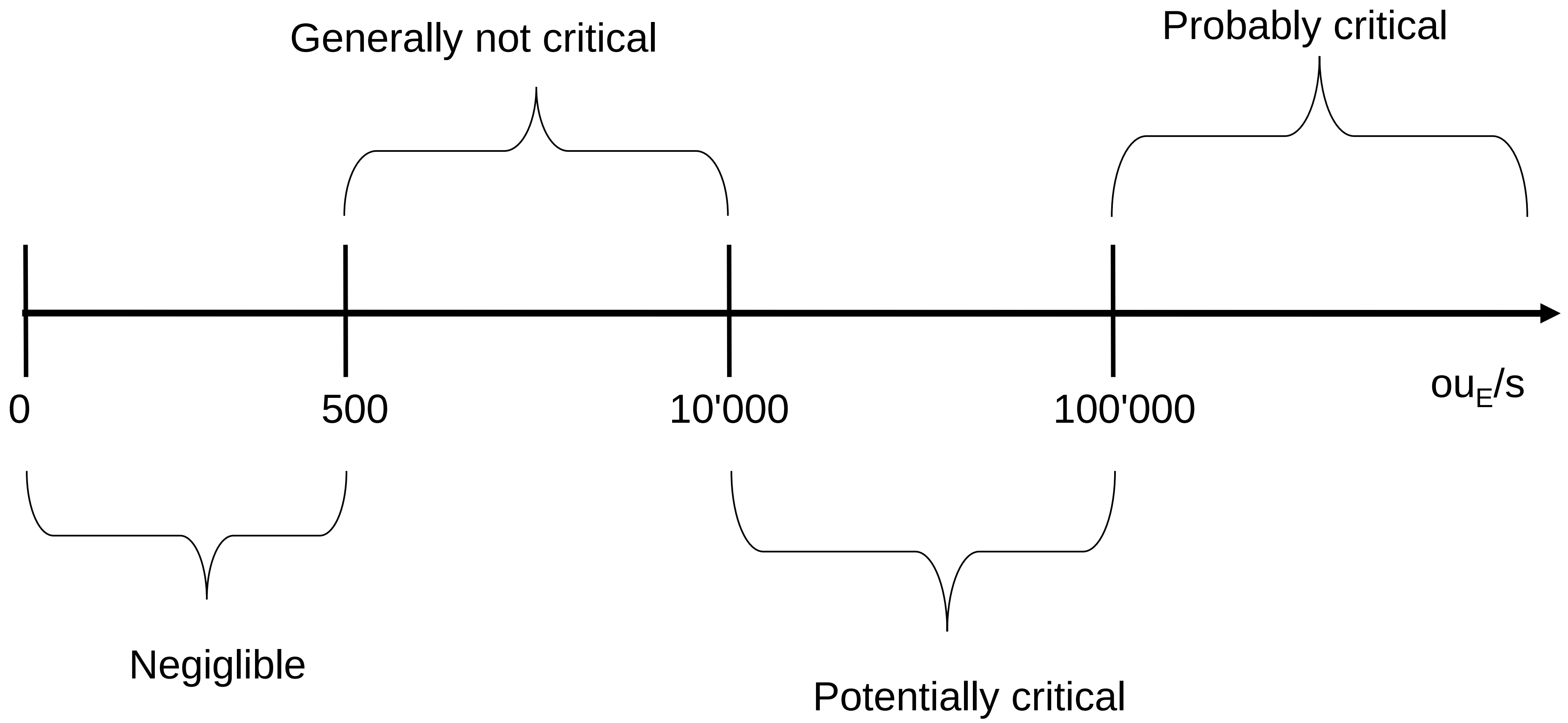
- insulate a portion of the emission surface
- insufflate a known neutral air flow and finally to
- measure the odour concentration at the outlet.

In Wind Tunnels, the carrier gas is introduced directionally to theoretically simulate the action of the wind on the sampled surface.

$$SOER = \frac{C_{od} \cdot Q_{air}}{A_{hood}}$$

Complex odour sources

Rules of thumb on odour flux (ou_E/s)



Dynamic Olfactometry (EN 13725): Pro and cons

Pro	Cons
• Recognised and standardised technique	• Only quantification, no qualification (=> impossible to recognise the source of the odour)
• Endpoint evaluation of olfactory effect	• Impossibility of continuous measurements
• High sensitivity (by definition up to OTV)	• High measurement uncertainty
• Possible implementation of atmospheric dispersion models (in order to estimate the impact at the receptor)	• Cannot be used directly in ambient air (at the receptor)

Olfactory impact assessment approaches

Humans

- Dynamic Olfactometry (EN 13725)
- **Field Inspection (EN 16841)**
- Citizen reports

Tools

- Chemical analysis with single compound qualification
- Non-specific chemical analysis
- Single gas analysis (i.e. H_2S, NH_3)
- IOMS

Field Inspection (EN 16841)

EN **16841:2016** Part 1 (Grid method) and Part 2 (Plume method) was published in November 2016:

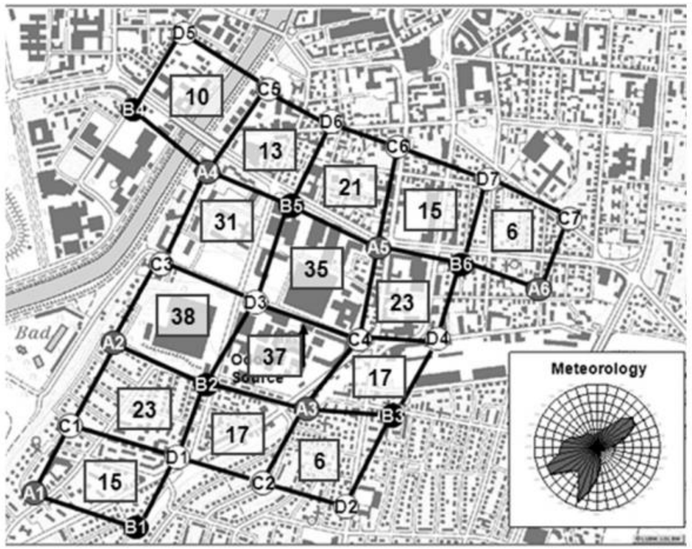
"This European Standard supplement the dynamic olfactometry method described in ***EN 13725 which is generally only suitable for measurement of odour emissions at source*** *as the practical lower detection limit is typically ≥10 ou_E/m^3, and."* **cannot be applied directly to determine odour exposure in the field**

"The methods for measuring odour presented in this European Standard make direct use of the effect of odorants on the human sense of smell. ***The standard involves the use of qualified human panel members in the field*** *to directly assess the presence of recognizable odour in ambient air, and provide data that can be used to characterize odour exposure in a defined assessment area."*

