Issues around field measurements with electronic noses : low concentration and specificity of odorous compounds

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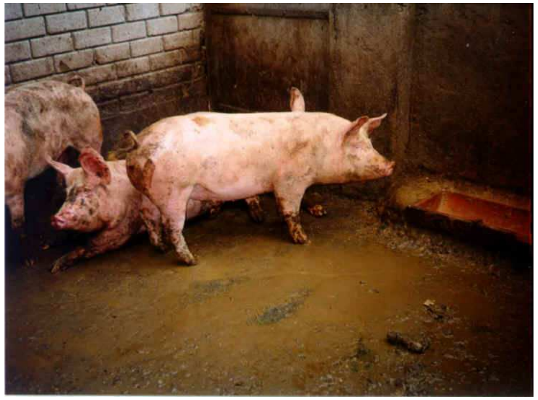
Main research topic : assessing the odour annoyance generated by different industrial or agricultural sources in the environment.

Landfill sites

Compost facilities

Waste water treatment plants

Settling ponds of sugar factories

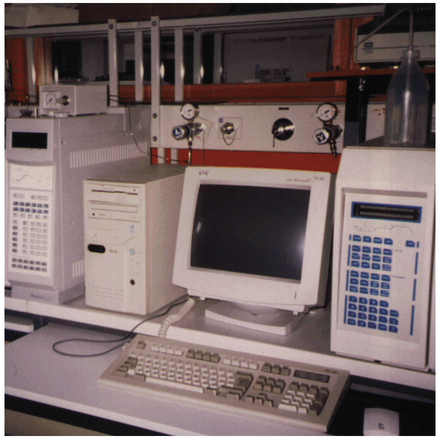


Piggeries, hen-houses

Detection of moulds in buildings

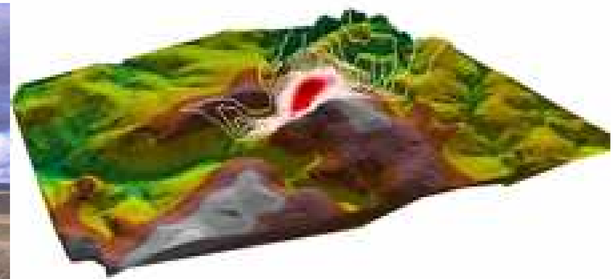
Different tools :

Lab analysis (GC-MS)



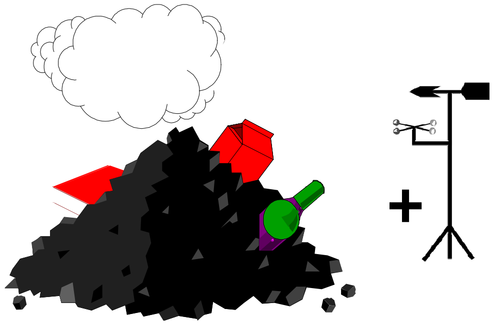
Dynamic olfactometry

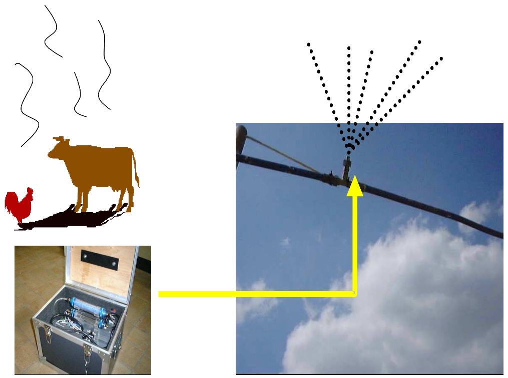
Field inspection + atmospheric dispersion modelling

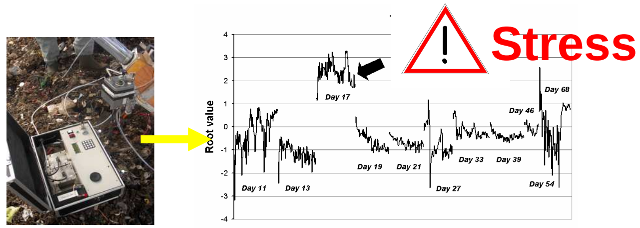


… and electronic nose

Very promising possibilities







Monitoring odour emission and trying to predict and measure odour annoyance in the surroundings

Controlling odour abatement system

Using the odour as a process variable to detect failures

Preconcentration is necessary to improve the detection performance of e-nose and to broaden the range of possible applications of e-nose in the environment

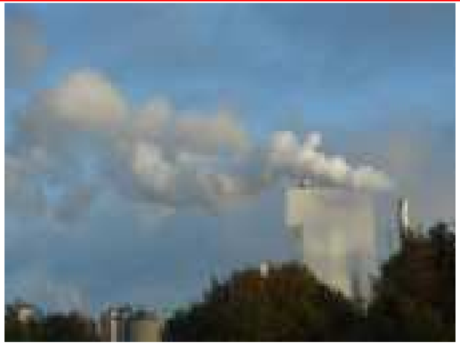
Only final users

➔Our role in a possible project =

expliciting the specifications of a "field preconcentrator"

- ➔ specifying the range of odour and VOC concentration observed in the field
- ➔ keeping in mind the relation between chemical composition and odour
- ➔ identifying key compounds particularly involved in odorous mixtures
- ➔ selecting material and condition of operation to avoid the risk of denaturing the sample
- ➔ choosing adequate sample time preconcentration to insure fast response for a dynamic odour detection
- ➔ testing prototypes in the field

1. Concentration comes down below the limit of detection of gas sensors

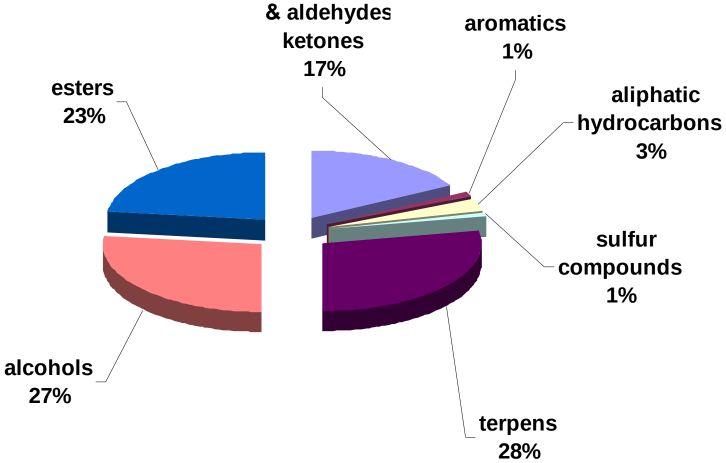


At the emission level, or in the immediate surrounding, an electronic nose is able to detect and to recognise an odour, but not in the environment.

