POLLUTION
ANALYTICAL EQUIPMENT

Application Note

Continuous and Automated Monitoring OF TBM or THT odorants compunds in Natural Gas Distribution Networks

PREFACE: Natural Gas, as well as Biomethane and LPG (Liquefafied Petroleum Gas), are gaseous mixtures which circulate in distribution areas or are stored in special tanks. These mixtures in themselves are totally, or almost, odourless. To ensure that leaks can also be detected without specific instruments, odorizing substances are added to these mixtures, to odorize them and make them perceptible to the human nose. There are two types of odorants: Tetrahydrothiophene (**THT**) and Tert-butyl mercaptan (**TBM**).

INTRODUCTION: The odorants used are THT and a mixture of TBM, IPM (IsoPropyl Mercaptan) and NPM (NormalPropyl Mercaptan), of which the TBM is always the most abundant (75 – 80%). The **UNI 7133 standard** indicates the minimum reference concentration for both substances: 32 mg/Sm^3 for THT, while for TBM the minimum reference concentration is 9.1 mg/Sm^3 if in the form of Natural Gas (21 mg/Sm^3 if the gas to be odorized is LPG). However, it is advisable **not to exceed the quantity of odorant introduced into the network**. A large amount of odorant increases the risk of any leakage being detected and continuously triggering emergency response teams, making security service management complicated. The costs of purchasing, transporting, and handling these substances are high, so adding large quantities increases the costs of running the network. The permitted total amount of **Sulphur** has recently been limited, and the trend is to reduce the quantity as much as possible for environmental reasons.

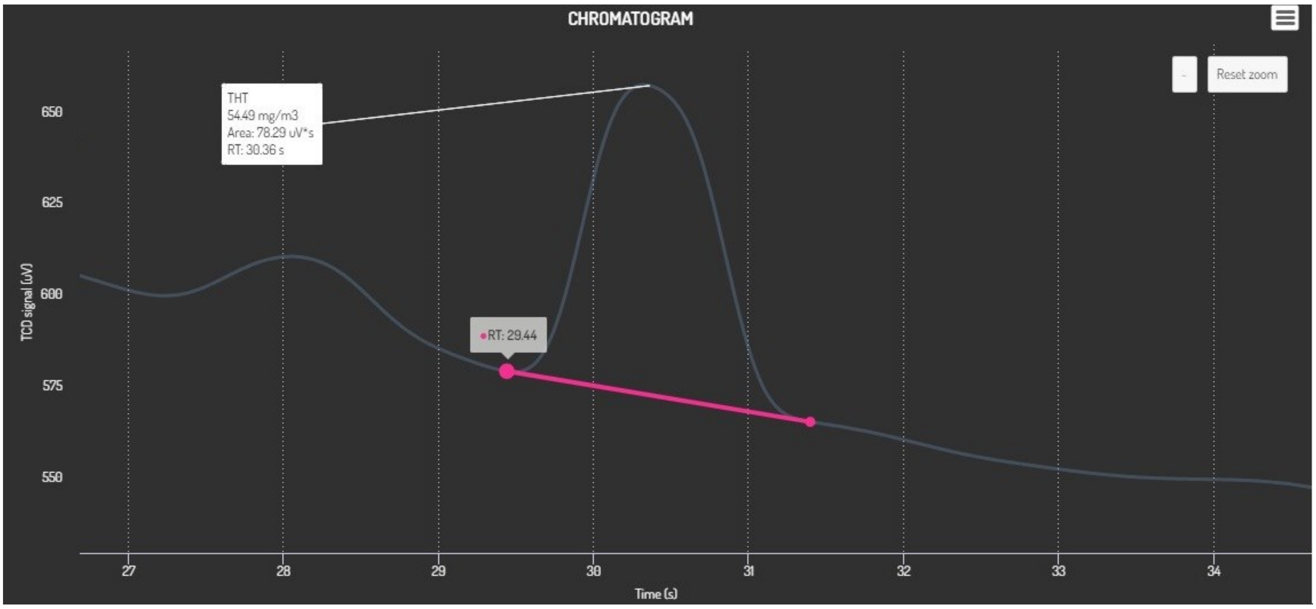
Currently, most of the work of checking and testing the level of odorization is carried out by **portable micro- gas chromatographs**, which are installed on special mobile vehicles and periodically carry out **analysis on the odorization's level** on predefined points of the network. This entails large operating costs in personnel, equipment, and consumables (such as vans, portable MicroGCs, carrier gas cylinders and standards) but above all it entails long periods of time between each measurement, during which the concentration level is unknown.

