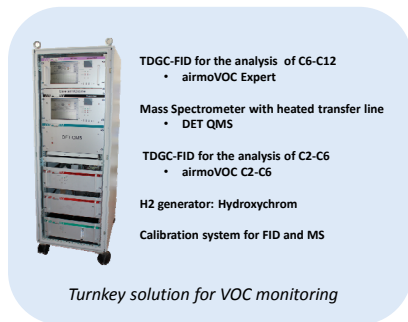


Ambient air is polluted by many VOCs coming from Petrochemical Industries. PAMS, Oxygenated, Chlorinated or Halogenated VOCs can be found in many ranges of concentrations between background and site fence line levels. These compounds are precursors of ozone and Industrial bodies need to identify them to be in compliance with the authorized limits and to improve their process. Chromatotec has developed a system capable of measuring on line and in field conditions a large number of VOCs from ppt to ppm. The device is required to identify automatically potential coeluted compounds by MS technology adapted to industrial context. The coupling of two different thermal desorption Gas Chromatographs equipped with Flame Ionization Detector to a Quadrupole Mass Spectrometer (TDGC-FID/MS) allowed by an elaborated multiplexer system is the originality of the project: one TDGC-FID for light compounds (C2-C6) and one TDGC-FID for heavy compounds (C6-C12) with specific trapping conditions and variable sampling volumes.



airmoSCAN_{xpert}

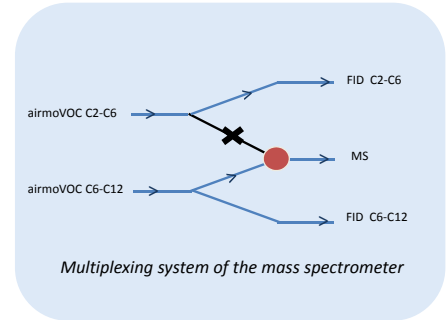
Combination of two technologies :

Gas Chromatography with Flame ionization detector

- Concentrate the compounds in a trap
- Compounds separated by column in pure hydrogen carrier gas
- First identification by RT
- Automatic quantification certified by different organisms

Quadrupole Mass Spectrometer

- Mass analysis Second identification by Mass Spectrum



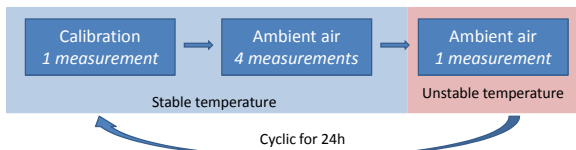
Automatic results without reprocess – MCERTS Certified in 2013¹

Laboratory tests

Modification of retention times induced by temperature variations:

Modification of external conditions is one of the most difficult problems when TDGC-FID technology is used. As the FID is not a selective detector, the retention time (or time at which compounds elute from the GC column) of VOCs is the only parameter that allows the identification of compounds. Therefore, changes of temperature can affect the temperature gradient on the column and modify the retention times of compounds, leading to incorrect identification. Here the MS will be used to solve this issue.

Experimental



Results

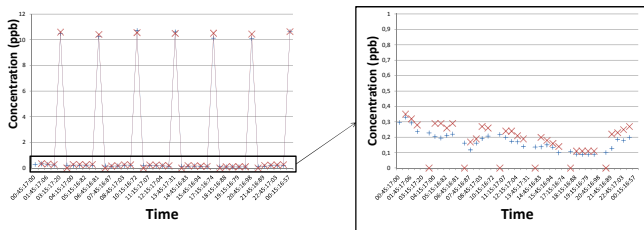


Figure 1: Trend for the measurement of Benzene for 24 Hours: Measurement with FID (in red) and mass spectrometer (in blue)

Every 5 analyses, the concentrations measured by the FID is 0 while the MS measures a concentration in the range of the expected concentration in ambient air (Figure 1). The modification of the temperature induces variations of retention times which do not allow the FID to identify Benzene. On the other hand, the MS can identify and quantify without problem. In Figure 2, the typical chromatograms obtained with FID and MS are shown. The selectivity of the MS (using MID mode) allows for automatic identification of benzene over one minute while 10 s are used for FID.