Olfactometric campaigns conducted in the field with a panel of trained examiners

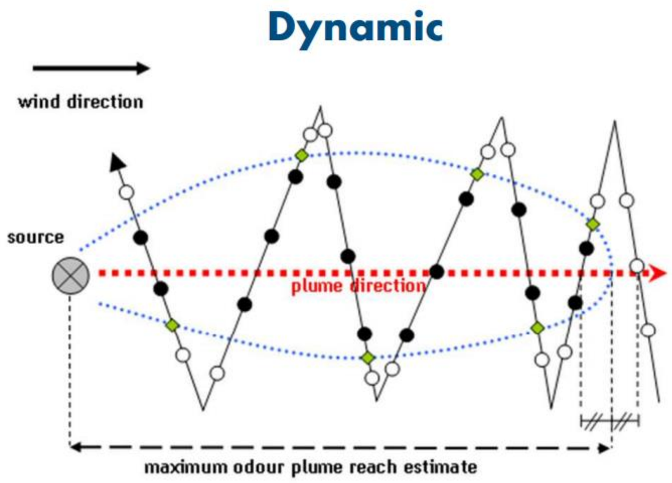
Grid method

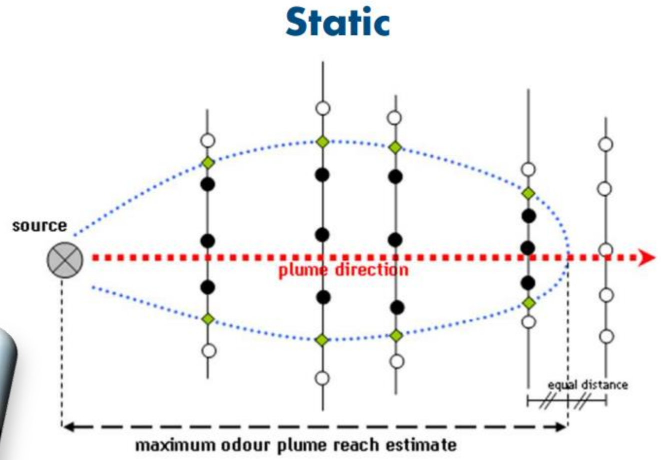
Long-term survey (1 year) in order to obtain a map of exposure to recognisable odours over a selected area

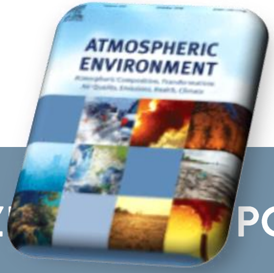


Plume method

Short-term method (10 or more surveys of a few hours with different weather conditions) to determine the extent of odour recognisable from a source







Field Inspection (EN 16841): Pro and cons

Pro | **Cons**

Pro

- Direct determination of odour impact in terms of frequency of occurrence or impact area of the odour at the receptor
- Possibility of comparing results with other methods

Cons

- Logistical difficulties related to the scheduling of surveys: night surveys, identification of walking paths (plume method)
- Difficulties in the formation of a suitable, available and not directly involved panel (grid method)
- High cost
- Lack of acceptable reference values

Olfactory impact assessment approaches

Humans

- Dynamic Olfactometry (EN 13725)
- Field Inspection (EN 16841)
- **Citizen reports**

Tools

- Chemical analysis with single compound qualification
- Non-specific chemical analysis
- Single gas analysis (i.e. H_2S, NH_3)
- IOMS

There are very different types of involvement of the resident population

D-NOSES

VDI 3883

ODOUR COLLECT

CEt

PoS

JCOM JOURNAL OF SCIENCE COMMUNICATION

CEt

CEt

Citizen reports: Pro and cons

Pro

- Low or no cost
- Useful to involve citizenship (psychological effect)

Cons

- Management difficulties
- Lack of scientific stability of data
- Lack of acceptable reference values
- Possibility of bias
- Long response times

Humans

- Dynamic Olfactometry (EN 13725)
- Field Inspection (EN 16841)
- Citizen reports

Tools

- **Chemical analysis with single compound qualification**
- Non-specific chemical analysis
- Single gas analysis (i.e. H_2S, NH_3)
- IOMS

Chemical analysis with single compound qualification

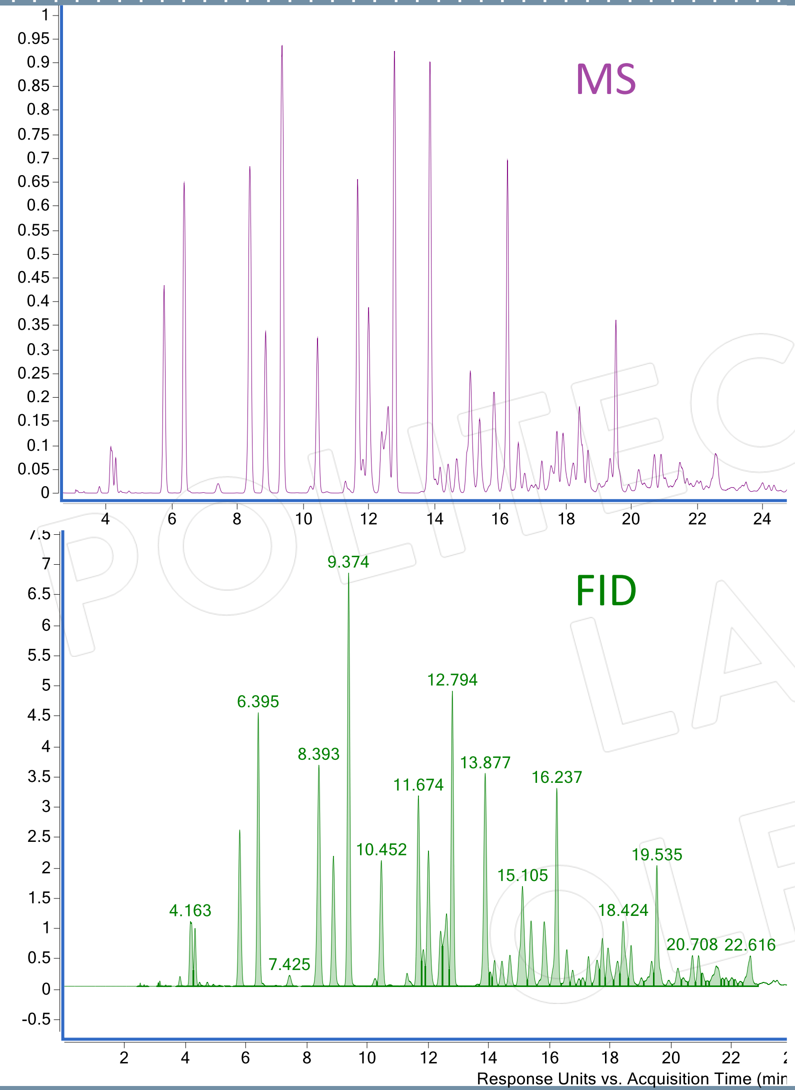
Among the analytical methods, the most widely used system for measuring odorous compounds is gas chromatography coupled to mass spectrometry (GC-MS).

The principle of the gas chromatographic (GC) method is the separation of the constituents of a mixture based on their affinity for a medium in a column through which the analyte streams in the gas stream.

The identification, and eventual quantification, of the chromatogram peaks, representative of the different separated substances constituting the odorous mixture under investigation, is carried out by means of mass spectrometry (MS).

In addition to MS, there exist different specific sensors for different kind of molecules e.g. FID, PID, FPD, PFPD, AED, NCD and eventually different separation techniques e.g. HPLC-MS

Chemical analysis with single compound qualification



?

