



Development of on-line and field dual TD-GC-FID/MS for automatic and continuous Volatile Organic Compounds (VOCs) ambient air and odour monitoring

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Ambient air is polluted by many Volatile Organic Compounds (VOCs) coming from anthropogenic and natural sources. VOCs from PAMS, TO14 and TO15 lists can be measured in many ranges of concentration, from ng/m^3 up to mg/m^3 depending on the location of the measurements. Due to the large number of molecules, the complete separation of all compounds is difficult to perform using chromatographic columns. Therefore, it is difficult to quantify precisely all compounds using a chromatograph equipped with a nonspecific detector. The goal of this study is to perform automatic and continuous identification and quantification of VOCs using a dual Thermal-Desorber Gas Chromatograph equipped with two Flame Ionization Detectors (FIDs) and one Mass Spectrometer (MS). The device is required to identify automatically coeluted compounds by MS technology adapted to industrial context. The coupling of two different TD-GC-FIDs to a Quadrupole MS allowed by an elaborated multiplexer system is the originality of the project: one TD-GC-FID for monitoring of light compounds and one for heavy compounds with specific analytical conditions for each system. A measurement campaign in petrochemical new site shows the concentration of about 100 compounds at different steps of the commissioning. Thanks to the continuous measurements every 30 minutes, variations of concentrations during specific hours can be monitored. Potentially coeluted compounds like terpenes or organochlorinated are identified and monitored at ppt level. This solution enables to monitor odorants compounds at level of concentration lower than what human nose can detect. It also offers good capabilities for odour monitoring with molecule speciation. This fully automatic system allows non-specialist operators to access expertise level results.

1. Introduction

Volatile Organic Compounds (VOCs) in the urban and industrial atmosphere are mainly originated from exhausts and other combustion processes utilizing fossil fuels, petroleum storage and distribution, solvent usage and other industrial processes (Cetin et al., 2003). The monitoring of potential sources of contaminants from petrochemical industries which may contribute to air pollution is a difficult job because of the complexity of the refining process, the unique nature of sources, the variety of emissions, the accessibility of some sources, and difficulties in the identification of some emissions (Kalabokas et al., 2001). VOCs which can be oxygenated or halogenated are emitted in a wide concentration range from background level to high concentrations near the site fence line. These compounds are ozone precursors and can significantly reduce lung function and induce respiratory inflammation (Cakmak et al., 2014). They are also responsible for unpleasant smells, even at low concentrations in atmospheric air (Cariou et al., 2016). Sensory techniques such as dynamic olfactometry, described in the standard EN 13725, are widely used to determine the odour concentration. However, they cannot determine which substances are behind the generation of the odour nuisance (Vera et al., 2016).

Industrial bodies need to identify these air pollutants to be in compliance with the authorized limits. Also, emission control is often a key factor to monitoring and improving industrial processes. The number of potential molecules to be analyzed and the wide range of concentrations require the use of Thermal Desorber

Gas Chromatographs (TDGCs) to pre-concentrate samples and analyze complex gas mixtures using different types of detectors. In gas chromatography, the mobile phase is a carrier gas, usually an ultra-pure gas such as helium, hydrogen, nitrogen or argon. The mobile phase carries the sample to be analyzed through a column in order to separate the compounds. The time at which the compounds elute from the column is used to identify the different species whereas the electrical intensity measured by the detector allows for quantification. This technique is commonly used in laboratories but requires trained people for instrument operation and result analysis. The complexity of such analyses often compels companies to send gas samples to laboratories. This procedure is expensive, not efficient for the measurement of one-time events, and not relevant for process monitoring. Also, the time between sampling and analyses is a crucial parameter when it comes to monitoring unstable compounds. Therefore, external laboratories cannot fulfill all the requirements for the monitoring of chemical emissions in petrochemical industries. For industrial use, there is a need for an instrument which combines the performances of laboratory instruments with the standard criteria of industrial monitoring systems. The challenge is to precisely analyze ambient air composition in different locations, to perform continuous analysis with automatic validation of results, to analyze more and more compounds in compliance with regulations. The instrument must be easy to start and to operate. Standard communication protocols used in the industry must be available to ensure data transfer.