Typical chemical composition ?

Composting facility

Waste water treatment



Nitrogen compounds	Ammonia Dimethylamine Methylamine Ethylamine Skatol Indole Cadaverine
Sulfur compounds	Dimethylsulfide Methanthiol Ethanethiol Hydrogen sulfide
Organic acids	Acetic acid Butyric acid Valeric acid
Aldehydes	Methanal Ethanal Buthanal
Ketones	Acetone

Typical chemical concentrations at the emission ?

Composting facility

Compound examples	ppm(v)
3-methyl-butanal	0.022
Butanoic acid, ethyl ester	0.019
2-butanol	0.038
Phenol	0.044
Ethyl-acetate	0.065
1-propanol	0.114
2-butanone	0.116
Limonene	3.340
Ethanol	1.155

Waste water treatment *(sludge stabilization)*

Compound examples	ppm(v)
Ammonia	25
Toluene	0.290
Dimethyl sulfide	0.360

Slaughterhouse*)*

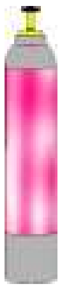
Compound examples	ppm(v)
Dimethyl disulfide	0.007
Dimethyl trisulfide	0.005
Tetramethyl pyrazine	0.001
Acetone	0.001

➔Rarely above 1 ppm(v)

➔But e-nose reacts on global volatile emission

➔Sum ? ➔ not representative of the global e-nose response

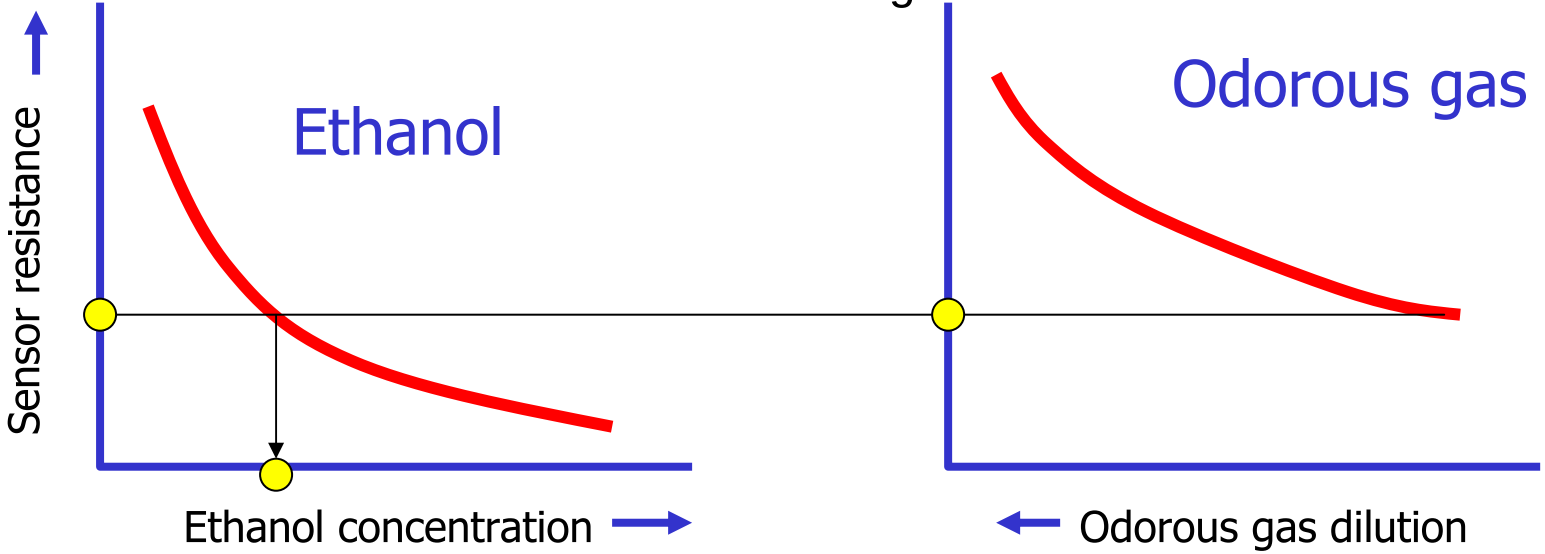
➔ not representative of the odour concentration