Odour activity value

$$OAV = \frac{m_i}{OTV_i}$$

Chemical analysis with single compound qualification

There is no known quantitative relationship linking the chemical composition of an osmogenic air with its odour concentration; a useful, albeit partial, piece of information is provided by the calculation of the Odour Activity Value (OAV) of the substances constituting an odorous mixture, obtained from the ratio between the concentration of each analyte and its Odour Threshold Concentration (OTC); the sum of the OAVs of a mixture is proportional *in the first approximation* to its odour concentration.

=> WE ARE NEGLECTING ADDITIVITY OR MASKING EFFECTS

$$C_{od} \approx\approx \sum_i OAV_i = \sum_i \frac{m_i}{OTV_i}$$

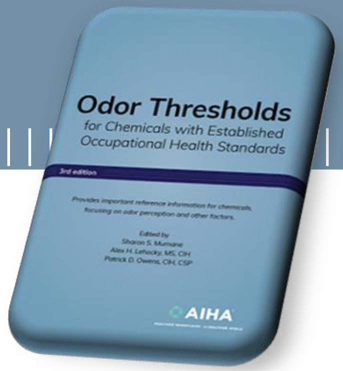
OTV H2S (Murnane et al. 2013)

Source	Type of Threshold	Odor Thresholds	
		mg/m³	ppm
Hydrogen Sulfide			
Valentin 1848, 1850		2	1.4
Lehmann 1897		<2	<1.4
Kulka & Homma 1910		0.2 - 0.3	0.14 - 0.22
Henderson & Haggard 1922		<0.001	<0.00072
Henning 1924	d	0.0001	0.00007
Katz & Talbert 1930	d	0.18	0.13
Thomas et al 1943		0.035	0.025
Loginova 1957		0.04	0.029
Duan - Fen - Djuy 1959		0.012 - 0.03	0.0086 - 0.022
Sanders & Dechant 1961		0.04 - 0.10	0.029 - 0.072
Baikov 1963		0.014 - 0.03	0.010 - 0.022
Young & Adams 1966	d	0.008 - 0.011	0.0057 - 0.0079
Cederlof et al 1966	d	0.01	0.0072
Sakuma et al 1967		0.007	0.005
Endo et al 1967		1.4	1
Basmadzhieva & Argirova 1968		0.012	0.0086
Adams et al 1968	d		
Leonardos et al 1969	r		
Pomeroy & Cruse 1969			
Wilby 1969	r		
Lindvall 1970	d		
Stephens 1971			
Nishida et al 1979	d	0.074	0.053
Winneke et al 1979	d	0.00265	0.0019
Thiele 1979	d	0.0016	0.0011

Source	Type of Threshold	Odor Thresholds	
		mg/m³	ppm
Bedborough & Trott 1979	d	0.0036	0.0026
Brunekreef & Harssema 1980		0.0011 - 0.0024	0.00079 - 0.0017
Anon. 1980	d	0.0007	0.0005
Anon. 1980	r	0.0078	0.0056
Thiele et al 1981		0.0013 - 0.0053	0.00093 - 0.0038
Thiele 1982		0.0028	0.062
Naus 1982	d	0.1	0.072
Naus 1982	r	5	3.6
Jensen & Flyger 1983		0.0038 - 0.0067	0.0027 - 0.0048
Kobal & Thiele 1983			
Bahmuller 1983			
Moriguchi et al 1983			
Bahmuller 1984			
Thiele 1984			
Roos et al 1985			
Roos et al 1985			
Don 1986			

Hermans 1989		0.000056 - 0.001545	**0.00004** - 0.0011
Nagy 1991	d	0.0055	0.0039
Hoshika et al 1993	d	0.0007	0.0005
Lotsch et al 1997		0.14 - 2.8	0.10 - 2
Mannebeck & Mannebeck 2002	d	0.000491 - 0.000946	0.00035 - 0.00068
Nagata 2003	d	0.00057	0.00041
		0.022	0.0157
		0.00070 - 0.003	0.0005 - 0.0022
	r	0.00064 - 0.0013	0.00046 - 0.00093
	d	0.00057 - 0.00142	0.00041 - 0.0010
	r	0.00071 - 0.0032	0.00051 - 0.0023
Glindemann et al 2006	d	0.001	0.00072
Ueno et al 2009		0.00045	0.00032
Ueno et al 2009		0.0018	0.013

Span of 5 Log!



INVE

Difficulties in chemical qualification / quantification: instrumental optimization

The chemical compounds present in an odorant gas are not known *a priori:* the problem is that instrumental sensitivity depends on different parameters which cannot be optimized prior to the analysis:

- **Sampling method**
- **Sample amount**
- **Chromatographic column**
- **Preconcentration adsorber material**
- **Detector**

Our target is try to have a sensitivity «as wide as possible»:

- **Wide range column**
- **Wide range adsorber**
- **Wide range detector**

Difficulties in chemical qualification / quantification: single compound calibration

The chemical compounds present in an odorant gas are not known *a priori* : it is almost impossible to have a single calibration curve of each detected odorous compound

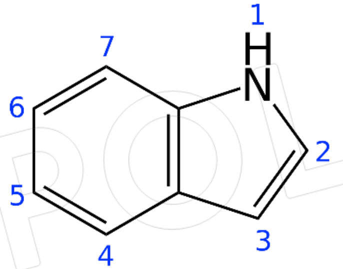
=> SEMIQUANTIFICATION: use of a reference molecule for the quantification of other different molecules (grouping)

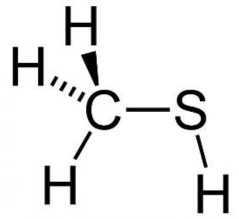
Categoria	Composto rappresentativo	CAS
Unknown	Toluene	108-88-3
Alcani C2-C6	Esano -n	110-54-3
Alcani C7-C20	Dodecano	112-40-3
Cicloalcani	Cicloesano	110-82-7
Alcheni, Alchini, Dieni	Propilene	115-07-1
Aromatici	Benzene	71-43-2
Policiclici	Toluene	108-88-3
Alcoli ed eteri	Isobutanolo	78-83-1
Terpeni	Limonene(R)+	5989-27-5
Acidi carbossilici	Acetone	67-64-1
Aldeidi e Chetoni	Acetone	67-64-1
Furani	Toluene	108-88-3
Esteri	Acetato di etile	141-78-6
Acrilati	Acrilato di butile	141-32-2
Solforati	Metilmercaptano	74-93-1
Azotati	Toluene	108-88-3
Alogenati	Cloroformio	67-66-3
Silani	Toluene	108-88-3

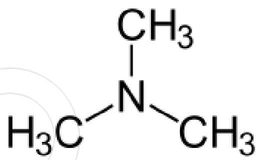
Difficulties in chemical qualification / quantification: super low OTV compound

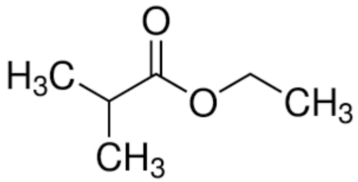
The chemical compounds present in an odorant gas are not known *a priori:* different molecules, also belonging to different categories shows very low OTV (from ppb to ppt).