In 2013, four Continuous Ambient Air Monitoring Systems (CAMS) have been tested by the National Physical Laboratory of London (NPL): two auto-TDGC-FID (airmoVOC C6-C12, Chromatotec[®], France) and two auto-TDGC-PID (airTOXIC, Chromatotec[®], France). For six months, the performances of the instruments have been checked in accordance with UKAS-accredited NPL Test Procedure QPAS/B/528a (and later on in the field) and compared against the performance criteria defined in the MCERTS (Monitoring Certification Scheme) standard for CAMS and EN 14662-3. Chromatotec[®] analyzers met the requirements for continuous monitoring of ambient air both indoors and outdoors. Following the tests carried out by the NPL, an improved version of the auto-TDGC-FID tested by the NPL has been developed to add a Process Mass Spectrometer as a detector. The instrument works with the same pre-concentrator, same column but has two detectors: a Flame Ionization Detector (FID) and an Electron Impact (EI) Mass Spectrometer (MS). The FID detector is very stable, linear and highly sensitive to VOCs. Nevertheless, it is not specific and does not allow deconvolution of coeluted peaks. On the other hand, the MS is a universal detector and specific at the same time. The combination of both technologies makes the system a unique tool for identifying and quantifying VOCs. The sum of the measured concentrations, C (mg m^{-3}), of these odorous substances can be converted into odour concentration of the mixture, C_{OD} ($\text{ou}_E \text{m}^{-3}$), according to the Eq(1).

$$C_{OD} = k_c \sum C_i / m_{OD,0} \quad (1)$$

The specific odour mass, $m_{OD,0}$, is set to 1 mg ou^{-1} to reach a proper measuring unit of the odour concentration and the proportionality constant k_c has to be determined by olfactometric measurements (Wu et al., 2016).

The main goal of this work was to develop an on-line auto TDGC-FID/MS system capable of measuring a large number of VOCs from ppt to ppm in field conditions. The device is required to automatically identify potential coeluted compounds by MS technology adapted to industrial context.

2. Materials and methods

2.1 AUTO-TD-GC-FID-MS

For the laboratory phase and field tests, an auto-TDGC-FID/MS (airmoSCANXpert, Chromatotec[®], France) was used to characterize the possibilities of the system. The integrated TD device comprises a mass flow controller to control the flow and time of pre-concentration, and a one phase trap specific for VOCs. There is no need to use a drying system for such trap, which reduces the risk of adsorption of analyt. The process MS (DET QMS, Chromatotec[®], France) uses Electron Impact ionization chamber, a quadrupole and two detectors: a faraday cup and a Secondary Electron Multiplier. The MS was used in scan mode (from 50 to 200 m/z) and in multiple ion detection mode.

One of the big advantages of this system is that the same MS can be coupled to two auto-TDGC-FID. As can be seen in Figure 1, one TDGC would be dedicated to the analysis of light compounds and the other TDGC for heavy compounds.

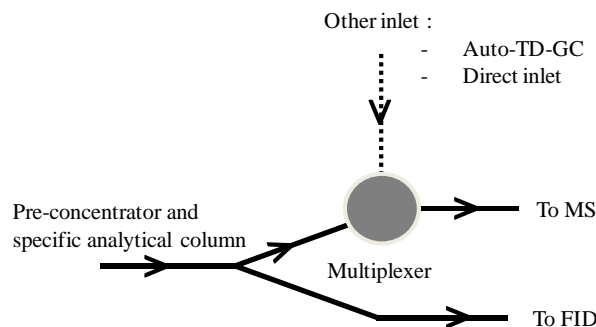


Figure 1: Pneumatic diagram of the airmoSCANxpert system.

