marcogaz
TECHNICAL ASSOCIATION
OF THE EUROPEAN NATURAL GAS INDUSTRY

Survey on Odorisation analysis

1. CONTEXT

At the end of 2013 MARCOGAZ WG Odorisation started a survey on Odorisation analysis, with the aim to know the similarity and differences in methods utilized for odorant analysis in natural gas (olfactory analyses are out of the scope of this survey). A form was sent to the MARCOGAZ Members, to collect information; there were received answers from 8 Countries (BE, CZ, EL, ES, FR, IT, NL and RO) out of the 20 MARCOGAZ Countries, with a total of 9 answers (two from Italy).

The analysis of the received information is presented in the following chapter.

2. METHODS AND INSTRUMENTS USED TO CHECK ODORISATION

4 answers are dealing on portable microGC (compact gaschromatographs using micro-thermal conductivity detectors [micro TCD detectors]); two answers refer to Sulphur dedicated gas chromatographs equipped with a Flame Photometric Detector [FPD]. Sensors are used in three cases: the difference between gas chromatographs and sensors is remarkable, while gas chromatographs can achieve better values of accuracy, reproducibility and documentation than sensors (the sensors, contrary to the gas chromatographs, cannot separate the different compounds that are present in the sample). The accuracy is expressed only for gas chromatographs, while sensors are often considered as "indicators", i.e. instruments that cannot be calibrated in reference to recognized standards and so they cannot give a result with a reference to a recognized measuring system.

The differences between microGC using micro TCD detectors and Sulphur dedicated gas chromatographs are several:

- microGC is often used for its functional capacity: it is very easy to take it outside laboratory and it is very fast in analyzing. Otherwise, it is limited in the minimum analyzable concentration and, moreover, its detector, the micro-TCD, is not selective, so the possible interferences are wider.
- Sulphur dedicated gas chromatographs (equipped with FPD or other detectors dedicated to Sulphur analysis) are, usually, Lab instruments with better analytical performances, but they are not created for on-site analyses, so it is necessary to install them into a dedicated van. The sensitivity is higher and they can analyze a wider range of Sulphur compounds. Usually time analysis is longer than with MicroGCs.

MicroGC in some cases is used as fixed gas chromatographs; dedicated gas chromatographs are used as Lab instruments, too with remote sampling.

Usually Lab analyses are performed for special aims (for example for legal purposes), when a better accuracy is needed; in this case the most important step is the sampling procedure, because odorant can be adsorbed/oxidized and the sample can be contaminated by air.

On site analyses with fixed gas chromatographs are used when special points must be checked, fixed on the grid, while the use of portable gas chromatographs is common when several points must be checked, varying in time.

Only the Italian Regulatory Authority (AEEGSI) at the moment has defined specific requirements, as far as minimum number of sampling points, incentives, documental verifications and direct execution of gas chromatographic analyses to verify Odorisation.

Round Robin Tests and accreditation of the test laboratories for the moment are not requested.

In general, the methodologies are considered satisfactory and no need of improvement was pointed out.

In the next tables data are reported on the different methods (please note that these data are at the moment based on few answers, so they cannot be representative of the entire landscape of gas market).

2.1 Portable microgc with microTCD

Analytical method (standard):	**ISO 19739 and national standard.**
Carrier:	**Helium**
Analytes:	**THT and TBM**
Number of analyses to stabilize the gaschromatograph before the measurement:	**5, or until a fixed value of standard deviation is achieved.**
Number of repetitions for a single result:	**Range from 3 to 10.**
Acceptance criteria of the results:	**Not always are specified. When are, the criteria is related to evaluation of the standard deviation.**
Range of analizable concentrations:	**The range is variable, depending on the calibration and on the national requirement. The wider range is 1-200 mg/m^3 for THT and 1-100 mg/m^3 for TBM.**
Uncertainty achieved by the Lab:	**THT: 10% (at 20-35 mg/m^3)**

	TBM: 13% (at 9 mg/m^3)
Calibration (levels):	**Usually 3**
Calibration (periodicity):	**At least monthly**
Compliance criteria of the result of the analysis:	**Direct comparison with the range of admissible values of concentration (national legislation).**
Sampling points locations:	**Odorisation plants (city gate distribution station);** **Relevant points of the grid (determined by the distribution grid operators);** **End points of the grid (especially on ramifications of the primary pipeline).**