=> super high analytical sensitivity would be required

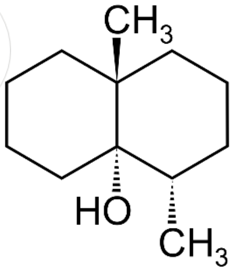


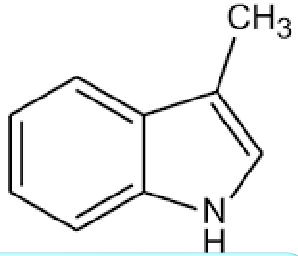


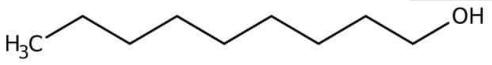




Compound	Class	CAS	PM [g/mol]	OTV [ppm]
n-Valeraldehyde	Aldeyide	110-62-3	86.13	4.10E-04
Acrolein	Aldeyde + =	107-02-8	56.06	3.60E-03
Geosmin	Cycloalkane	19700-21-1	182.3	6.50E-06
Methyl mercaptane	Sulphur	74-93-1	48.11	7.00E-05
Trimethylamine	Amine	75-50-3	59.11	3.20E-05
Indole	Aromatic + N	120-72-9	117.15	3.00E-04
Skatole	Aromatic + N	83-34-1	131.17	5.60E-06
p-Diethylbenzene	Aromatic	105-05-5	134.22	3.90E-04
Ethyl isobutyrate	Ester	97-62-1	116.16	2.20E-05
n-Nonanol	Alcohol	28473-21-4	144.26	9.00E-04
p-Cresol	Aromatic + OH	106-44-5	108.14	5.40E-05







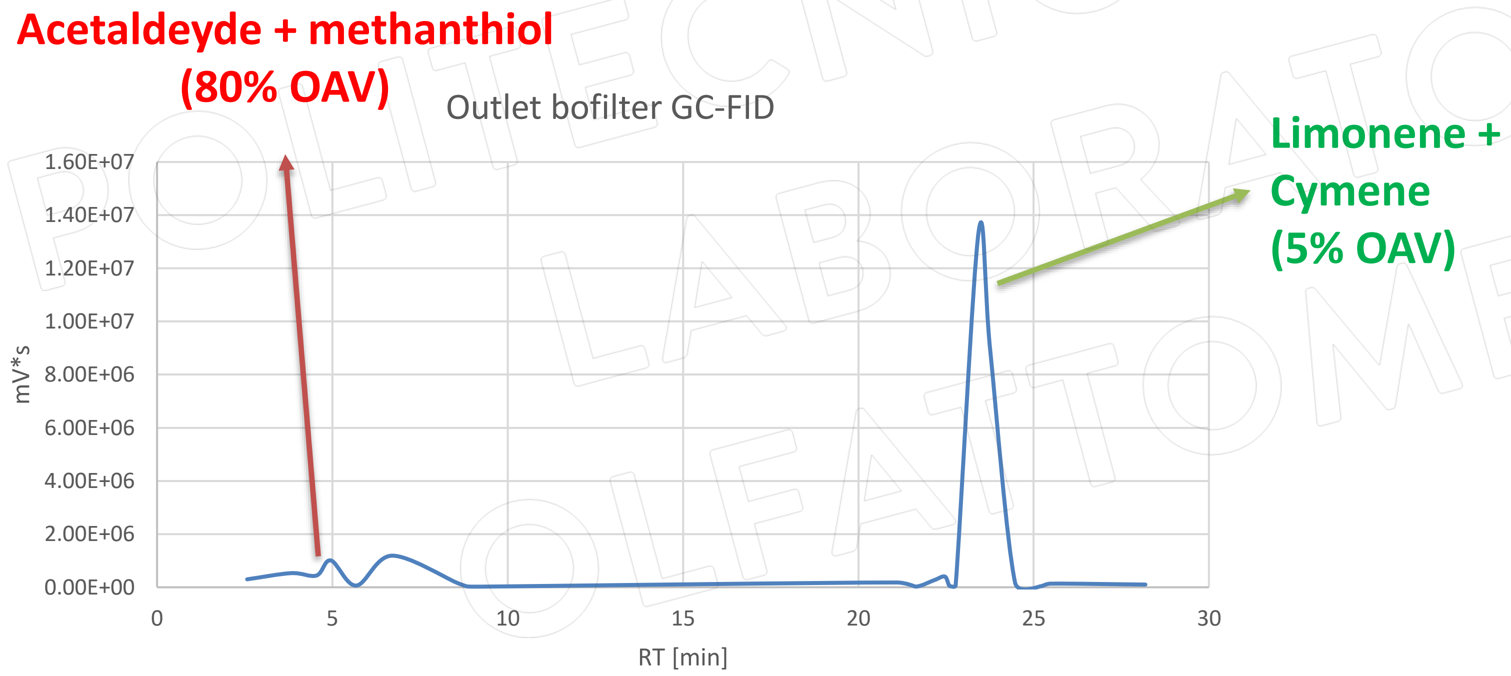
Nagata 2003

Difficulties in chemical qualification / quantification: super low OTV compound

The chemical compounds present in an odorant gas are not known *a priori:* different molecules, also belonging to different categories shows very low OTV (from ppb to ppt).

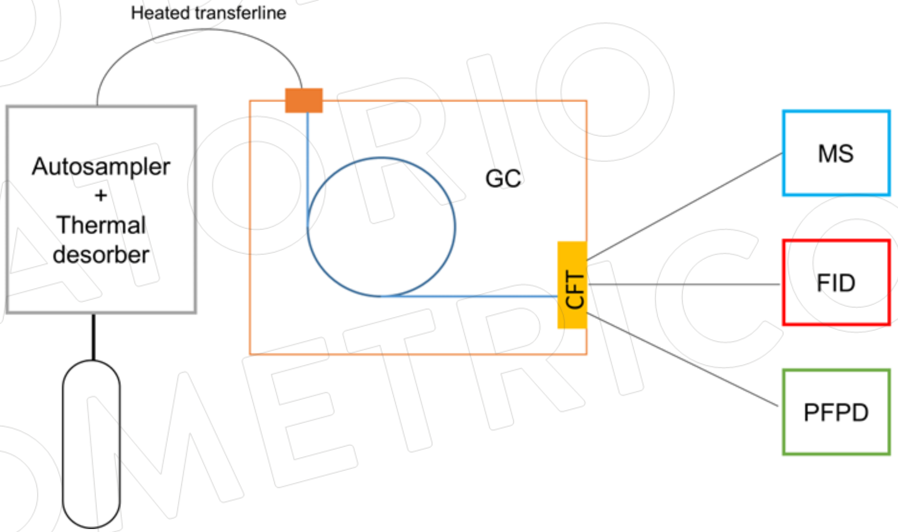
=> high analytical sensitivity required

=> problem overlapping with non odorous high-concentration substances



Composto	mg/ m3	OTV [mg/	OAV
Methane	NQ		
Acetaldehyde	3.8	2.7E-03	1407.3
Methanethiol	0.1	1.4E-04	876.3
Ethanol	7.2	1.0E+00	7.3
Acetone	0.5	1.0E+02	0.0
Dimethyl sulfide	0.4	7.6E-03	54.9
2-Butanone	0.9	1.3E+00	0.7
2-Butanol	0.1	6.7E-01	0.2
Ethyl Acetate	0.1	3.1E+00	0.0
α-Pinene	0.4	1.0E-01	4.3
Cyclohexane, 1-methylene-4-(1-methylethenyl)-	0.1		
3-Carene	1.1	9.3E+00	0.1
β-Pinene	1.6	1.8E-01	8.8
Decnae	0.1	3.6E+00	0.0
Unknown	0.2		
p-Cymene	28.8	7.2E+00	4.0
Limonene	35.7	2.1E-01	168.6
γ-Terpinene	0.7	5.5E+01	0.0
Unknown	0.1		
Undecane	0.8	5.6E+00	0.1
Tetradecane	1.6		