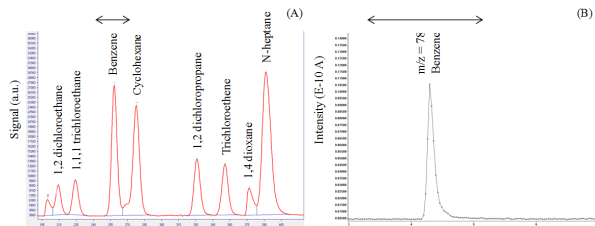


Figure 2: TDGC-FID/MS chromatogram: FID (A) and MS (B)

Field measurements

Validation of GC results by Mass spectrometer:

The concentration variations for selected C2-C6 compounds, obtained for one week of measurements at the petrochemical site, are shown in the table 1. The maximum concentrations of ethane and propane are 119,88 and 121,14 ppb respectively. These anomalous high concentrations which are characteristic from production issues must be confirmed by Mass spectrometer. In the Figure 3 are displayed the MS chromatograms obtained at the maximum of concentration and few days after at low concentration. The MS spectrum and intensity confirm the identification and quantification obtained by FID.

Week 5	ETHANE	PROPANE	N-BUTANE	ACETYLENE	CYCLOPENTANE	N-PENTANE	1-3-BUTADIENE	CYCLOHEXANE	N-HEXANE
mean (ppb)	22,26	18,75	9,25	0,03	0,49	2,67	0,15	0,16	1,45
std dev	25,87	24,81	11,43	0,14	2,56	4,00	0,10	0,35	1,50
min (ppb)	2,35	1,27	0,84	0,00	0,00	0,00	0,00	0,00	0,00
max (ppb)	121,14	119,88	55,23	1,17	16,93	20,54	0,38	1,53	8,06

Table 1: Concentration variations for one week of measurements for the C2-C6

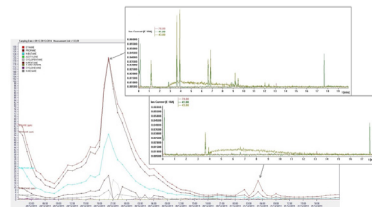


Figure 3: GC-FID validation with mass spectrometer

Identification and quantification of unknown compounds on C6-C12:

In the table 2 are shown the concentration variations for selected C6-C12 compounds. From this table we cannot observe anomalous fluctuation of ambient air concentrations. For example O-xylene varies from 0,05 to 0,72 ppb. Nevertheless, we can see in the Figure 4 (A) that the main peak observed on the FID chromatogram is saturated and not identified. The mass spectrometer will be used for both identification and quantification of the molecule.

Week 1	N-HEXANE	BENZENE	CCl4	CYCLOHEXANE	TOLUENE	N-OCTANE	ETHYLBENZENE	M&P-XYLENES	STYRENE	O-XYLENE	N-DECANE	N-DODECANE
mean (ppb)	0,80	2,07	0,00	0,27	2,40	0,17	0,68	0,71	0,08	0,31	0,64	0,19
std dev	0,52	1,33	0,00	0,23	0,79	0,12	0,20	0,32	0,06	0,11	0,15	0,06
min (ppb)	0,13	0,20	0,00	0,00	1,28	0,00	0,00	0,00	0,02	0,05	0,06	0,00
max (ppb)	1,89	5,35	0,00	0,74	4,75	0,46	1,26	1,78	0,39	0,72	0,94	0,32

Table 2: Concentration variations for one week of measurements for the C6-C12

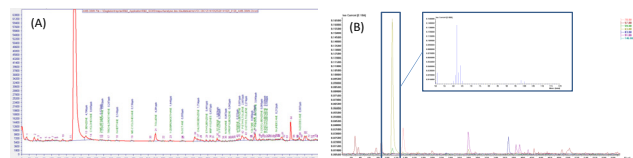


Figure 4: TDGC-FID/MS chromatograms obtained at the petrochemical site

Using the MS chromatogram and spectrum we are able to characterize the unknown compound at a concentration of 120 ppb.² After this identification, the compound can be added to the list of molecules analyzed automatically.

The ability of coupling in continuous two different TDGCs to a unique MS and the automatic identification is a new advance in the technology of industrial TDGC-FID/MS. The big advantage is the possibility to play with two different trapping and thermodesorption techniques linked to one MS. This fully automatic system allows non-specialist operators to access to expertise level results.

¹ MCERTS Certified by SIRA with tests carried out by the NPL of London according to EN 14662-3: Method to establish the performance criteria for the measurement of Benzene concentration using an automated sampling pump with in-situ gas chromatography.

² Due to confidentiality reasons, we cannot give the nature of the compound.