2.2 Fixed (process) microGC with microTCD

Analytical method (standard):	**ISO 19739 and national standard.**
Carrier:	**Helium**
Analytes:	**THT, H_2S, COS, MM, TBM**
Number of analyses to stabilize the gaschromatograph before the measurement:	**Not applicable: continuous control.**
Number of repetitions for a single result:	**1.**
Acceptance criteria of the results:	**Reproducibility, in one case.**
Range of analizable concentrations:	**THT: (5-10)–200 mg/m^3** **Not specified for other sulphur compounds.**
Uncertainty achieved by the Lab:	**THT: ±3mg/m^3 between 15 to 40 mg/m^3**
Calibration (levels):	**1**
Calibration (periodicity):	**The calibration is automated. It can be executed on an hours/daily or monthly basis.**
Compliance criteria of the result of the analysis:	**Direct comparison with the admissible values of concentration, taking into account the accepted deviation in the response factor.**
Sampling points locations:	**Odorisation plants, hubs of the transmission grid, critical points in the network.**

2.3 Laboratory gas chromatographs, even when installed on vehicles (FPD - SCD detectors)

Analytical method (standard):	**EN ISO 19739**
Carrier:	**Helium**
Analytes:	**THT, TBM, DMS, H_2S, COS, EM (C_2H_5SH) and other Sulphur compounds.**
Number of analyses to stabilize the gaschromatograph before the measurement:	**5 or until achievement of the prescribed value of standard deviation**
Number of repetitions for a single result:	**1 - 3**
Acceptance criteria of the results:	**Standard deviation.**
Range of analizable concentrations:	**THT: from 0,01 – 0,1 to 100 mg/m^3** **TBM: from 0,5 – 1 to 100 mg/m^3**
Uncertainty achieved by the Lab:	**Not known**
Calibration (levels):	**From 1 to 3**
Calibration (periodicity):	**Before every analysis cycle** **6 months**
Compliance criteria of the result of the analysis:	**Direct comparison with the range of admissible value of concentration (national legislation)**
Sampling points locations:	**End points and relevant points of the grid - especially on ramifications of the primary pipeline and at city gates and at main distribution stations.**

2.4 On site sensors (Electrochemical detectors)

Analytical method (standard):	**The method is not described in standard.**
Carrier:	**-**
Analytes:	**THT, TBM, Sulphur-free odorant, EM, H_2S.**
Number of repetitions for a single result:	**-**
Acceptance criteria of the results:	**Repeatability**
Range of analizable concentrations:	**THT: 0-100 mg/m^3; TBM: 0-3,6 mg/m^3; Sulphur-free odorant: 0-8 mg/m^3; EM: 0-30 mg/m^3; H_2S: 0-141**

	mg/m^3.
Uncertainty achieved by the Lab:	**-**
Calibration (levels):	**For the calibration, a test gas is required containing the odorant to be detected in the same range of concentration**
Calibration (periodicity):	**A calibration must be performed on each day of measurement**
Compliance criteria of the result of the analysis:	**Direct comparison with the minimum admissible value of concentration**
Analysis locations:	**Relevant points on site after Odorisation.** **Endpoints of the grid, especially on ramifications of the primary pipeline and at city gates and at main distribution stations.**

3. REMARKS

Even if, analysing the answers, there is no evidence of the necessity to improve the standardization of the methods for odorant analysis, probably a better harmonization could be useful. A common reference is ISO 19739 "Natural gas - Determination of sulfur compounds using gas chromatography".
No standards for odorant analysis performed by sensors is available at the moment.
With a bigger diffusion of the participation to interlaboratory tests it will be possible to know more about the different performances of the methods and instruments; a critical aspect is the number and the quality of the calibration mixtures, that highly influences the analysis results.

4. DEFINITIONS OF THE ABBREVIATIONS

ABBREVIATION	DEFINITION
GC	Gas chromatograph
FPD	Flame photometric detector
TCD	Thermal conductivity detector
THT	Tetrahydro thiophene
TBM	Tertiary butyl mercaptan
COS	Carbonyl sulfide
DMS	Dimethyl sulfide
EM	Ethyl mercaptan (C_2H_5SH)
H_2S	Hydrogen sulfide
MM	Methyl mercaptan
Sulphur free odorant	Odorant without Sulphur compounds, based on Acrylates