Difficulties in chemical qualification / quantification: edges of hope



Qualitative *information not specific (TIC mode)*

Specific detection *and* ***quantitative*** *information about* ***organic compounds***

Specific detection *and* ***quantitative information*** *about* ***sulphur*** *compounds*

Difficulties in chemical qualification / quantification: edges of hope

RT [min]	Composto	CAS	Area detector	Detector	mg/ m3	OTV [mg/m3]	OAV
3.78	Acetaldehyde	75-07-0	3.94E+05	FID	0.56	2.70E-03	206.4
4.791	Trimethylamine	75-50-3	1.97E+05	FID	0.28	7.74E-05	3604.0
4.929	Ethanol	64-17-5	1.28E+06	FID	1.81	9.99E-01	1.8
5.549	Unknown sulphur compound		1.24E+06	PFPD	0.11		
5.653	Acetone	67-64-1	7.70E+05	FID	1.09	9.98E+01	0.01
5.882	Isopropyl Alcohol	67-63-0	3.78E+05	FID	0.53	6.39E+01	0.01
6.733	Dimethyl sulfide	75-18-3	3.57E+06	PFPD	0.63	7.62E-03	82.4
7.432	Carbon disulfide	75-15-0	1.56E+05	PFPD	0.02	6.54E-01	0.0
7.521	1-Propanol	71-23-8	1.91E+05	FID	0.27	2.31E-01	1.2
7.9	Silanol, trimethyl-	1066-40-6	2.02E+05	FID	0.29		
8.563	2-Butanone	78-93-3	4.60E+05	FID	0.65	1.30E+00	0.5
8.855	2-Butanol	78-92-2	4.90E+05	FID	0.69	6.67E-01	1.0
9.359	Unknown		1.26E+05	FID	0.18		
9.7	1-Propanol, 2-methyl-	78-83-1	2.55E+05	FID	0.36	3.33E-02	10.8
10.848	1-Butanol	71-36-3	8.67E+05	FID	1.23	1.15E-01	10.6
13.313	1-Pentene, 2,4,4-trimethyl-	107-39-1	1.33E+05	FID	0.19		
14.043	Disulfide, dimethyl	624-92-0	1.80E+07	PFPD	2.40	8.48E-03	283.0
14.99	Toluene	108-88-3	1.31E+06	FID	1.85	1.24E+00	1.5
15.801	tert-Butyldimethylsilanol	18173-64-3	1.21E+05	FID	0.17		
16.222	Octane	111-65-9	2.02E+05	FID	0.29	7.94E+00	0.04
17.711	Benzene, chloro-	108-90-7	1.89E+05	FID	0.27	5.93E+01	0.005
18.514	p+m-Xylene	106-42-3	3.59E+05	FID	0.51	2.52E-01	2.0
19.343	o-Xylene	95-47-6	1.21E+05	FID	0.17	1.65E+00	0.1
21.831	Dimethyl trisulfide	3658-80-8	8.45E+05	PFPD	0.10	1.40E-02	7.2
22.615	Mesitylene + Decane		8.01E+05	FID	1.13		
23.04	1-Hexanol, 2-ethyl-	104-76-7	8.82E+05	FID	1.25	8.00E-01	1.6
23.771	D-Limonene	5989-27-5	1.50E+05	FID	0.21	4.50E-02	4.7
25.504	Undecane	1120-21-4	4.70E+05	FID	0.66	5.56E+00	0.1
28.194	Dodecane	112-40-3	2.01E+05	FID	0.28	7.66E-01	0.4

Dyanmic olfactometry odour concentration [ouE/m3]	6’900
∑ OAV	4’219

With the identification of low odour threshold compounds, the measured odour concentration and the sum of the OAVs obtained may be mutually consistent.

Difficulties in chemical qualification / quantification: edges of hope

RT [min]	Composto	CAS	Area detector	Detector	mg/ m3	OTV [mg/m3]	OAV
2.536	Methane		1.82E+05	FID	**NQ**		
3.1	Sulfur dioxide	7446-09-5		PFPD	**NQ**	2.3E+00	
3.805	Acetaldehyde	75-07-0	2.52E+05	FID	**1.80**	2.7E-03	666
4.519	Methanethiol	74-93-1	5.79E+05	PFPD	**0.16**	1.4E-04	1145
4.945	Ethanol	64-17-5	1.29E+06	FID	**9.22**	1.0E+00	9
5.667	Acetone	67-64-1	7.32E+04	FID	**0.52**	1.0E+02	0
6.7	Dimethyl sulfide	75-18-3	1.36E+05	PFPD	**0.05**	7.6E-03	6
7.4	Carbon disulfide	75-15-0	1.98E+05	PFPD	**0.04**	6.5E-01	0
7.521	1-Propanol	71-23-8	8.68E+04	FID	**0.36**	2.3E-01	2
8.56	2-Butanone	78-93-3	2.48E+05	FID	**1.34**	1.3E+00	1
8.855	2-Butanol	78-92-2	9.12E+04	FID	**0.38**	6.7E-01	1
9.219	Ethyl Acetate	141-78-6	4.53E+04	FID	**0.22**	3.1E+00	0
21.083	α-Pinene	80-56-8	1.73E+05	FID	**0.41**	1.0E-01	4
22.169	3-Carene	13466-78-9	1.80E+05	FID	**0.72**	9.3E+00	0
22.465	β-Pinene + Decane		2.74E+05	FID	**0.78**		
23.427	p-Cymene	99-87-6	4.93E+06	FID	**10.59**	7.2E+00	1
23.758	Limonene	138-86-3	6.16E+06	FID	**24.64**	2.1E-01	116
24.47	γ-Terpinene	99-85-4	1.03E+05	FID	**0.41**	5.5E+01	0
25.42	2-Carene + Undecane		4.09E+04	FID	**0.12**		
27.278	o+m-Cymene	527-84-4	3.78E+04	FID	**0.08**	4.0E-03	20
28.181	Tetradecane	629-59-4	9.36E+04	FID	**1.44**		

Dyanmic olfactometry odour concentration [ouE/m3]	**1'300**
∑ OAV	**1'972**

With the identification of low odour threshold compounds, the measured odour concentration and the sum of the OAVs obtained may be mutually consistent.

