International Gas Union Research Conference 2011

NEW METHODOLOGIES TO HELP NATURAL GAS ODORISATION.

Author:
F. Cagnon
GDF SUEZ – DRI-GRIGEN
France

ABSTRACT

Although gas odorisation is used since the beginning of the gas industry as a key measure to ensure the safety of gas distribution, the odorants used have not readily changed since the introduction of Thiophane (THT) and TertioButylMercaptan (TBM). One of the reason is that human olfaction is still not very well understood, a major breakthrough on its understanding dating back only about 20 years. The complexity of its functioning means that although the industry is able to measure odorant concentration in the gas in a satisfactory manner, we still don't have any instrument able to measure an odour.

The legal requirements ask that distributed gas has a detectable and characteristic smell gas companies. Thus gas companies have to rely on human noses to demonstrate that it is achieved. However, the poor reproducibility of the olfaction added to the lack of standardised procedures means that it is quite difficult to compare and understand results produced by different laboratories.

When traditional odorants are used, the experience of the various gas companies using them can be brought forward as an additional mean of demonstration. If one wants to introduce a new odorant this becomes paralysing. Thus gas odorisation is a conservative activity.

This paper presents the potential advantages coming from the implementation of standardised procedures and gives examples of some new developments in the field.

1. INTRODUCTION

Gas odorisation was born with the gas industry. Town gas was odorised thanks to the presence of reduced sulphur and distillate residues giving it a peculiar smell and enabling the detection of leaks. The introduction of natural gas didn't readily change that picture although the lack of odoriferous compounds in most treated gases meant that once natural gas is processed to pipeline quality it generally is devoid of any smell. Thus odorants have been developed and are added to the gas as trace elements in order to achieve what is now a legal requirement all around the world for distributed gas: **It shall smell!**

This legal requirement can be formulated in various ways but fundamentally it states that:

- The smell of gas shall be perceived before the gas concentration builds up to significant level, the one fifth of the LEL (Lower Explosive Limit) being often the target.
- The smell of gas has to be characteristic in order not to be confused with smell existing in the environment.

The way to achieve this target may be stated in standards or technical codes (*[1]*, *[2]*, *[3]*) but it is usually up to the gas companies to define their procedures for odorising the gas and for checking that the requirement is fulfilled. As odorisation is a complex matter where mistakes have a disastrous impact, new developments are difficult and often the subject is treated as "If it is not broken, don't fix it!". One of the issues is that it is quite difficult for gas companies to share their experience. Some recent methodological developments are discussed in this paper that could help pooling the experience and thus ease the development of new odorant or practices.

2. THE SENSE OF SMELL

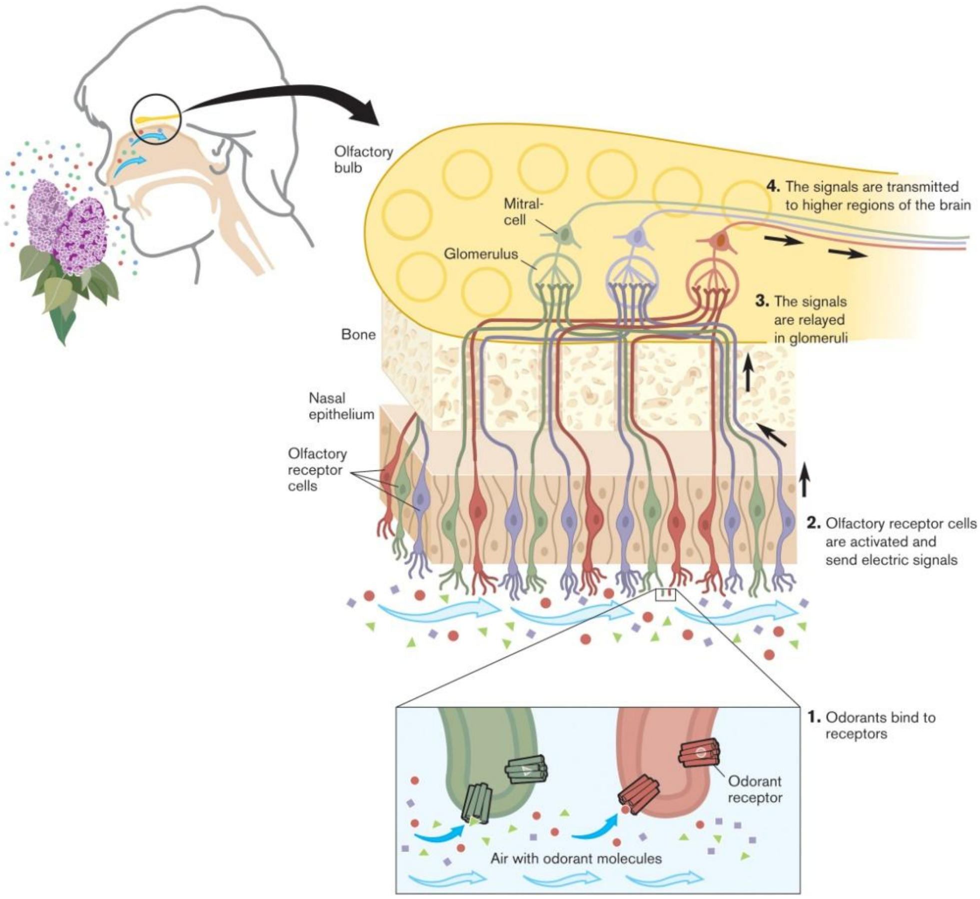
The sense of smell is shared by a lot of earth species. First communication means for social insects, primary tools for hunting or detecting hunters for mammals, the sense of smell is not knowingly a major sense for humans. Nevertheless it is a key element in the pleasures associated with food, in the recognition of kin's and it is found as being closely associated with the brain structures linked to emotional states and memory. Although they are said to be able to discriminate more than 10 000 different odours, some even say 400 000, without training human beings are just able to share about smells in terms of pleasure and strength. All other discourses about odours are based upon the relationship of the smell with its support, i.e. "*it smells as a rose/an apple/...*." Significantly human languages have no words uniquely dedicated to naming odours as we have for colours for instance.