Automatically monitoring the odorization's level online directly on the network's most strategic points has the operational advantage of **intercepting any odorant deficiency or any increase in concentration**, taking the necessary countermeasures automatically or semi-automatically (depending on the level of automation required). The high level of automation and remote connection potential allow the various operating units to be interconnected, to **optimize the quantity of odorant used**, minimizing its consumption and thus improving all costs related to consumption, management and transport of THT and/or TBM substances.

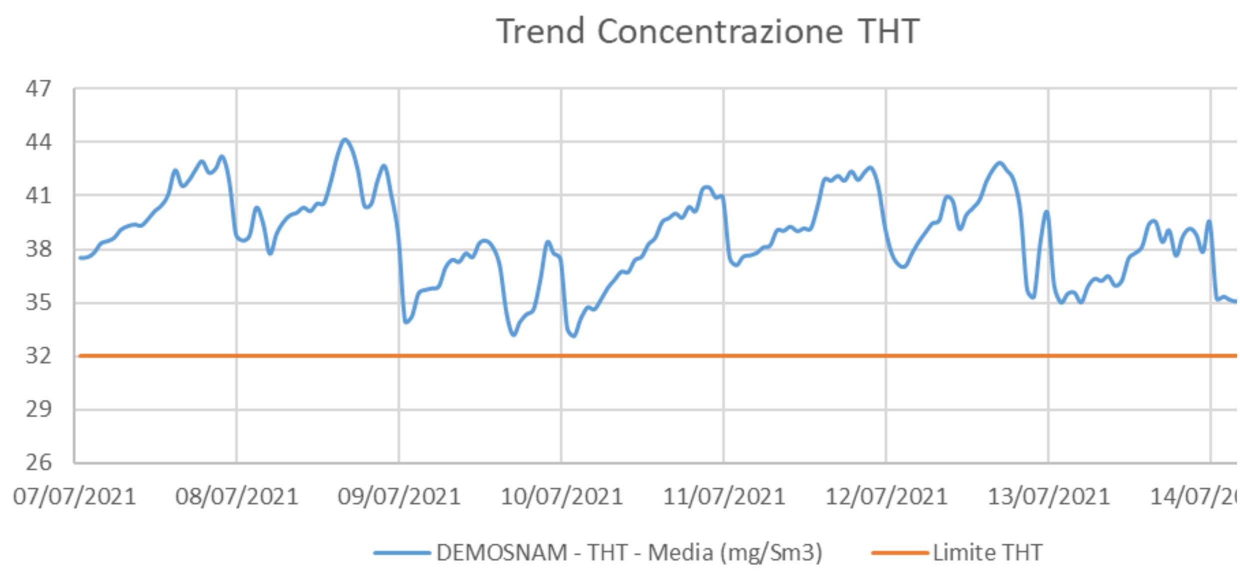
ANALYTICAL SOLUTION: For this application, Pollution Analytical Equipment has developed a **miniaturized and automated gas chromatograph**, which can be installed close to the grid and autonomously carry out analysis. The equipment consists of an injector, an analytical column and a detector (µTCD). The injector and the detector are based on **MEMS technology (Micro Electro Mechanic Systems)**. The columns differ depending on the type of odorant being measured.

The solutions differ depending on the type of column being used. The containment and communication and management system are shared for both solutions.

