Continuous Monitoring of Odourous Compounds in Waste Water Treatment Plants - Sensory approach or Physico-chemical solution?

Odour measurement is a demanding topic to manage due to the complexity of existing solution and the methodology used.

"For years, WWTP as prestigious as SIAAP in France or stations in the UAE have placed a lot of trust in Chromatotec solutions. A measurement network has been deployed on site and data is centralised on SCADA systems."

Authors/Contact Details:
Jean Philippe AMIET, Louis VIVOLA
Chromatotec
15 rue d'Artiguelongue
33240 SAINT-ANTOINE
France
Tel: +33 (0)557 940 627 /
+ 33(0)762 667 658
Fax : +33 (0)557 940 620
Email : louis.vivola@chromatotec.com

Market needs

When an odour is perceived, the first approach is to try to identify its origin. This approach requires solutions able to track very low concentrations due to air dilution effects.

Several solutions can be provided:

- Sensory approach
- Physicochemical approach

Sensory approach: dynamic olfactometry

Dynamic olfactometry relies on human nose evaluation. Samples are collected at the source and sent to a certified laboratory working according to standard methodology (EN 13725, ASTM 679-E04, VDI 390). Samples are automatically diluted and smelt by a sensory panelist with dedicated equipment; a dynamic olfactometer.

This approach is not easy as the time between sampling and measurement must be reduced to avoid reactions and adsorption of unstable molecules in the gas mixture (i.e.: sulphur compounds).

This method offers a spot measurement which does not take into account process or meteorological variations because results are available only after a few days.

Electronic nose is an alternative and complementary approach on dynamic olfactometry as they can offer online measurement of odour emissions. Electronic nose technology may use non-specific sensors such as metal oxide sensors (MOS), gas chromatography or mass spectrometry. For these last two technologies, the systems provide odour and chemical fingerprints and can identify and quantify contaminants in comparison with MOS sensors which cannot provide such results.

In both cases, chemical profiles are compared to sensory evaluation to check possible correlation between instrumental and sensory evaluation. An odour index can be defined to monitor odour intensity according to specific methodology if needed.

These global approaches help to rank odour sources on site (dynamic olfactometry) and allow users to focus on the most emissive sources to treat odour issues with adequate deodourising process.

With e-noses, the main limit is the training of the equipment (called the learning stage) as it is needed to realise several analysis of samples with dynamic olfactometry to train the e-noses.

On the other hand, when odour occurs it is quite difficult to understand which step of the process may explain the odour emission due to the lack of information on chemical concentration (i.e. in a Waste Water Treatment Plant (WWTP))

The physico-chemical approach: alternative solution to quantify odourants!

Several solutions exist for the quantification of odourous molecules. Solutions are deployed and designed depending on the expected sensitivity.

Portable sensors used as indicators located in the environment provide alerts as soon as values exceed a reference value. These indicators require annual replacement of sensors.

As they rely on electrochemical cells, electrolyte is consumed over time and also needs annual replacement. These sensors may be good indicators of process drift or chemical leakage but predictive concentration is not accurate as no calibration is provided.

Sulphur concentration is estimated with a global approach and it is not possible to discriminate H_2S from Mercaptans concentration. If the user is interested in several molecules, several units need to be deployed (one per targeted molecule).

To quantify several molecules, it is compulsory to have multiple and sensitive analysers.

In WWTP, site managers are familiar with odour and chemical profiles as they are exclusively focused on sulphur compounds measurement. These molecules are used as process drift indicators and offer a good criteria of process performance. Hydrogen Sulphide (H_2S), Methyl Mercaptan (MM), Ethyl Mercaptan (EM), dimethyl sulphur (DMS) or Di-Methyl-di sulphur (DMDS) and sulphur dioxide (SO_2) provide a better understanding of odour emissions. For example, high sulphur concentrations have been measured on primary clarifiers contaminated by effluents coming from tanneries and responsible of complaints from the neighbourhood.

So with this quantification step, it is easy to link odour perception to its origin and be alerted when level of concentration exceed specific reference values.

In addition, as operators on site are not experts in chemical analysis, it is very important to provide turnkey solution with automatic result validation and a friendly user interface.

TRS MEDOR for on-line monitoring of Sulphurs from ppt to ppb or ppm levels

The reduced sulphur compounds, such as the Mercaptans and organic sulphides, tend to be the most odourous, based on their relatively low odour threshold concentrations.

Chromatotec offers a complete and turnkey solution with the TRS MEDOR which is a 24/7 unattended online air monitoring system dedicated on sulphur compounds quantification.

Equipment offers excellent linearity over its entire range of measurement. Alert thresholds are defined to start or stop process according to chemical concentration levels.