A key insight to the olfactory system was given in the 1990's by L. Buck and R. Axel (Nobel Prize in 2004) when they discovered the gene family coding the olfactory receptor's proteins. These genes, representing about 3% of the human genome, allow for the production of thousands of different receptors each one able to interact with a small number of molecules. Similar receptors types are connected to particular micro structure in the olfactory bulb called glomerulus. Thus the odorant molecule will activate some type of receptors that will in turn stimulate the corresponding glomeruli generating an activation pattern in the olfactory bulbs. This pattern is interpreted by the brain and associated with a smell through experience and learning (see Figure 1).

The complexity of the olfactory sense means that for the time being no instrument has been built able to measure a smell. Gas chromatograph can measure the concentration of an odorant molecule in a gas but says nothing about the actual smell. This can be easily demonstrated if more than one odorant molecule is present. Although the individual concentrations of odorants would be known it is not possible to induce from those the resulting odour unless one has a previous experience of the smell. The *electronic noses* which are built around an array of non specific gas detectors those signals are interpreted via a formal neuronal network are called as such more because their operation is mimicking the nose than because they are able to smell. Their first generation for instance was based on semiconductors sensors which sensitivity to water vapour and alcanes is well known, unlike that of human nose.

This obviously puts a limitation to daily work around gas odorisation as the gas industry has no instrument able to demonstrate easily that the gas smells. Thus, although it is easy to demonstrate that the odorisation is "nominal" it is difficult to demonstrate that it is adequate. Furthermore any new development about odorants has to go through the tedious path of human jury assessment, extensive laboratory testing and field testing. That may be a reason why gas odorisation is quite conservative.

Figure 1: Odorant receptors and the organization of the olfactory system (Nobelprize.org)



3. GAS ODORANTS: ARE THEY EVOLUTION FORESEEN?

The first odorants were sulphides and mercaptans obtained as by-product of the oil industry *[4]*. In the 1940's and 1950's the chemical industry started to produce tertioButylMercaptan (TBM) and Thiophane (THT) that are still the main odorants for natural gas. Interesting to note that TertioButyl Mercaptan was a by-product of di-tertiary Butyl Sulfide used during the Second World War to recycle natural rubber.

Thiophane is quite odorant when compared to other sulphides although its smell is quite low relatively to mercaptans. Its main advantages are that it can be used pure and that it is a very stable molecule. It is the sole odorant that is used as a pure substance which is an asset for evaporation odoriser. It means also that the analytical control of its concentration in the gas allows for a direct relationship with the smell of the gas assuming that no interfering molecule could change its smell. This is generally the case with natural gases as it has no odour or, if it has, it is due to sulfides or mercaptans that would enhance the smell.

Its main drawback is that it can get adsorbed on material surface leading to a loss of smell when commissioning new pipelines. This means also that when a gas leak occurs on underground networks some odorant could be adsorbed by soil. Although significant amount of adsorption have been observed in laboratory experiments *[5]*, they also have shown that moisture is heavily limiting the amount of THT that can be adsorbed. In practice this means that real leaks in normally wet ground will not adsorbed so much THT that a gas leak could go undetected.