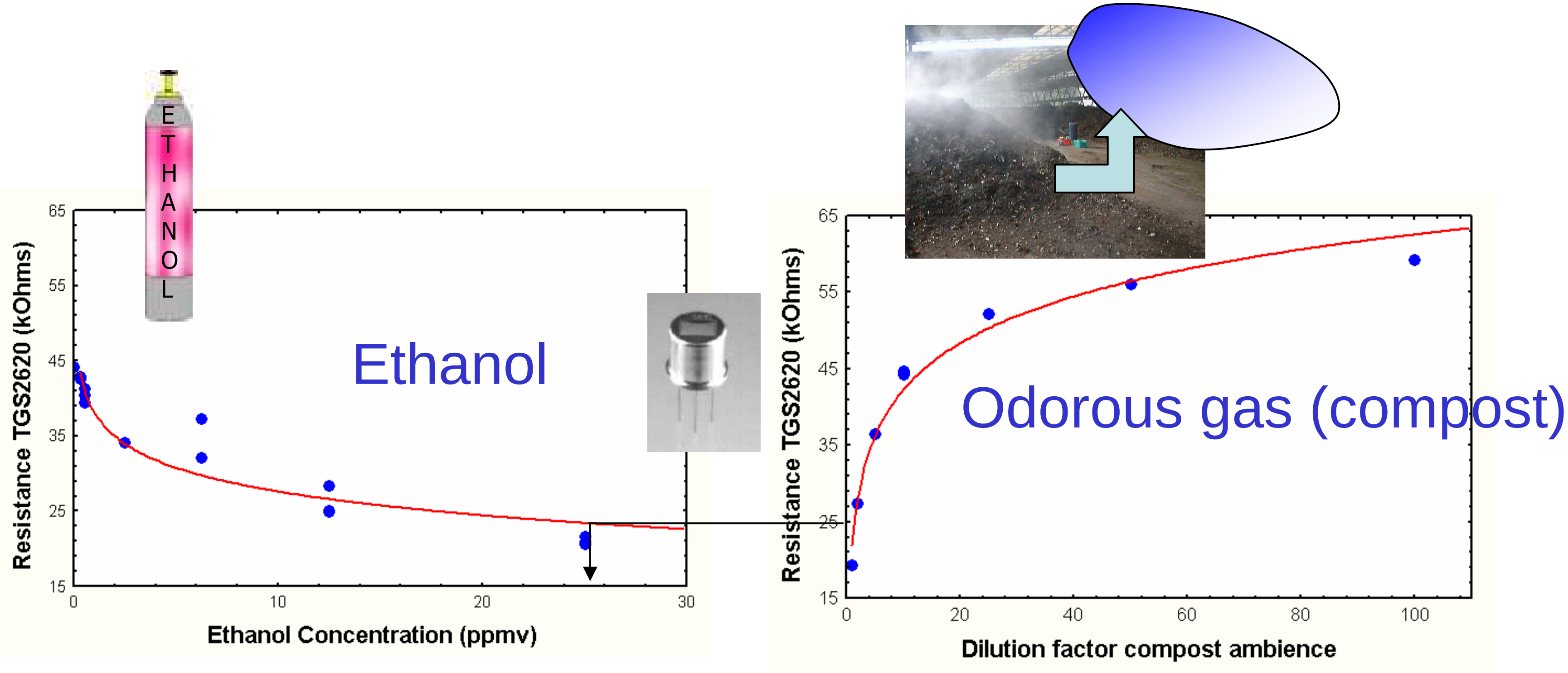


To have an idea of the order of the "global chemical concentration" detected by the sensor array

➔ Finding an equivalence between the global "chemical concentration" of the odorous gas mixture and the concentration of ethanol vapour

➔ Common features = sensor signals





➔ 1 … 25 ppmv ethanol-equivalent

Limit of detection in "ethanol equivalent" ?

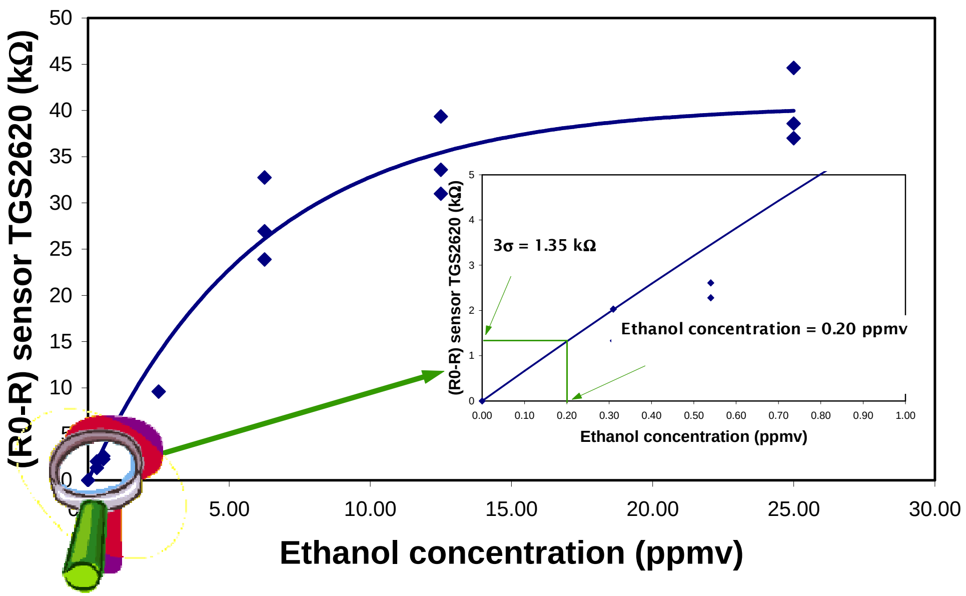
Limit of detection ➔ signal-to-noise ratio S/N = 3

Noise = standard deviation σ of the stabilised signal (e.g. in kΩ)

For our configuration ➔ $\sigma \in [0.07, 1.8 k\Omega]$ according to the sensor type

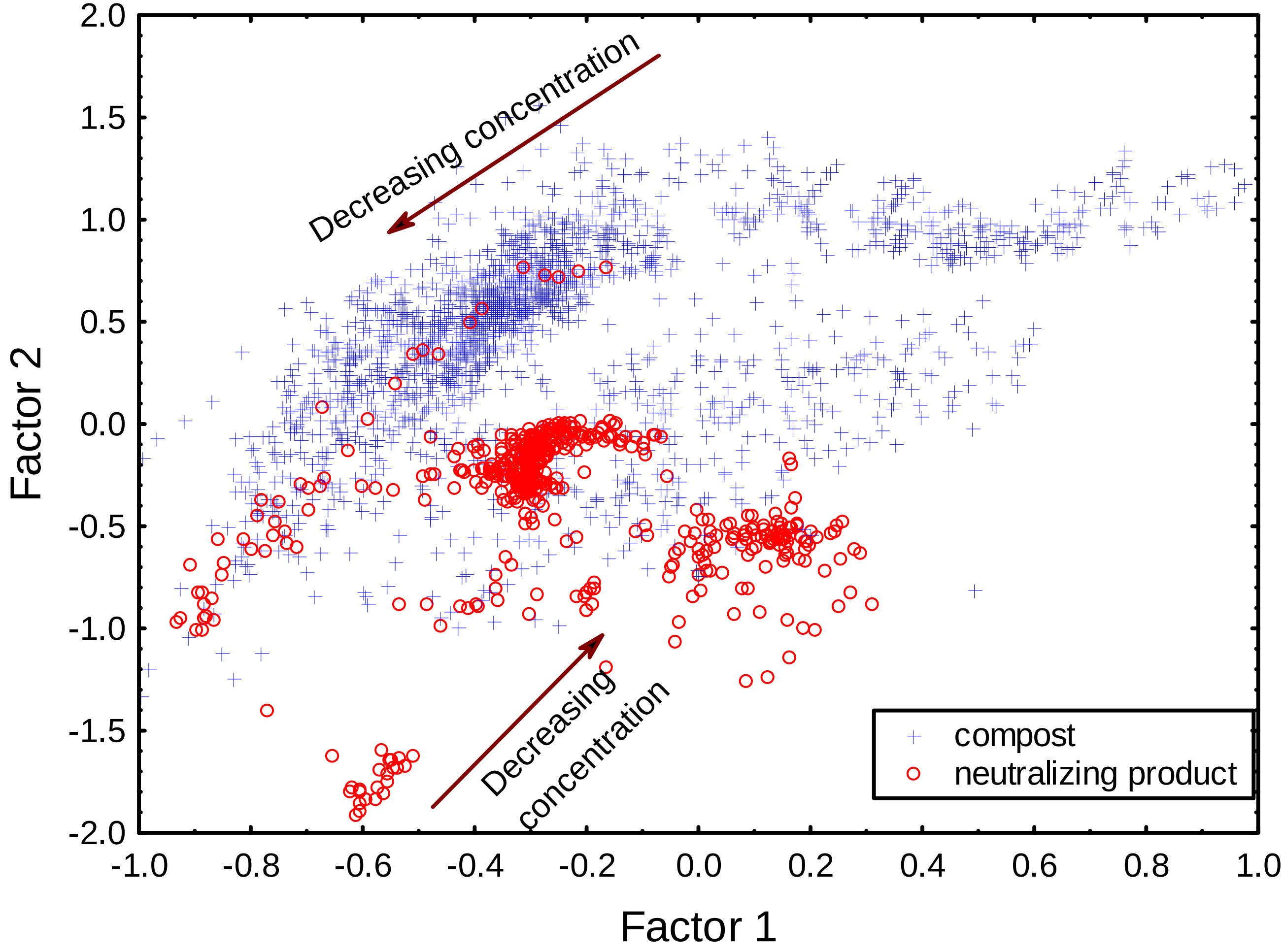
Corresponds to 0.04 … 1.03 ppm(v) in ethanol equivalent