THT IN NATURAL GAS: Shown below you can see the chromatogram and the graph showing the separation of THT from other hydrocarbons in natural gas, and the concentration trend of THT. These graphs are obtained with an online monitoring system installed directly on a Natural Gas distribution network. In Graph 1, you can see how the concentration of THT odorant is kept above the minimum limit of 32 mg/Sm^3 and how at the same time **the added THT quantity gets optimized**, also considering the oscillations due to multiple factors, such as temperature, pressure, and flow rate. If measured only punctually, THT concentrations may show high or low levels depending on the moment of that each analysis.

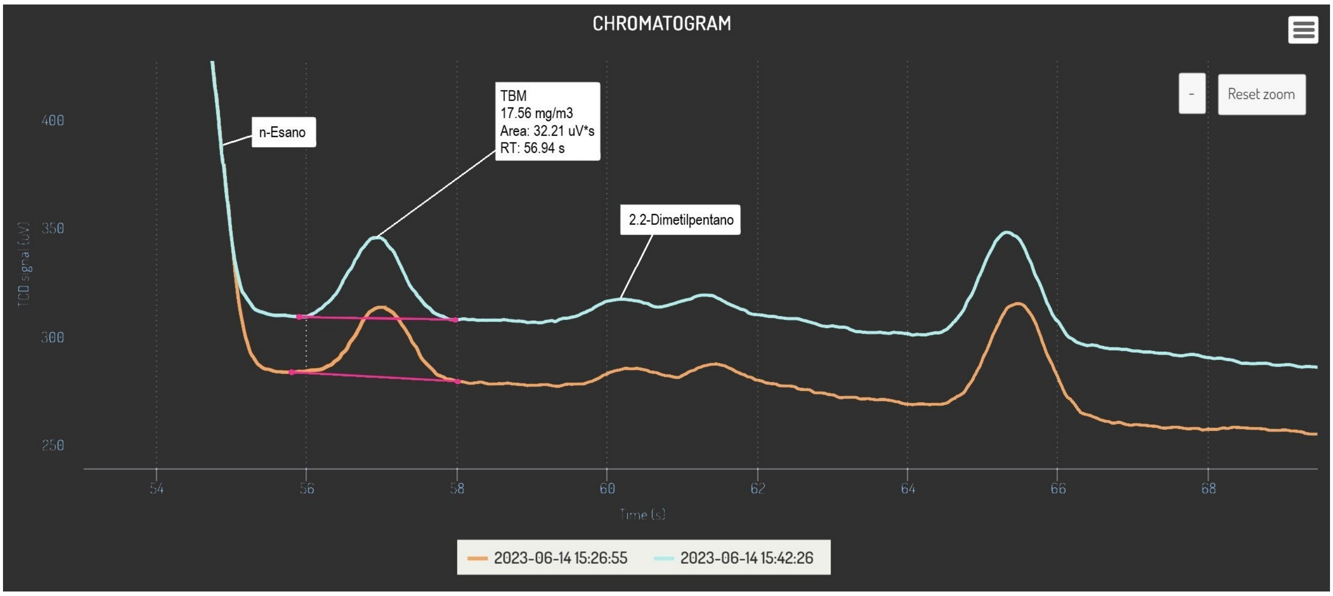


Chromatogram 1: CP Sil 19CB — THT 50,5 mg/Sm^3 in natural gas

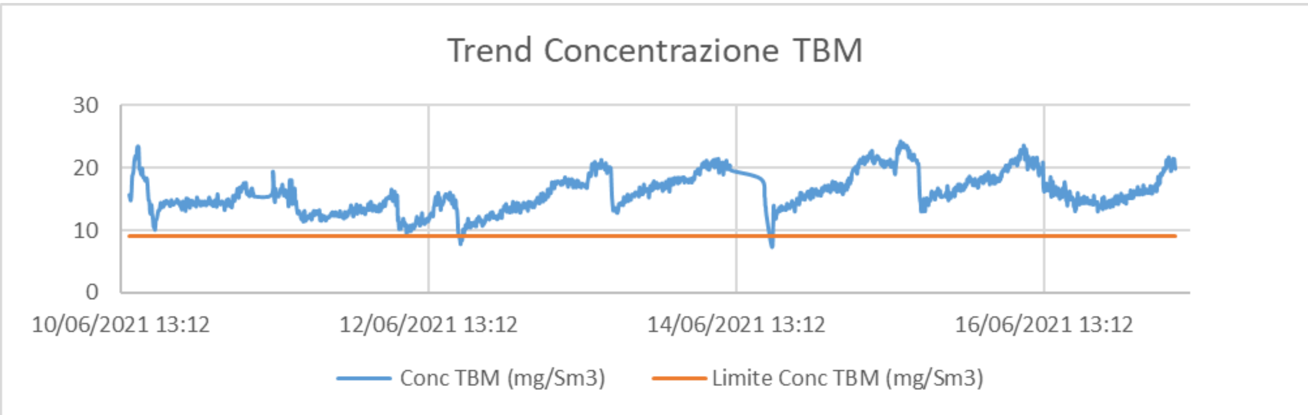


Graph 1: Weekly report of the continuous measurement of the concentration of THT in the natural gas network.

TBM IN NATURAL GAS: In Chromatogram 2, you can see the right separation between TBM and other potentially interfering hydrocarbons, in particular 2,2-dimethylpentane, which if not separated correctly can be the main responsible for any false alarms. Shown below you can see the weekly report of the TBM concentration measured in a specific point, which appears particularly subject to possible out-of-specification of a distribution network.



Cromatogram 2: CP Sil 13 CB — TBM 15,4 mg/Sm^3 in natural gas



Graph 2: Weekly report of the continuous measurement of the concentration of TBM in the natural gas network

RESULTS AND DISCUSSION: As shown by the previous chromatograms, the separation of odorants from other hydrocarbons present in natural gas is correct. In tab 1 and 2, the evaluation of repeatability was carried out with five replications for the TBM and seven replications for the THT, by using standard gas with a concentration of 10,50 mg/Sm3 (2,82 ppm) and 3,71 mg/Sm3 (1,01 ppm). The repeatability expressed as standard