TertioButylMercaptan is, as all mercaptans, very odorant. It is also the most stable of all mercaptans which are known to react with oxygen, coming from for instance by iron oxide, to form disulphides with little odour. Unfortunately its freezing point is so high, 0°C, that it can't be used as a pure substance and has to be mixed with other mercaptans or sulphides which can be bringing additional smell but can also be considered as mere antifreezing agents. For this reason TBM is a widely used odorant for natural gases but always in a mixture, with sulphides as DimethylSulphide (DMS), MethylEthylSulfide (MES) or THT or with other mercaptans, one famous mixture being 80-85% TBM with isopropyl an n-propyl mercaptan.

These odorants, THT and TBM blends, have been odorising all gases distributed in the world for the last 40 years with a very good record. Although their use has been sanctioned by history and experienced rather than by systematic laboratory studies they are considered as giving a characteristic odour to the gas.

In the last years they have been starting to be questioned because of their sulphur content. Sulphur represents about a third of the mass of THT or TBM. Depending on the odorant used the added sulphur coming from odorisation varies from +2 to +5 mgS/m^3 for TBM blends and + 10 mgS/m^3 for THT when the usual amounts are used. This is quite a small amount, for instance the added SO_2 emissions coming from gas odorisation in Europe where pure THT is the preferred odorant represents only about 0.2 % of Europe anthropogenic sulphur dioxide emissions. Nevertheless it may be a drawback for some applications:

- Fuel cells whose catalyst may be poisoned by sulphur with a reduced lifetime,
- Natural gas vehicle application, where the oxidised sulphur may poison the catalytic material of the exhaust.

These reasons are enticing the development of low sulphur odorants. In Japan where the fuel cell application is targeted, Tokyo Gas is substituting its traditional TBM:DMS blend by a mixture of TBM in cyclo-hexane. This change is quite straightforward as the smell is not dramatically modified, TBM being the main odorant in the two products. DMS is not very odorant and cyclo-hexane is virtually non odorant when compared with TBM. With that change the sulphur content of the gas should come from $\approx$4.4 mgS/m^3 to $\approx$1.8 mgS/m^3 as the LNG's supplied in Japan are totally sulphur free.

In Germany a more drastic approach has been undertaken with the development of a sulphur free odorant. This proposal, a mixture of acrylates and methylethylpyrazine called GASODOR® S-Free, has been first introduced in test fields about 10 years ago and has found some measure of success since *[6]*. True to its name it is totally without sulphur but its odour is quite different to that of the traditional sulphured odorants. This means that a change to this new product shall be made cautiously with accompanying information to the population. Furthermore one can question its ability to give a characteristic odour to the gas *[7]*.

These evolutions could lead to a renewal of research on gas odorant following those that were made in the 1970's *[8]*. At that time the main issues were already sulphur but also the loss of odorant in the pipe or ground and the best answers were found to be TBM blends.

4. IS MY ODORISATION MEETING THE REQUIREMENT?

4.1. IS THE ODOUR CHARACTERISTIC?

Regulation requirements are twofold. The odour shall be characteristic and it shall be detectable, some say *"readily detectable"*, by the public.