Or to a dilution of 40…100 for a typical compost sample



… and the limit of resolution may still be higher

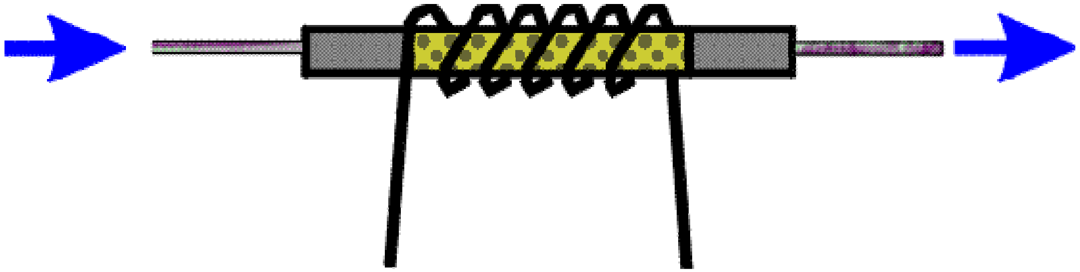
(e.g. recognition of compost odour among others)



Far away from the source the "global" concentration comes down below the limit of detection of gas sensors

10 ppm … 1 ppm … 100 ppb … 10 ppb

Improving the sample uptake is essential



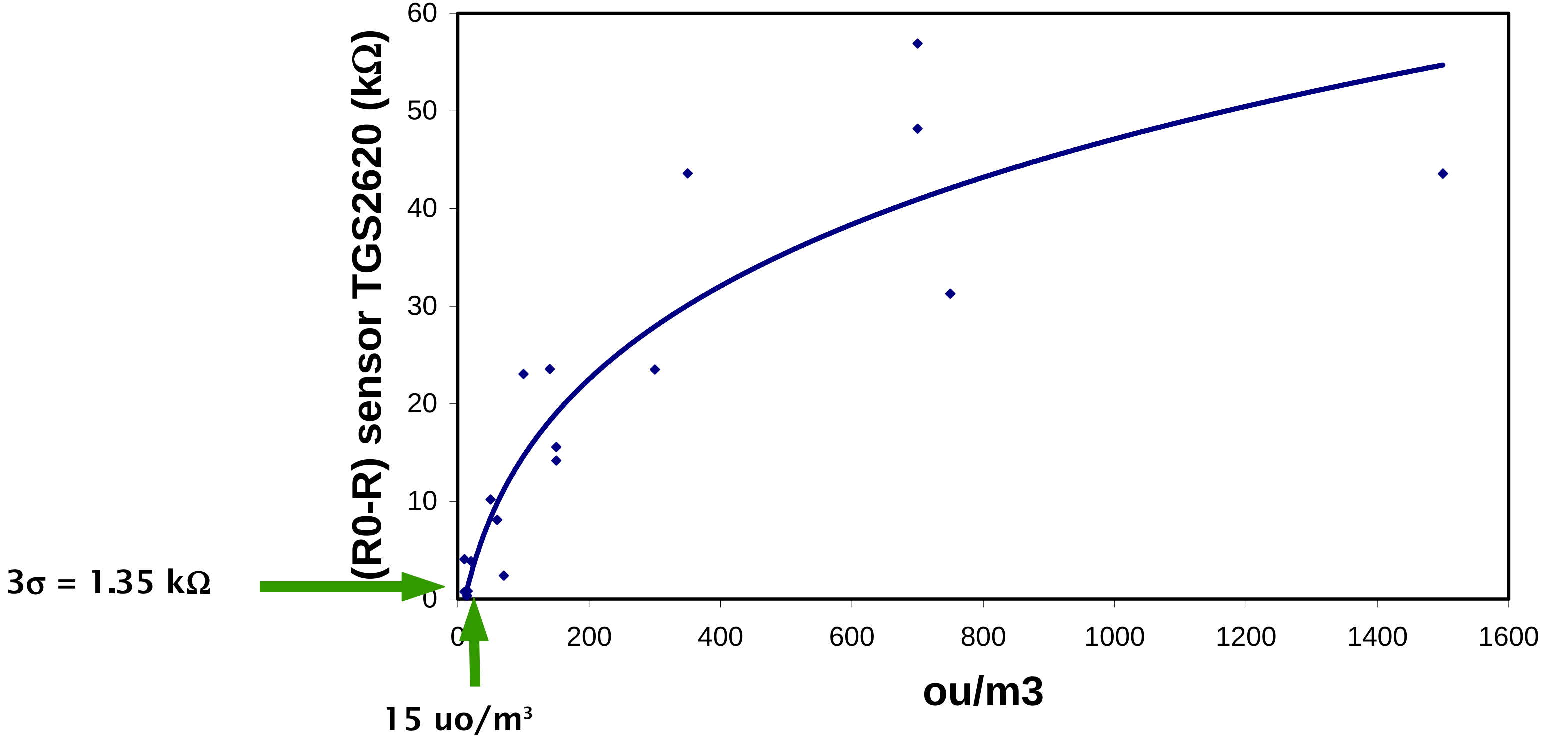
Correspondance with "odour concentration"

Measurement method : dynamic olfactometry

Assessment of odour concentration expressed in ou/m^3

1 ou/m^3 = perception threshold

"Calibration curve" between odour concentration and sensor signals



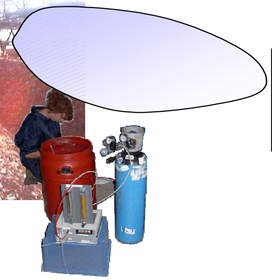
For compost emission, the odour concentration corresponding to the limit of detection of the sensors is low and close to the odour perception threshold of human nose, defined as 1 uo/m3.

For the different sensors : from 10 to 80 ou/m3.