For the analysis of C2–C6 hydrocarbons, 99.19 ml of sample was drawn into the system with a flow rate of 9.92 ml.min⁻¹ (air sample is integrated over 10 min). The sample passed first through a dryer (airmoDry, Chromatotec[®], France) to remove the humidity and then hydrocarbons were pre-concentrated at -10 °C on a trap filled with a mixture of Carboxen and Carboxen. The pre-concentrated air sample was thermally desorbed at 220°C for 4 minutes and directly injected in a 25 m Al₂O₃/Na₂SO₄ column (PLOT column, 0.32 mm ID, 5.0 µm dF) located inside the heated oven of the GC. Within the first minute of the analytical procedure, the oven temperature rose from 36°C to 38°C. Afterwards a constant heating rate of 10 °C.min⁻¹ was applied to 100 °C and then 15°C.min⁻¹ until 190°C. Then the temperature is kept at 190°C for 500s before cooling.

For the analysis of C6–C12 hydrocarbons, 990 ml of ambient air was drawn into the system with a flow rate of 44 ml.min⁻¹ (air sample is integrated over 22.5 min). The hydrocarbons were pre-concentrated at room temperature on a trap filled with Carboxen. The pre-concentrated air sample was thermally desorbed at 380 °C for 4 minutes and directly injected in a 30 m MXT 1 column (0.28 mm ID, 1.0 µm dF) located inside the heated oven of the GC. During the first 7 minutes of the analytical procedure, the oven temperature rose from 36 °C to 50 °C. Afterwards a constant heating rate of 10 °C.min⁻¹ was applied for 3 minutes followed by a heating rate of 15 °C.min⁻¹ for 8 minutes. The temperature reached 200°C by the heating time. Then the temperature is kept at 200 °C for 240 s before cooling.

Hydrogen was used for the FID flame and as carrier gas at 30 mL/min and Air was also used for the FID flame, as well as for valve actuations of the auto-TDGC-FIDs and drying of samples at 180 mL/min. Air generators (airmopure, Chromatotec[®], France) and Hydrogen generators 99.9999% with dew point below -15 °C (Hydroxychrom, Chromatotec[®], France) were used. The VOCs content of gas generated by both generators was verified experimentally using auto-TDGC-FID and Non-Methanic Hydrocarbon Concentration (NMTHC) for both analyzers was below 0.1 µg.m⁻³.

Along with the development of the analytical system, a specific software has been developed to integrate all data and to display the final results. The system has been first tested in our laboratory where field conditions were reproduced (modification of temperature, humidity, nature of matrix gas, electrical shutdown, etc). Here, results obtained when the system undergoes temperature modifications are presented. The second part will show results from an instrument working in a petrochemical area where important pollutions of unknown compounds were measured.

2.2 Calibration and results validation

Calibrations of the instruments were performed using NIST certified cylinders. TO15, TO14 and PAMS 58 cylinders (Takachio, Japan) were used for the calibration of instruments and response factor calculations for the VOCs, in accordance with the requirement of the ISO:17025 for benzene calibration. The relative response factors to benzene were determined experimentally and then values were compared with the theoretical relative response factors obtained using the equivalent number theory. Less than 10% difference between theoretical and experimental values were obtained, which indicates that the system is suited for such measurement. The linearity tests were performed using 1 ppm cylinder containing 31 VOCs and a dilution system equipped with two mass flow controllers and a dilution chamber (airmoCAL MFC, Chromatotec[®], France). With this system, concentrations ranging from 2 ppb up to 20 ppb were generated from the 1 ppm

cylinder. 5 measurements were performed for each concentration. Both detectors gave an excellent correlation between their response and the concentration ($R^2=0,999$). However, sensitivity and linearity obtained for FID with respect to MS was better over the same concentration range, as shown in Figure 2 for Toluene.