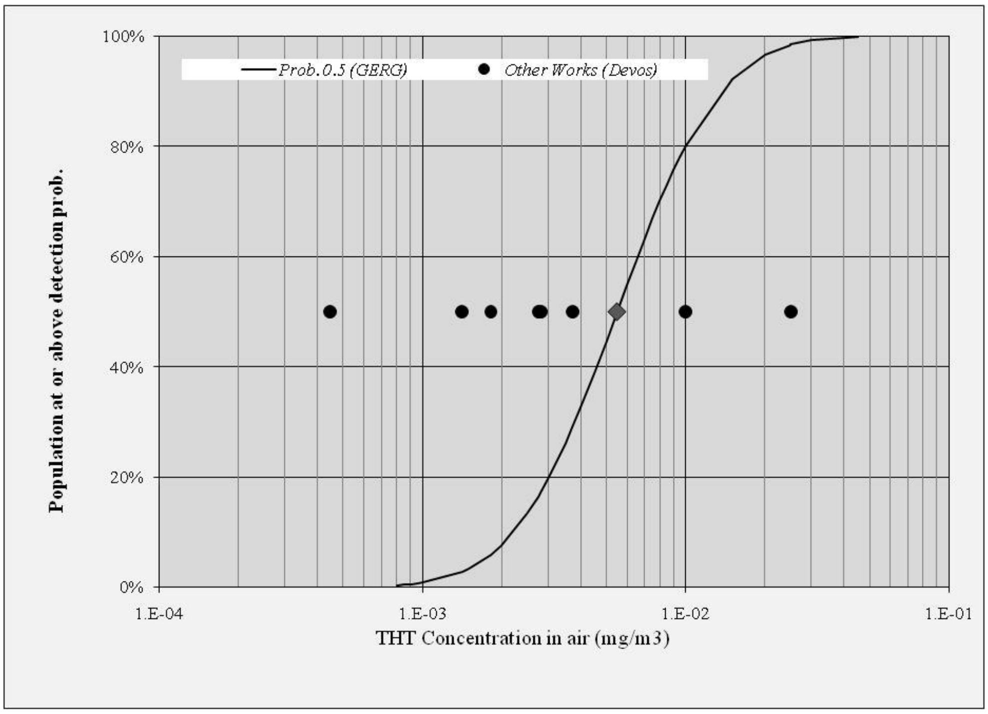
The first requirement is generally not questioned if traditional odorants are used. THT and TBM blends have an odour that is quite similar for untrained people and their use is so widely associated with gas odorisation that it is assumed that these odorants are giving a characteristic odour to gas providing that they are not reacting with the pipe walls or chemicals in the gas to be either stripped from the gas flow or chemically modified. As mentioned above the question is more complex for new odorants based on different formula with an odour not related to that of traditional odorants. The demonstration shall then be made prior to introducing the product as odorant that its odour is different from the ones that can be present in the environment and that it is sufficiently *worrying* to raise an alarm.

This demonstration needs a consumer panel approach. Because of the possible cultural bias and the mere variety of the public perception of smell such an approach shall be based on large sample of people and a *blind* process is necessary to avoid any forced association between the smells and gas. Furthermore the use of reference smells for which the response of the population samples can be obtained to compare that with those of the new odour would be necessary. Such an approach has been used by GDF SUEZ *[7]* however the methodology could probably be improved and harmonised.

4.2. IS THE SMELL DETECTABLE?

To determine if the smell is detectable raises the questions of what detectable means and by whom? Figure 2 presents the evolution of percentage of population able to detect the presence of THT with a probability of 0.5 (S curve from GERG *[9]*). There is one order of magnitude in concentrations between the first and last decile, which represents only the dispersion of the human nose as all people were subjected to the same procedure. By definition this work established the population detection threshold (50% of the population having a 0.5 or more probability to detect THT) at ≈5.5 µg/m^3 in air. Various studies compiled by Devos and col. *[10]* are distributing THT detection thresholds on nearly two orders of magnitude as the different procedures used for testing are increasing the dispersion.

Figure 2: Perception of THT in air (from GERG)



Thus it is important to know who shall be taken into account to estimate the necessary level of odorant in the gas. For instance the French regulation states that the odour shall be detectable by an *average* nose with reference to EN 13725 *[11]* jury selection process that eliminates people over or under sensitive by screening.

Then the procedure used to evaluate the level of odorant that this target group is able to detect shall be defined. Obviously the threshold concentration shall not be retained as it is a concentration that people have one chance out of two to detect. GERG has defined a certainty of perception as the concentration that 99% of the population will be able to detect with a probability of 0.99. With this approach the certainty of detection for THT was 50 $\mu g/m^3(n)$ in air, ten times the threshold concentration. The minimum concentration to be found in the gas would then be at least based on that figure to achieve the certainty of detection when gas is diluted to 20% LEL.

A different approach is given in the German standard VDI 3882 *[12]*. It is based on the free judgement of the panelists who have to state how strong the odour is. Based on this answer the K-Value, i.e. the minimum concentration to be found in the gas, can be calculated when 84 % of the panelists judge the odour as strong. A recent review *[13]* of the K-value led to the lowering of the K-Value of TBM to level around 1 $\mu g/m^3$ leading to minimum TBM concentrations in the gas of about 0.1 mg/m^3 with THT k-Value measured in the same conditions being $\approx$50 $\mu g/m^3$ close to the certainty of detection as found by GERG.

A study conducted by GERG *[14]* more recently has compared the different approaches used in European countries for odorant evaluation. It identified that, although the material everyone is using and the objectives are similar, the differences in vocabulary, training of the operators and procedures for testing made it really difficult to understand results that others have obtained. Thus GERG proposes a methodology to assess the odour intensity of odorants based on:

- A common olfactory scale defined by a series of THT concentrations
- Procedures for training (calibrating) the operators against that scale
- Methods for taking into account the measurement uncertainty.

This methodology has been proposed to ISO TC 193 to draft a new standard and hopefully should be discussed in the next future.