The TRS MEDOR monitors the odour control performance and warns the user if process drift appears.

Thanks to a multiplexer unit, one system can monitor odours before and after the deodourisation process in different locations to limit budget.

The TRS-MEDOR includes, as standard, automatic calibration with permeation tube using DMS at 25 ppb and Air generator (Airmopure)

Is MEDOR as sensitive as the human nose?

The results provided in figure 1 illustrate the MEDOR capabilities for sulphur quantification. There are on-line results without any data processing. An NPL[1] Standard Certified tank was used for the evaluation.

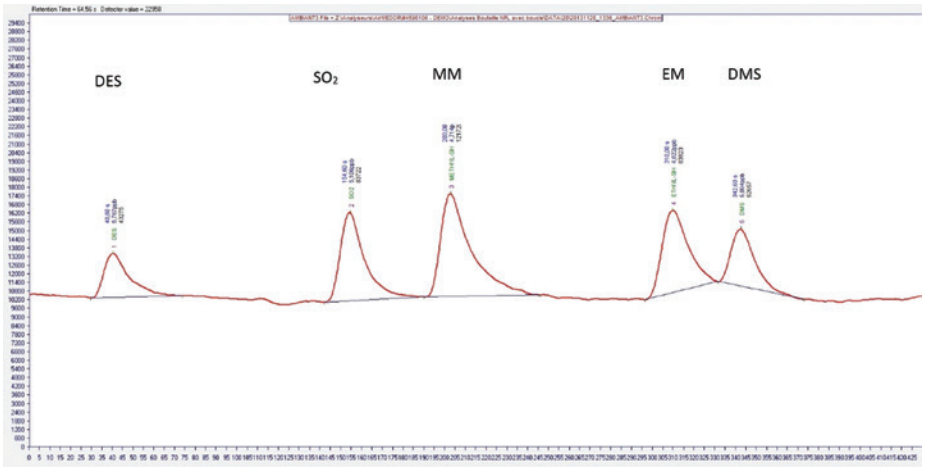


Figure 1 : Chromatogram for Mercaptan and sulphurs using NPL Certified gas bottle

Repeatability tests have been conducted on 19 measurements on MM, EM, DMS, DES. SO_2 was considered too as it was present in the mixture.

The results have shown that sensitivity obtained with a MEDOR is better than the human nose with repeatability at less than 5% for Mercaptan and sulphur compounds. This enables the ability to anticipate odour issues before they affect our human nose.

	Average(*) concentration (ppb)	Standard deviation (ppb)	Repeatability (%)	Limit Of Quantification - LOQ[2]	Human nose detection threshold [3]
METHYL-SH (MM)	4,87 ppb	0,24 ppb	4,86%	0.11 ppb	~0.25 to 40 ppb
ETHYL-SH (EM)	4,48 ppb	0,14 ppb	3,07%	0.11 ppb	~ 0.3 to 20 ppb
DMS	5,02 ppb	0,17 ppb	3,41%	0.19 ppb	~ 1 to 6 ppb
DES	5,54 ppb	0,23 ppb	4,15%	0.26 ppb	~ 2 to 20 ppb
SO_2	5,20 ppb	0,29 ppb	5,59%	0.12 ppb	500 to 3000 ppb

(*) number of measurements: 19

Figure 2 : Repeatability results

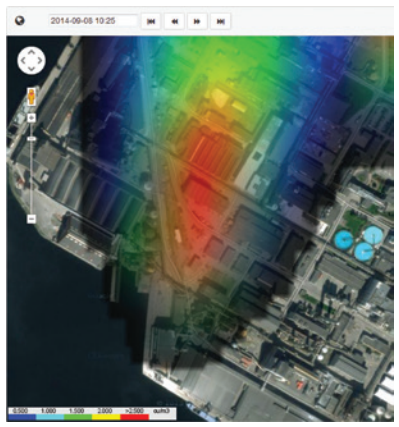
Case study with the TRS MEDOR in WWTP

Several WWTP as prestigious as SIAAP in France or stations in the UAE have placed for years a lot of trust on Chromatotec solutions.

A measurement network has been deployed onsite and data was centralised on SCADA systems.

The quantification of gases was conducted according to the methods ISO 6326/2 & DIN51855/7 ASTM D 7493-08. It was possible to monitor with one unique instrument and multiplexer several points of interest focusing on Mercaptans (H2S/MM/ EM/PM), sulphurs (DES/DMS/DMDS) or SO_2.

To ensure the performance and the representativeness of measurement, automatic calibration (AIRMOCAL) was performed to automatically validate the results and this, without any human intervention.