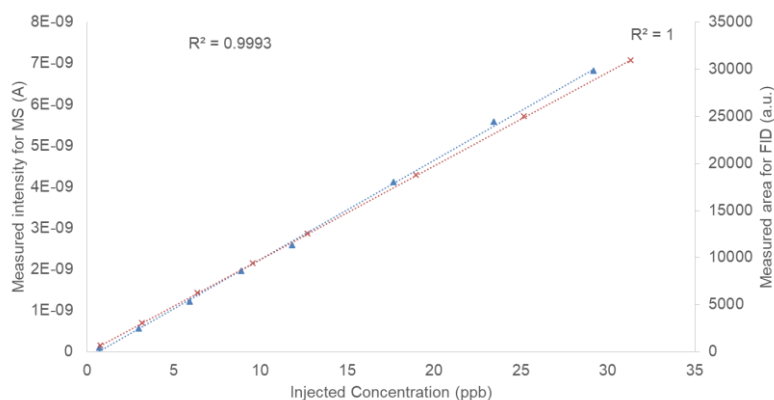


Figure 2: MS (red) and FID (blue) response for Toluene as a function of the concentration.

3. Results and discussion

3.1 Laboratory tests

Laboratory tests have been carried out to test and highlight the advantages of this system. In field conditions, temperature around the analyzer or humidity of the sample can vary a lot and modify by few seconds the time at which compounds elute from the column (also called retention time). This will affect the results as the TDGC-FID will use this parameter to identify the different compounds. For the first test, the temperature of the column was changed to induce a punctual modification of retention times every 5 measurements. In Figure 3, benzene concentrations measured every 30 min in ambient air with the MS and FID are shown.

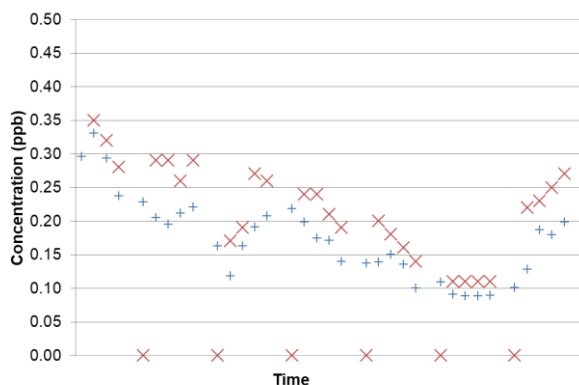


Figure 3: 24 hours measurement of benzene concentrations in ambient air obtained with the MS (+ in blue) and the FID (X in red).

The FID is very stable, linear, and sensitive but it is not selective: any molecules which can burn give an electric signal. Therefore, the only way to identify a compound is to use the retention time. When the peaks elute few seconds before or after the expected time because of temperature variation, the automatic identification of the molecule is not possible: FID measures 0 ppb. On the other hand, the MS allows the monitoring of specific ions which are characteristic of each molecule and measures a concentration corresponding to an expected benzene concentration in ambient air despite the modifications. Chromatograms obtained with the FID and MS are displayed in Figure 4.

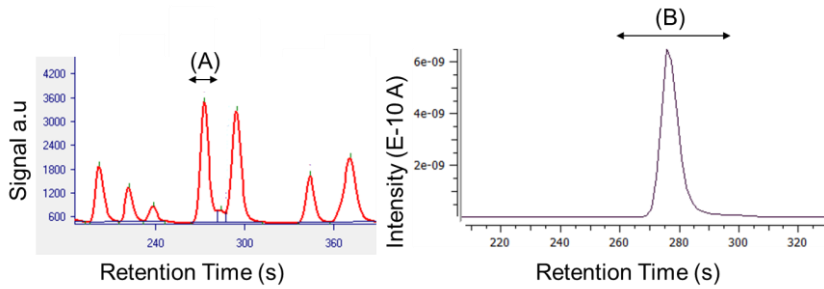


Figure 4: Chromatograms obtained with the FID (a) and the MS (b). The blue arrows represent the period time when the analyzers search for benzene signal: 262-284s for FID and 260-300s for MS.

In Figure 4 b, the intensity of the ion 78 m/z obtained with the MS is displayed. Only one peak can be seen because benzene is the only molecule which can produce this ion (during this period of time). The instrument uses this specific ion identification and quantification and will not be disrupted by a modification of the retention time. Also, the software has been developed to intercompare results from the FID and MS so that the operator is informed of any analytical problem without analyzing the results.