4.3. HOW TO DEMONSTRATE THAT IN THE FIELD?

Once the odorant is chosen and its minimum concentration is defined, gas utility has the duty to check that the gas it distributes is correctly odorised. Two options are available, rhynoanalysis and analytical control *[15]*.

Rhynoanalysis asks that operators sample the gas and smell it to evaluate if its smell is alright. It gives a direct assessment of the smell but can be affected by a rather large uncertainty. The training of the operators is a key element of each evaluation and needs to be thoroughly documented. Thus, even if it seems a straightforward procedure it may be difficult to use.

Analytical control can give an accurate evaluation of the odorant concentration in the gas but to conclude on the odour one shall have a clear relationship between the measurement and the odour. Interfering products shall be identified and if the odorant is a multi component blend, each component shall be measured which may become a challenge. Furthermore, if the interactions of the odorant with the gas or the pipes change the blend composition, by specifically filtering one component for instance, then the response on the modified odorant has to be evaluated.

In general, analytical control is preferred for the routine evaluation of the odorisation as it is much more simple and accurate than olfactory measurement. It is easy to have accurate and representative measurement when the odorant is THT. It is more difficult for the measurement of TBM as the concentrations injected are closing to the detection limit of most of the instruments. Thus analytical controls are generally used to check if the level of odorant in the gas is nominal. This may not be sufficient to demonstrate that the gas is correctly odorised. For instance in the UK and US, utilities have to go through olfactory measurements to establish the quality of their odorisation procedure as the legal system does not consider that a concentration measurement proves that the smell is there.

5. CONCLUSION

As far as innovation is concerned gas odorisation has nothing in common with information technologies. The difficulties to develop a new odorant, the complexity of its evaluation and testing may explain that the gas industry has been relying on the same products for the last 60 years. As no breakthrough is expected in the measurement of smell the sole instrument available, the human nose, shall be used. By using the best methods available in sensory evaluation and by unifying them, the gas industry can and should share the results that are available. With a common view on the odorants it is using the gas industry will be able to pool the different experiences and have a better understanding about what can be the best practices. It can also help the development of new odorants, based on the existing molecules or new formulations as their evaluation can be widely shared.

This can lead to a drastic reduction of the number of odorant in use and a better understanding of their limits and advantages. Along with the improvement of analytical instruments it will be easier for gas utilities to demonstrate the adequacy of their odorisation practice.

REFERENCES

1- UNI 7133, "Gas odorisation for domestic and similar uses – Procedures, characteristics and tests", Italian standard

2 DVGW-Arbeitsblatt G 280-1 (2004): Gasodorierung. Wirtschafts- und Verlagsgesellschaft Gas und Wasser mbH, Bonn, 2004

3 ISO TS 16922 "Natural gas — Guidelines for odorizing gases"

4 S. Robertson, "History of gas odorisation", Symposium of Gas Odorisation conference, Chicago, August 1980

5 M. Palócz, H. Driesen, "Verhalten von Odoriermitteln im Erdboden. Teil 3", gwf Gas-Erdgas, 131 Nr1, p.28-36, 1990.

6 F. Graf, "Current developments in the odorization of natural gas in Germany", IGRC 2008, Paris.

7 F. Cagnon, A. Louvat, V. Vasseur, "The gas smell: a study of the public perception of gas odorants.", IGRC 2011.

8 F. Sullivan, "New Gas Odorants", Symposium of Gas Odorisation Conference, Chicago, August 1980

9 Cagnon F., Hagge E., Heimlich F., Kaesler H., Kuiper Van Loo E., Lopez Zurita J.M., Rijnaarts S., Robinson C., Salati E. and Vinck H., “New testing method helps optimize odorization levels”, IGT Symposium, Chicago 2000.

10 Devos, Patte, Rouault, Laffort, Van Gemert, "Standardised Human Ofactory Thresholds", OIRL Press, 1990, ISBN 0-19-963146-8.

11 EN 13725, "Air quality — Determination of odour concentration by dynamic olfactometry".

12 VDI 3882 sheet 1, "Olfactometry - Determination of Odour Intensity.", Verein Deutscher Ingenieure. October 1992

13 S. Krauss, B. Maxeiner, M. Goschin, "Vergleidchende Bestimmung der K-Werte für die Odoriermittel TBM und THT durch Olfaktometrie", Gas-Erdgas 147(2006), N° 9.

14 E. Salati et Col., "GERG Project: Review of olfactory methods for evaluation of odour intensity – a new proposal for olfactometry, " proposal for new ISO standard to ISO TC 193, WG 5.

15 F. Cagnon, E. Salati, "Sniff test and analytical control: an European view", IGT Odorisation symposium, Chicago, 2001.