An embedded PC provides odour index and sulphur gas concentrations (In addition, VOC option can be added using others analysers with GC/PID or GC/FID on line instruments).

Recently, the solution allows for the integration of meteorological data from weather stations and dispersion modelling software to display odour and chemical plume to evaluate the odour and chemical impact of the site on neighborhood. It is now possible to integrate data coming from other complementary technologies, display all the results and manage complaints on a unique interface offering the user at-a-glance results from source to environment.

On a specific WWTP several areas were monitored: Screening area (stripping), deodourisation unit area and H_2S filter management area.

On screening area: stripping, MEDOR was capable of measuring H_2S and Mercaptans in ambient air. Compounds like Tertio-Butyl-SH, Propyl-SH, Methyl- Ethyl-S, 2-Butyl-SH or n-butyl-SH were measured in addition. An unexpected Mercaptan for user was discovered in the process. Considered as a confidential one, this sulphur compound may explain some particular events in the process.

The measuring range of the two compounds is between 1 ppb to 1000 ppm. A visual and audible alarm are activated when threshold levels are reached. Equipment are housed in a temperature controlled cabinet to ensure continued reliable operations.

Results are obtained at a glance on a table thanks to VISTACHROM software. Chromatograms can be explored to validate TRS MEDOR performance. An example is given figure 3.

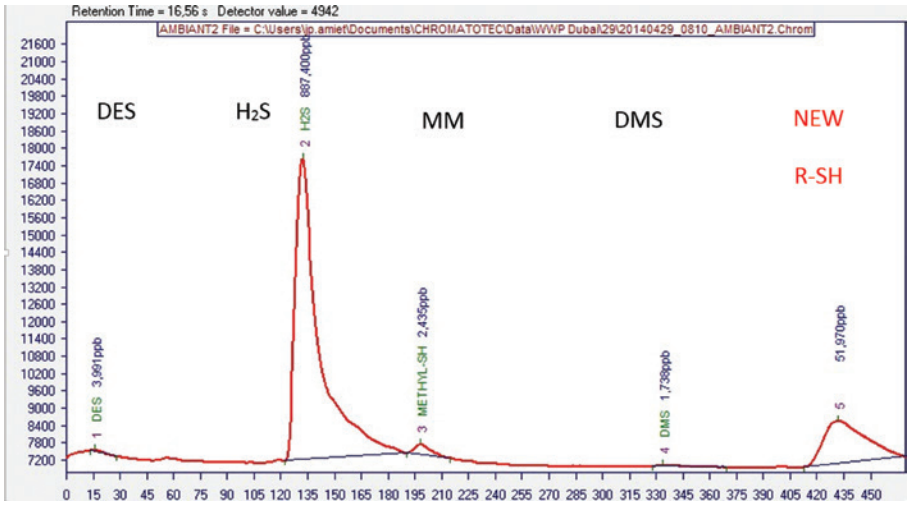


Figure 3 : Quantification on Screening Area (stripping)

One TRS MEDOR was located at the outlet of the stripping process on deodourisation area. It monitors H_2S concentrations and pilot the adjunction of calcium nitrate allowing users to save time and money by reducing and optimising the consumption of calcium nitrate used.

The second TRS MEDOR was located on a Hygiene, Sludge dewatering and H_2S filter management area. ATEX certified, this TRS MEDOR was located in a harsh environment with a measurement cycle of 3 minutes. It was used to check filter performance with only one unit coupled with a stream selector.

This installation allowed users to check gas emissions from 5 digesters, and provided warnings when replacement of the filter was needed.

TRS MEDOR: ALTERNATIVE SOLUTION FOR ODOURANTS MONITORING ON WWTP

With the quantification at low ppb of H_2S, MM, EM, DMS, DMDS, DES, SO_2, the TRS-MEDOR may be considered as one of the Best Available Technologies for sulphurs analysis in ambient air. With LOQ of less 0.3 ppb and repeatability of less than 5% for Mercaptans (MM & EM) and sulphurs (DES & DMS), the system offer full traceability with peak areas for each molecule. TRS concentration is evaluated by calculations considering H_2S, MM, EM, DMS, DES, and DMDS.

Additionally, the instrument shows his capability to detect and quantify SO_2 with the same equipment. Generally SO_2 is measured using Fluorescence detector. New predictive algorithm allows to define an odour index in WWTP to give a full understanding of emission generation and predict odour and chemical impact. Additionally, the internal auto calibration allows users to automatically validate the robustness of the results.

(1) National Physical Laboratory in UK

(2) LOQ= Low Quantification Limit in automatic / LOQ calculation with minimum area value of 2 000 (amplification 3)

(3) ADEME and INERIS sources