3.2 Field tests

The intercomparison of the results obtained with the two detectors integrated are very useful in field conditions for two reasons: identification of interferences and accurate quantification of the affected compounds. In Figure 5, an unknown compound is measured a few seconds before the benzene peak at high concentration. This is highlighted in Figure 6, where the ion 63 m/z (unknown compound) coelute with the ion 78 m/z (benzene).

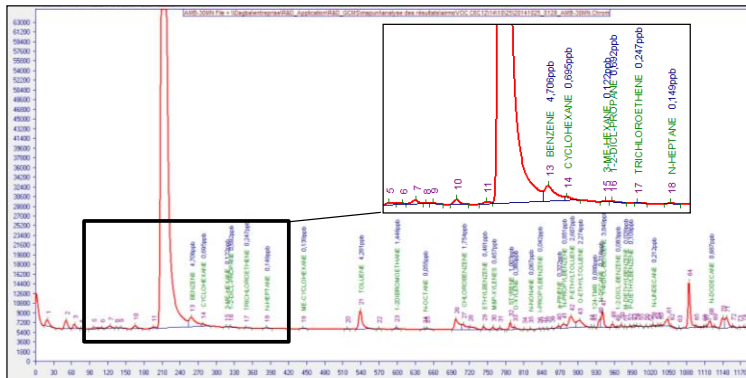


Figure 5: FID chromatogram obtained.

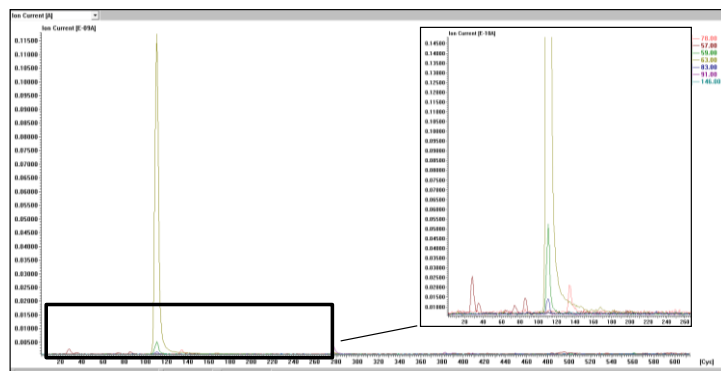


Figure 6: MS chromatogram obtained.

This will affect the benzene integration on FID and induce an overestimation of the concentration. Measured concentrations on FID and MS were of 4.7 and 1.0 ppb respectively. In this case, the system will inform the operator that benzene concentration is overestimated. Once the benzene concentration corrected, the MS has been used to identify the unknown compounds. A scan analysis from 50 to 200 m/z allowed to identify the unknown compound as 1,2-dichloroethane. It has been added to the list of compounds to be measured continuously.

4. Conclusions

The ability of coupling continuous TDGC to a unique process MS and the automatic process of all data is a new advancement in the technology of industrial TDGC-MS. The software integrates all data from both detectors and combines them to ensure the accuracy of the identification and quantification of compounds. One of the big advantages is the possibility to play with two different trapping and thermodesorption techniques linked to one MS. The other advantage is the ability to detect coelutions automatically and then to have the possibility to quantify each compound. This fully automatic system allows non-specialist operators to access to expertise level results. The instrument is perfectly suited for the monitoring and improvement of processes which do not require very short analysis cycles (knowing that measurements take between 5 and 30 minutes with TDGCs). This technique allows measuring the concentration of individual chemical compounds to perform the characterization of complex mixtures such as odour emissions and to obtain their molecular fingerprint. GC-MS allows continuous and field measurements at ppt concentration levels, lower than the human nose detection threshold. Potential harmful effects on human health are therefore more easily prevented through early detections of dangerous release events. However, it does not give information about the odour perception. Thus, there is a need for the application of different complementary techniques for odour measurement such as dynamic olfactometry.

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