1. Concentration comes down below the limit of detection of gas sensors

2. Risk of denaturing the sample

Very important for odour measurement (olfactometry) to avoid interaction between sampling material and sampled air



The bag must be

➔odour free

➔without reaction or adsorption with the sample

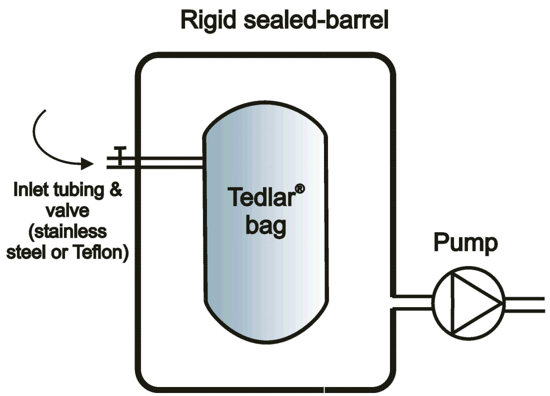
➔impervious, to prevent significant losses before measurement

Pumping system cannot interact with the sample

➔Tedlar® bags (PVF)

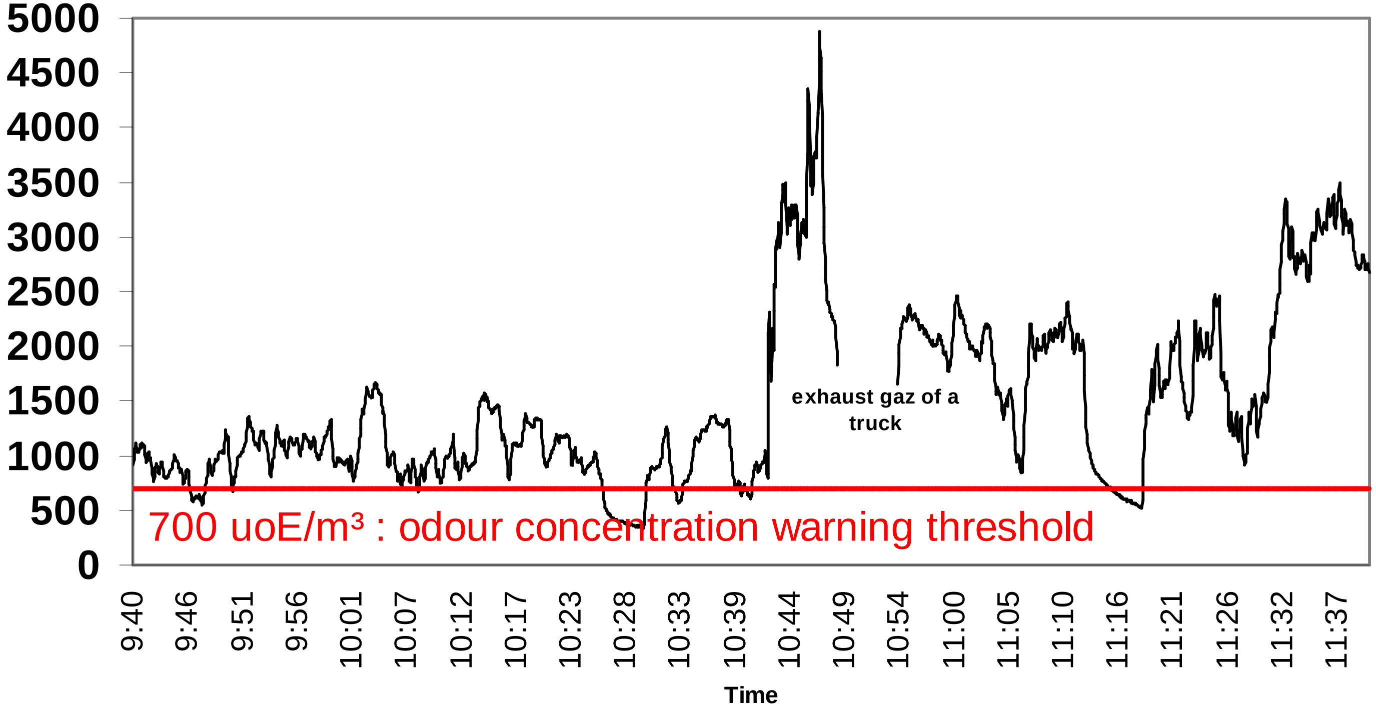
➔Sealed-barrel maintained under negative pressure

➔Air drawn into the bag by the pressure difference



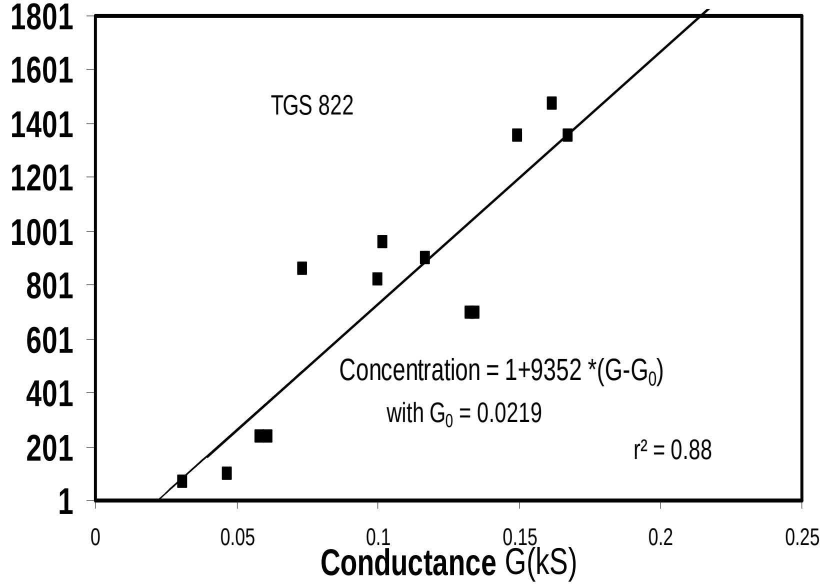
➔ ideally, same precautions for a preconcentrator at the e-nose inlet