deviation relative % (%RSD) on the area value was found to be 2.08% for TBM and 4.16% for THT. While on the Retention Time (RT) value it is 0.03 for the TBM and 0.23 for THT (relative to the above concentrations). The RSD calculated in the tests just discussed for both RT and Area, demonstrated **excellent accuracy of THT and TBM**, which proves that this analytics platform is ideal for **online monitoring of odorants**. The accuracy also proved to be very high, as evidenced by the measurements reported in the tables below.

n°	TBM (mg/Sm^3)	TBM (ppm)	Area (µVs)	RT (s)
1	11.03	2.90	28.03	78.81
2	10.74	2.82	27.27	78.84
3	10.43	2.74	26.49	78.79
4	10.45	2.74	26.55	78.81
5	10.74	2.82	27.28	78.85
DEV.STD.	0.22	0.06	0.56	0.02
Average	10.68	2.80	27.13	78.82
% RSD	2.08	2.08	2.08	0.03

Tab 1

n°	THT (mg/Sm^3)	THT (ppm)	Area (µVs)	RT (s)
1	3.71	0.99	11.21	44.04
2	3.84	1.03	11.60	43.96
3	3.60	0.97	10.90	44.08
4	3.92	1.05	11.85	44.04
5	3.70	0.99	11.20	44.00
6	3.51	0.94	10.60	44.16
7	3.47	0.93	10.49	44.28
DEV.STD.	0.15	0.04	0.46	0.10
Average	3.68	0.99	11.12	44.08
% RSD	4.16	4.16	4.16	0.23

Tab 2

CONCLUSIONS: Online monitoring of odorant concentrations with automated gas chromatography systems allows you to always have **control over the levels of odorants** in the network, even in the trickiest points. At the same time, it is possible to make substantial and significant savings over the long term, on the quantity of odorant that is transported, handled, and added annually in the network. Analytical performances are guaranteed by the innovative gas chromatographic technology of Pollution Analytical Equipment, and they allow you to accurately measure the concentrations of the two odorants without the risk of interferences and false negatives or positives. The analysis system **can be integrated with Ilot industrial automation systems and a proprietary Cloud platform, Pollution Guardian**, to implement **remote access** and control capabilities by the company's technical staff.