Chemical analysis with single compound qualification: Pro and cons

Pro	Cons
• Historical, recognised, repeatable technique	• Non-obvious correlation with odour concentration
• Possibility of single species determination (health impact analysis)	• Customized instrumentation and techniques
	• High technical capacity required
• Possibility of emission and receptor analysis	• Detection thresholds are often >> of OTVs
• Possible implementation of atmospheric dispersion models	• Reproducibility not taken for granted (instrumentation dependence)

Humans

- Dynamic Olfactometry (EN 13725)
- Field Inspection (EN 16841)
- Citizen reports

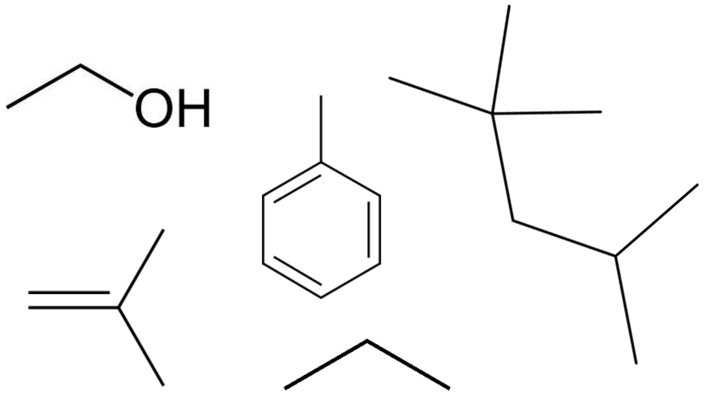
Tools

- Chemical analysis with single compound qualification
- **Non-specific chemical analysis**
- Single gas analysis (i.e. H_2S, NH_3)
- IOMS

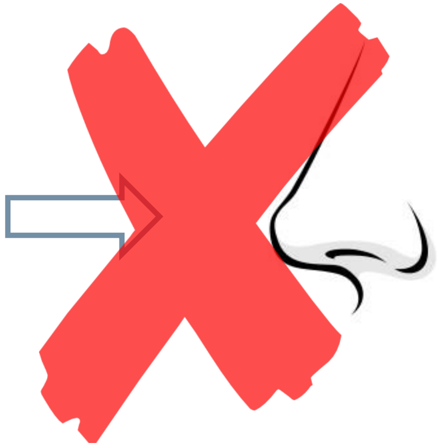
Non-specific chemical analysis

The class of Volatile Organic Compounds, or VOCs, comprises various chemical compounds made up of molecules containing carbon atoms, having different functional groups, having different physical and chemical behaviours, but characterised by a certain volatility.

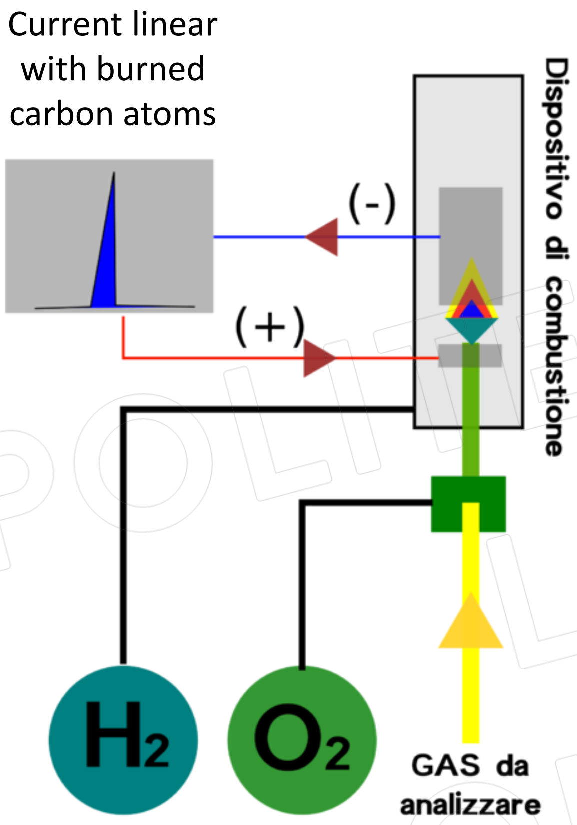
VOC sensors (FID or PID) are able to give an idea of the total concentration of organic compounds, but this is non-specific, non-massive and expressed in ppm (or ppb) equivalents.

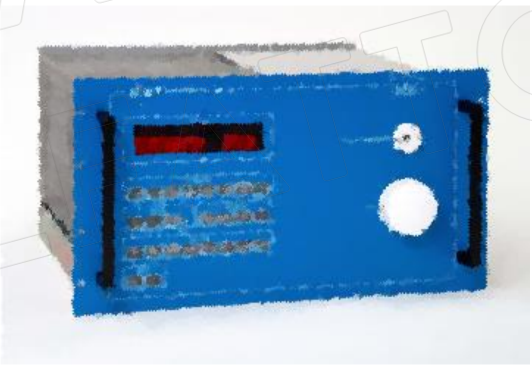


ppm_{eq}
(CH_4, C_3H_8, C_4H_8)



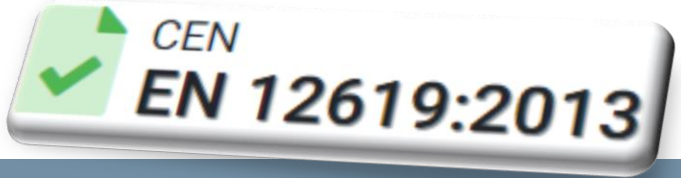
Flame Ionization Detector, FID

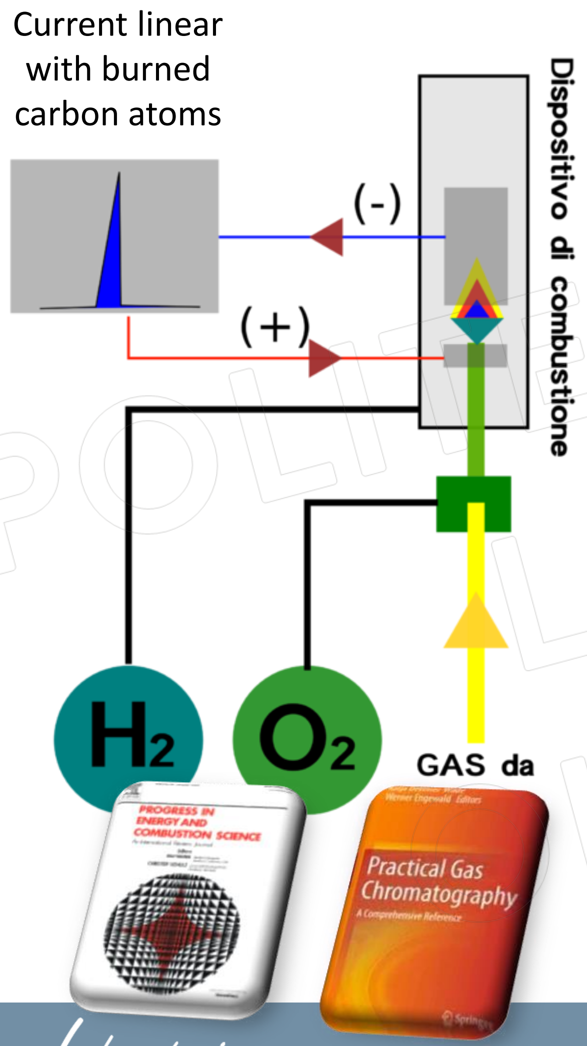




The FID, is a measuring instrument used for the detection of hydrocarbons. It has a linear detection range of 6 to 7 orders of magnitude (10^6-10^7), with a lower detection limit of less than one picogram.