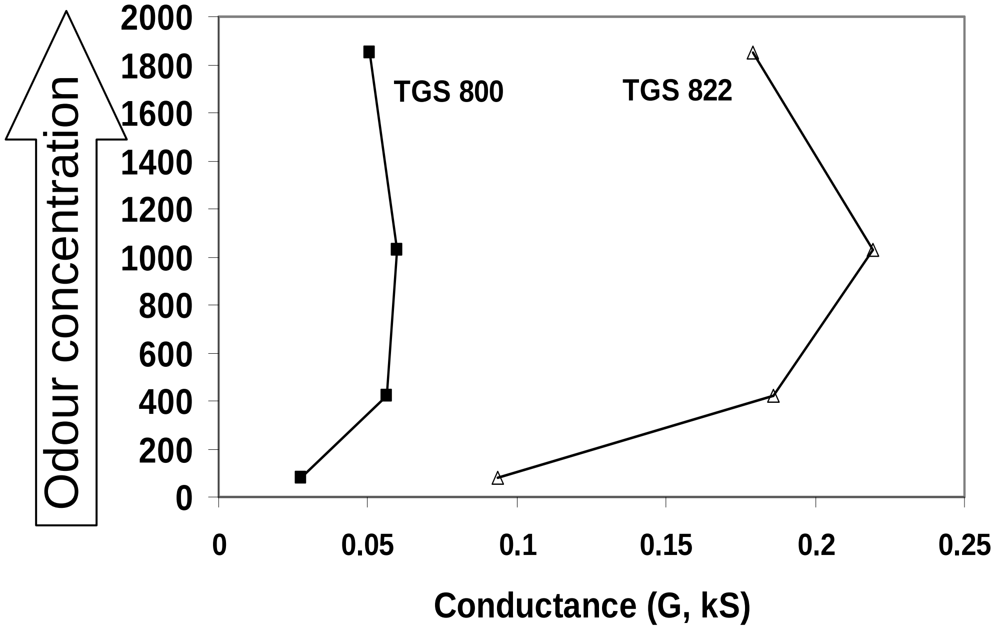
Purpose of e-nose : recognising an odour (e.g. compost emission) and monitoring it
e.g. : detecting that the odour level is over a "warning threshold"



But : gas sensors respond to both odorous and odourless compounds

➔ The global e-nose signal ≈ "odour" if "chemical" concentration is correlated to odour concentration





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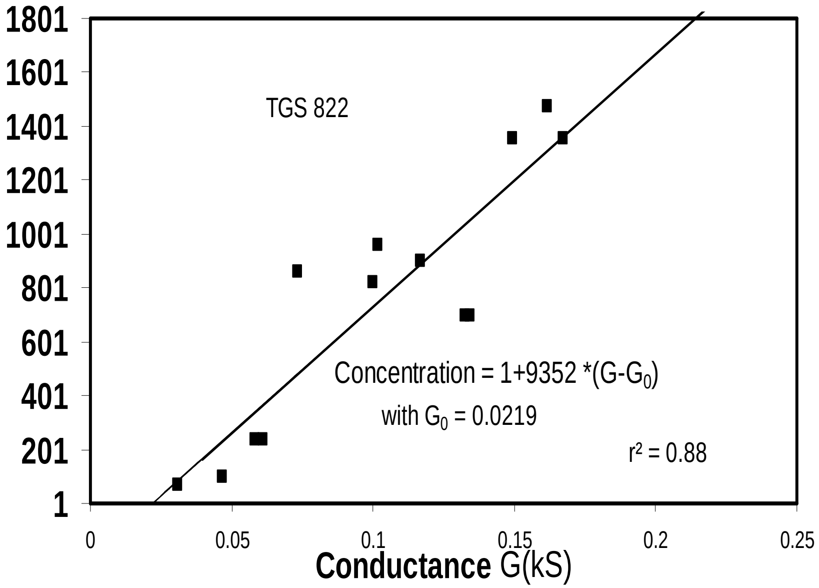


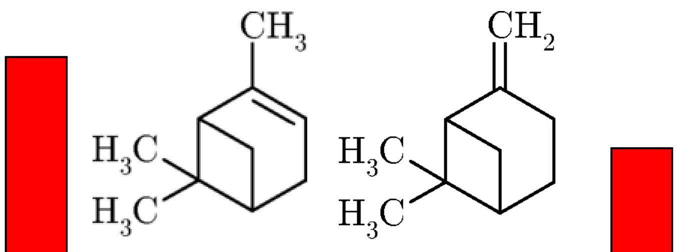
Odour concentration

Keeping that relationship after preconcentration

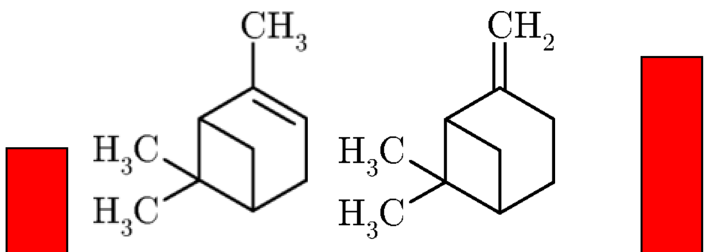
Sometimes : no specific compound but characteristic "signature"

Example (indoor air pollution) :
detection of mould contamination of wood material

Typical fungal signature ("musty smell") does not necessary involve new specific compounds with respect to original material



α-pinene β-pinene



α-pinene β-pinene

In indoor air, simple sampling is not sensitive enough for the VOC detection

➔Requires pre-concentration

➔Best = active sampling process

➔But suitable analyte recovery is essential

In some cases, selective pre-concentration could also be interesting

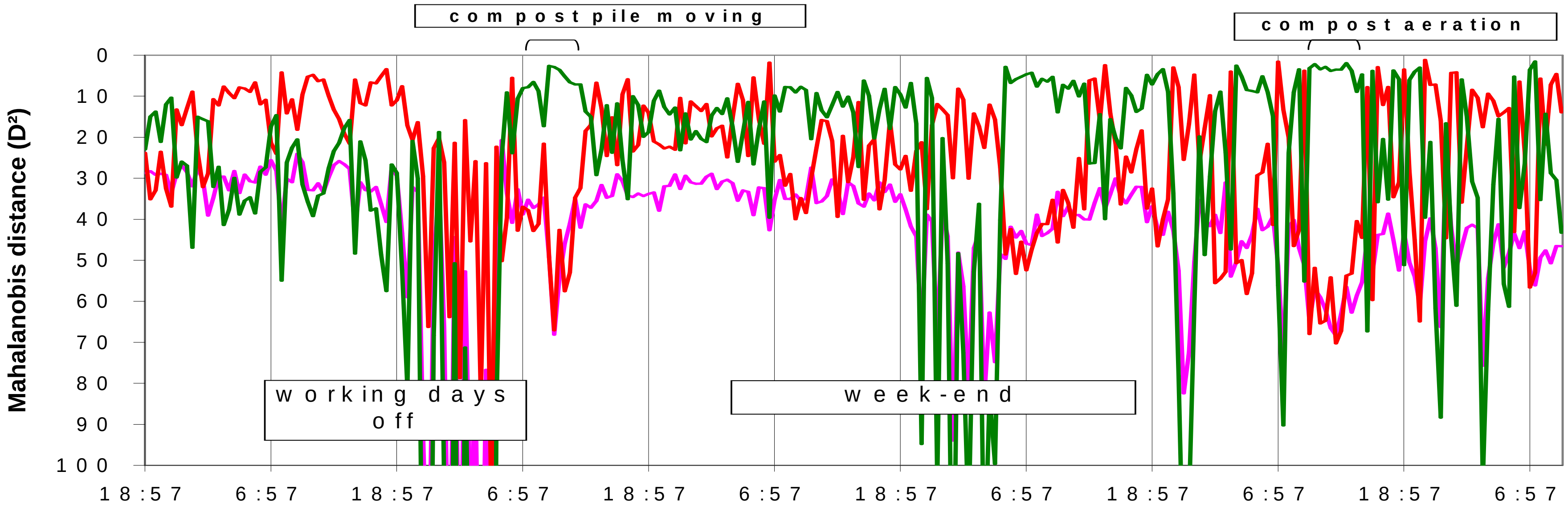
If the recovered chemicals are precisely those which are typical of the odour or pollution

1. Concentration comes down below the limit of detection of gas sensors

2. Risk of denaturing the sample

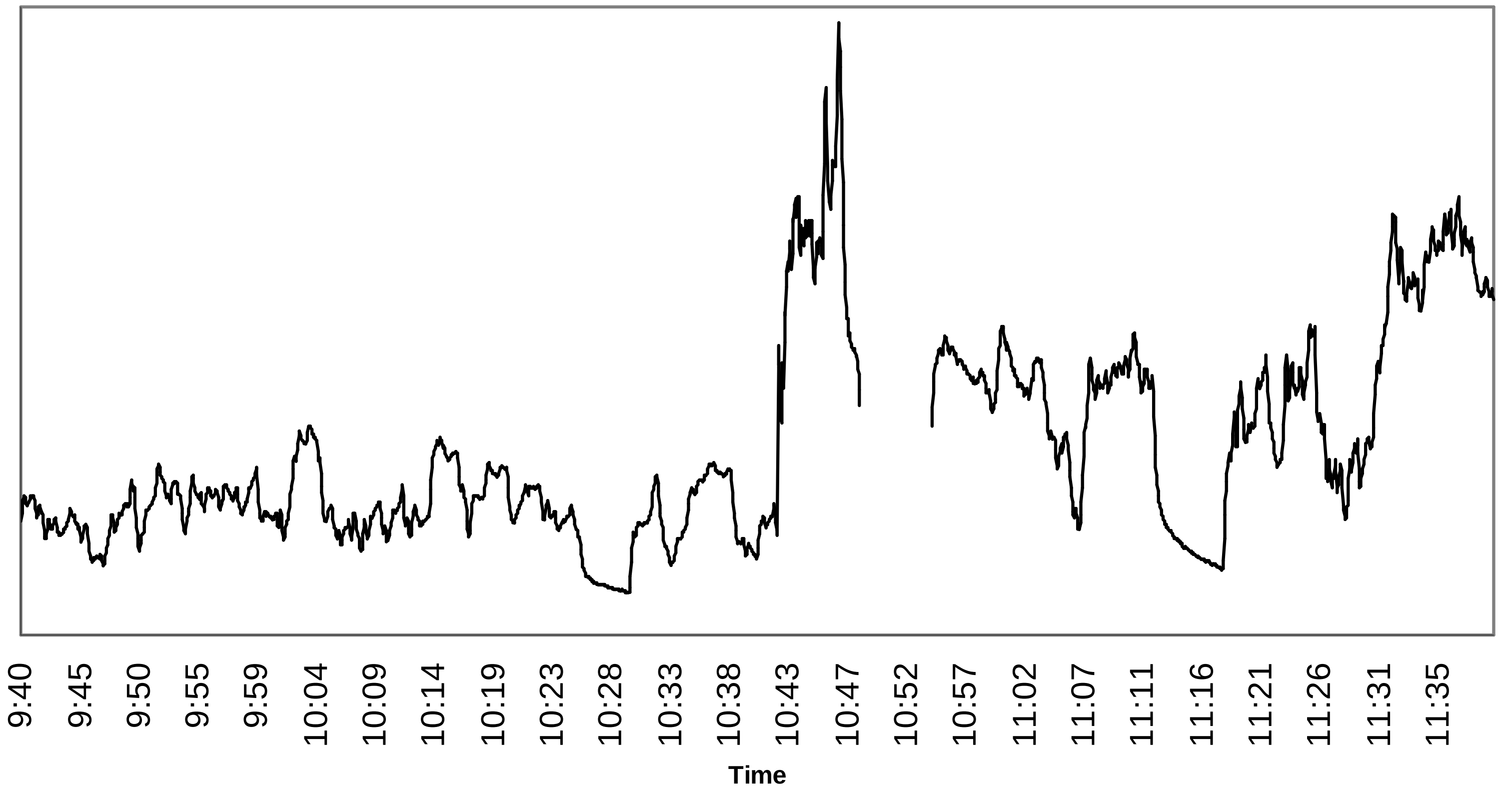
3. Preserving the dynamics of the detection