Despite its use as a GC detector for the quantification of organic compounds, the FID is used for Total Organic Carbon quantification (EN12619)





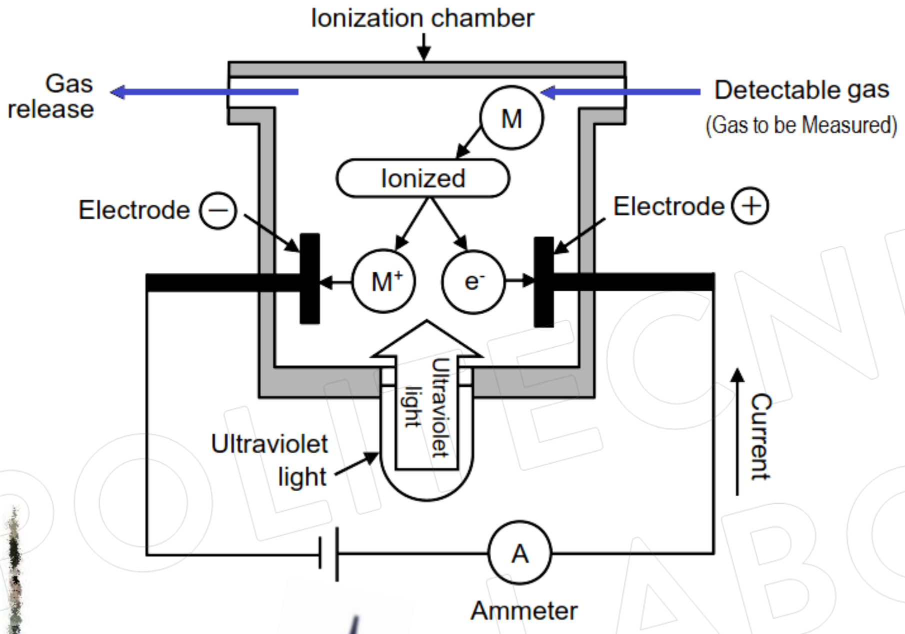
Its limitation is that is not able to discriminate which kind of Carbon atoms is burning:

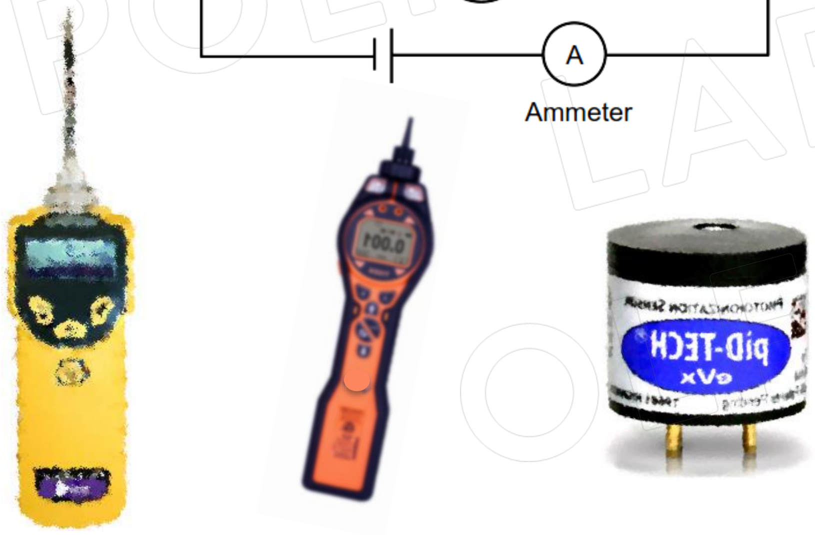
The same FID response [10 mg_C/Nm^3] can be provided for:

Compound	Formula	Conc [mg/m3]	OTV [mg/m3]	OAV
Methane	CH4	13	None	0
Benzene	C6H6	11	8.6	1
Acetaldehyde	CH3CHO	18	0.003	6000
Methyl mercaptan	CH3SH	40	1.38E-04	290000

It cannot discriminate compounds in mix!

PhotoIonization Detector, PID



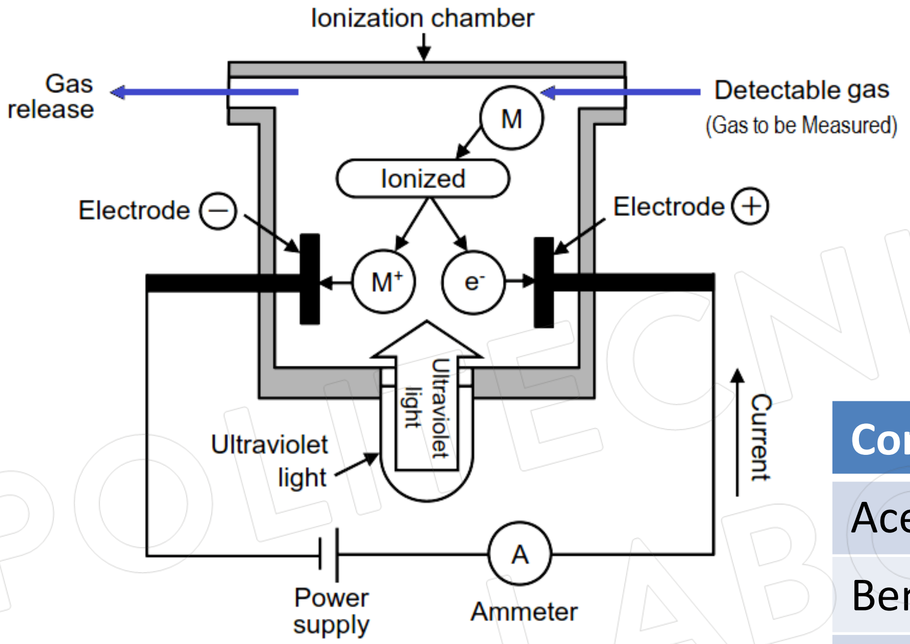


Typical PID measures VOC and other gases in concentrations from sub parts per billion to 10 000 parts per million (ppm).

The PID is an efficient and inexpensive detector for many gas and vapor analytes.

PIDs produce instantaneous readings, operate continuously, and are commonly used as detectors for gas chromatography or as hand-held portable instruments.

PhotoIonization Detector, PID



Its limitation is that is not able to discriminate which kind of molecules is ionizing:

The same PID response [10 ppm_{C4H8eq}] can be provided for (10.6 eV lamp type IONSCIENCE):

Compound	Formula	Conc [ppm]	OTV [ppm]	OAV
Acetic acid	CH3COOH	280	0.006	47000
Benzene	C6H6	5	2.7	2
Acetaldehyde	CH3CHO	60	0.0015	40000
Methyl mercaptan	CH3SH	7	0.00007	100000
Hydrogen sulfide	H2S	40	0.00041	98000
Ammonia	NH3	85	1.5	57
Nitrogen dioxide	NO2	130	0.12	1000

PhotoIonization Detector, PID: response dependence on lamp energy

Chemical name	Formula	CAS no.	IE, eV	Lamp Type (RF)			notes
				11.7 eV	10.6 eV	10 eV	
Isoeugenol	C10H12O2	97-54-1	~9	NA	0.4	NA	
Isoflurane	C3H2ClF5O	26675-46-7	~11	50	ZR	ZR	
Isoheptane	C7H16	591-76-4	9.84	NA	1.2	NA	
Isojasmone	C11H18O	95-41-0	~9	NA	0.7	NA	
Isomenthone	C10H18O	1196-31-2	9.86	NA	0.6	NA	
Isononanal	C9H18O	5435-64-3	~9.6	**0.5**	**0.9**	**1.4**	
Isononanol	C9H20O	3452-97-9	~9.8	1	1.5	NA	
Isooctane	C8H18	540-84-1	9.86	**0.51**	**1.1**	**3.2**	
Isooctanol	C8H18O	26952-21-6	~9.8	1	1.7	NA	
Isopentane	C5H12	78-78-4	10.32	4	4	ZR	
Isopentanol	C5H12O	137-32-6	9.86	**0.8**	**2.0**	**6**	
Isopentene	C5H10	563-46-2	9.12	NA	0.8	NA	
Isophorone	C9H14O	78-59-1	9.07	**1.1**	**0.8**	**1.0**	
Isophorone diisocyanate	C12H18N2O2	4098-71-9	~9	NA	0.6	NA	
Isoprene	C5H8	78-79-5	8.85	[illegible]	[illegible]	[illegible]	
Isopropanol	C3H8O	67-63-0	10.1[illegible]	**2**	**4.0**	**25**	
Isopropanolamine	C3H9NO	78-96-6	~ 9.6	[illegible]	[illegible]	NA	S V X
Isopropoxyethanol, 2-	C5H12O2	109-59-1	~10.3	**0.8**	**1.2**	**1.5**	
Isopropyl acetate	C5H10O2	108-21-4	9.99	**1.1**	**2.4**	**8**	

Non-specific chemical analysis: Pro and cons

Pro

- Possibility of making measurements both at the receptor or at emission
- Low cost, ease of use (PID)
- Continuous measurement
- Possibility to control accidental emissions

Cons

- Unable to correlate with odour concentration (different RF, different OTV)
- Impossible to recognise source (many interferers, no speciation)
- Dependence of results on instrument and sensor type

Humans

- Dynamic Olfactometry (EN 13725)
- Field Inspection (EN 16841)
- Citizen reports

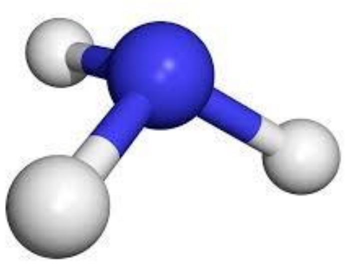
Tools

- Chemical analysis with single compound qualification
- Non-specific chemical analysis
- **Single gas analysis (i.e. H_2S, NH_3)**
- IOMS

Single gas analysis

Inorganic gas analysis at the receptor is an effective approach in cases where low OTV chemicals, e.g. **hydrogen sulphide or ammonia** (not so low OTV), can be detected that may be tractable and representative of the particular odour emission of interest (landfill gas, paper mill waste, livestock, etc.).

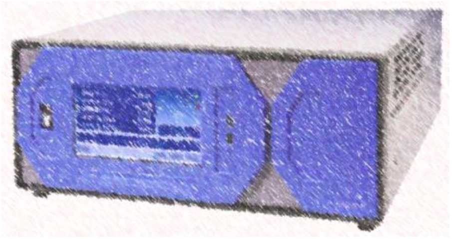
Due to the fact that almost never a single gas is responsible for the odour nuisance, this analysis can be used as a *surrogate analysys:* it is necessary that the ratio between the concentration of the surrogate parameter and the odour concentration is relatively constant and known



Single gas analysis

Analysers up to the olfactory threshold (even to ppb)

- Gold foil H2S analysers
- Chemiluminescence NH3 analysers

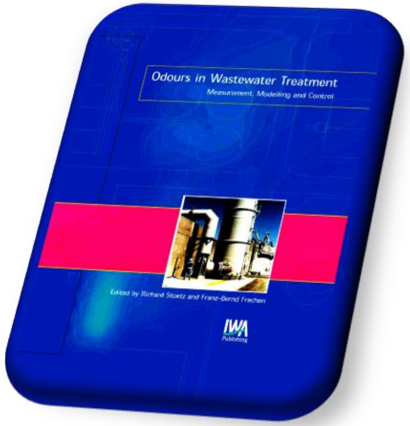


Possibility of using electrochemical cells (much cheaper) but they have high detection limits => not very useful for evaluating odour at the receptor

Single gas analysis: risk of interferences

Table 6.3. Jerome 631-X response to reduced sulphur compounds (Winegar and Schulz 1998).

Compound	Response factor (%)
Hydrogen sulphide	100
Methyl mercaptan	45
Dimethyl disulphide	40
n-propyl mercaptan	40
Carbonyl sulphide	36
t-butyl mercaptan	35
n-butyl mercaptan	33
Diethyl sulphide	25
Diethyl disulphide	17
Tetrahyrothiophene	10
Dimethyl sulphide	7
Thiophene	0.8
Carbon disulphide	0.01



Single gas analysis: risk of interferences

Ref	Gas	POD detection range, ppm	pins	bias	Position compatibility	Resolution*, ppm	LOD*, ppm	Application	Interference, +/- % of reading in presence:
03	NH_3	1875	3	0	A1 type	0.5	1.5	High concentration	-30% SO2
04	NH_3	3750	3	0	A1 type	1	3	Wery high concentration	-60% SO2
05	H_2S	10	3	0	A1 type	0.01	0.03	High sensitivity, High temperature	-10% SO2; -35% NO2
06	H_2S	13	3	0	A1 type	0.01	0.03	High sensitivity	-30% NO2; -25% Cl2; +10% SO2
07	H_2S	188	3	0	A1 type	0.1	0.3	High concentration	-20% NO2; -15% Cl2; 20% NO; +20% SO2
10	NO_2+O_3	15	3	0	A1 type	0.01	0.03	Very high sensitivity, NO2+O3 total detection, H2S filter	+100% Cl2
11	NO_2+O_3	25	3	0	A1 type	0.015	0.045	High sensitivity, NO2+O3 total detection, H2S filter	+100% Cl2
12	SO_2	38	3	0	A1 type	0.01	0.03	High sensitivity	-130% NO2; -60% Cl2; +40% C2H4
13	SO_2	30	3	0	A1 type	0.01	0.03	High sensitivity, Low interference	-100% NO2; -20% Cl2
14	SO_2	75	3	0	A1 type	0.02	0.06	High concentration	-100% NO2; -40% Cl2
16	NO	38	3	300	A1 type	0.015	0.045	High concentration	+10% H2S; +2% NO2, +3% SO2
17	NO	38	3	300	A1 type	0.015	0.045	High concentration	+15% NO2; 25% H2S

Single gas analysis: Pro and cons

Pro	Cons
Low cost, ease of use (electrochem)	Difficult correlation with odour concentration
Possibility to make measurements at the receptor	Need for a source with a particular type of emission
Possibility for incidental emission control (where tracer gas is present)	Dependence of results on instrument and sensor type (possible interactions)
Continuous measurement	High costs (gold plate, chemilum)

Humans

- Dynamic Olfactometry (EN 13725)
- Field Inspection (EN 16841)
- Citizen reports

Tools

- Chemical analysis with single compound qualification
- Non-specific chemical analysis
- Single gas analysis (i.e. H_2S, NH_3)
- **IOMS**


HELP ME OBI WAN KENOBI
IOMS
YOU'RE MY ONLY HOPE

Q&A

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