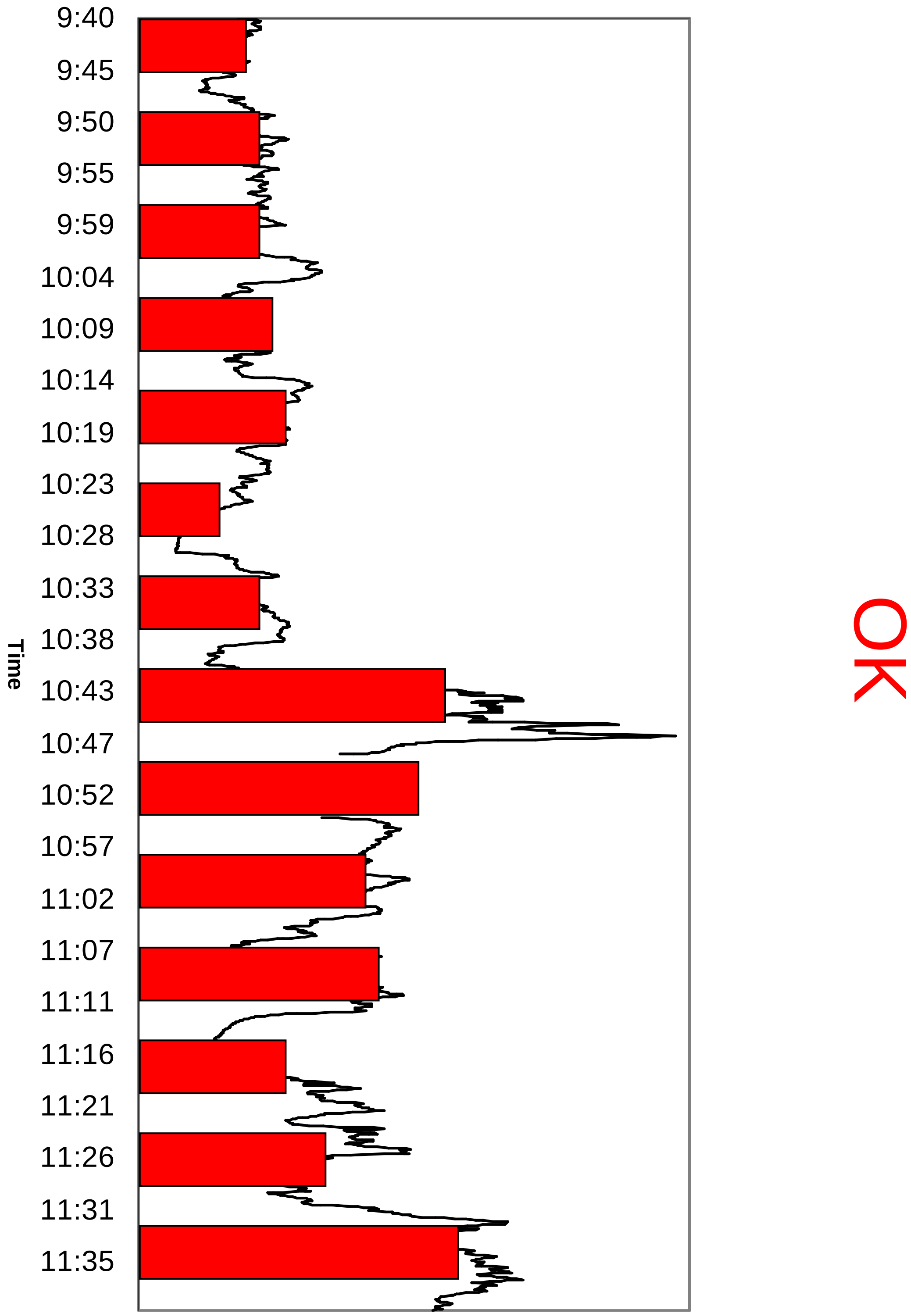
Continuous monitoring



Ideally

- Pre-concentrator should work continuously with improved cycling time to allow a greater number of samples to be analyzed in a given time period.




9:40
9:45
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10:04
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10:19
10:23
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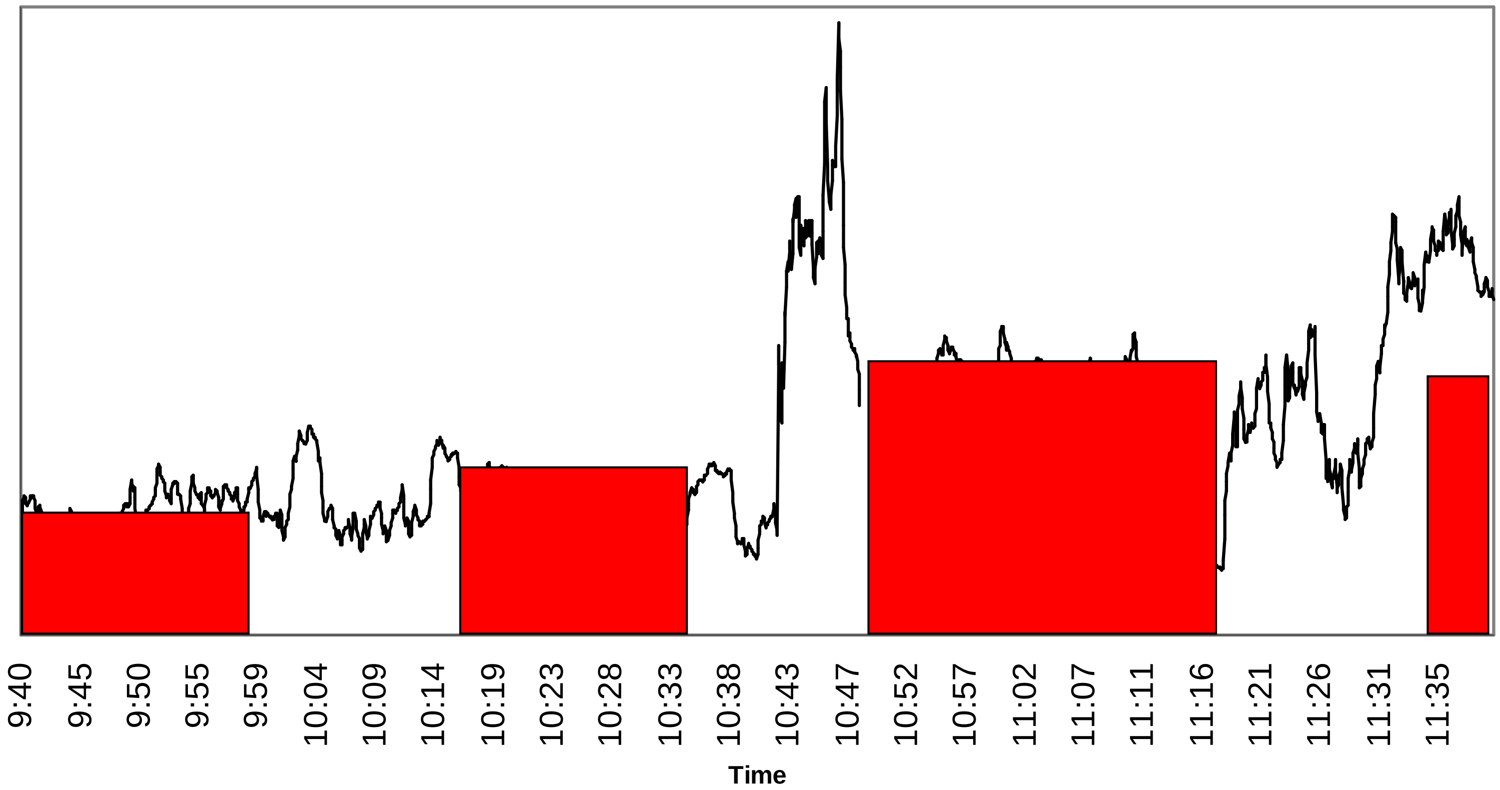
10:33
10:38
10:43
10:47
10:52
10:57
11:02
11:07
11:11
11:16
11:21
11:26
11:31
11:35
Time
OK

Too much "filtering"



Conclusions

Pre-concentration is needed for many applications of ambient gas monitoring in the environment (odour, indoor air pollution, …) with electronic nose

- ➔ gas concentration is often below the limit of detection of sensors

Final users may contribute to the development

- ➔ writing the "specification sheet"
  - ❑ typical gas composition and concentration of ambiences
  - ❑ relation chemistry/odour
  - ❑ dynamics of gas monitoring in the field
  - ❑ …
- ➔ testing prototypes
  - ❑ in the lab
  - ❑ in the field