

AUTONOMOUS AND FIELD DUAL TD-GC-MS/FID FOR AUTOMATIC AND CONTINUOUS AMBIENT AIR MONITORING

Chromatotec has hardened and automated a complete GCMS system composed by two different automatic trap GC-FIDs and one single process Quadrupole MS



GCMS system at National Institute

Ambient air is polluted by many semi-Volatile and Volatile Organic Compounds (SVOCs and VOCs) coming from anthropogenic and natural sources. They contribute significantly to the formation of tropospheric (ground-level) ozone (O₃), resulting primarily from the reaction of VOCs with NO_x (NO and NO₂) in the presence of sunlight, and Secondary Organic Aerosol (SOA) by oxidation. They can also have adverse effects on human health due to the well-known toxicity of several compounds, such as benzene (carcinogen) and toluene (central nervous system toxicant).

Automatic, continuous and easy identification and quantification of VOCs in ambient and indoor air is critical to improve the understanding of the exposure to toxicants released into the environment, and hence improve people's safety.

Due to the large number of molecules, the complete separation of all compounds is difficult to perform using chromatographic columns. Mass Spectrometry (MS) detection must be added to identify with expertise individual compounds monitored and identify unknown compounds.

Chromatotec® solutions

Chromatotec Group® is specialized in the manufacturing and developing of autonomous gas analyzers based in automatic Gas Chromatography (autoGCs) for online monitoring. The turnkey solutions provided allow tracking in automatic VOCs at very low concentration levels (from ppt) as well as up to high concentration (ppm level) during industrial big pollution events.

Chromatotec® is permanently involved in new turn-key solution

developments for gas analysis at industrial sites. In order to answer to the customer demand willing to have fully automatic system providing automatically validated data, a new GCMS solution has been developed: the airmOzone expert with DET QMS system.

This standalone system provides automatically and continuously validated results for the identification and quantification of more than 120 different VOCs in standard directly on the field without the need of any daily operator.

USEPA validation and list of molecules

The airmOzone expert has been selected by the United States Environmental Protection Agency (USEPA). The USEPA requires Photochemical Assessment Monitoring Stations (PAMS) to ensure the required collection of ambient air pollutant and meteorological data to meet the need for more comprehensive air quality database for ozone and its precursors and attainment of the National Ambient Air Quality Standard (NAAQS) for ozone nationwide.

The EPA conducted an evaluation of auto-GCs, with on-board gas generators and internal calibration, to replace the old equipment used at PAMS sites for effective tracking of VOC concentrations believed to be important ozone precursors. After both laboratory evaluation and a field deployment evaluation, the EPA concluded that the PAMS network require 12 additional airmOzone systems from Chromatotec on field over the US.

Ambient concentrations of ozone precursors will be used to better characterize the nature and extent of the ozone problem, and prepare air quality trends. In addition, data from the PAMS will provide an improved database for evaluation of photochemical model performance, especially for future control strategy mid-course corrections as part of the continuing air quality management process. The data will be particularly useful to States in ensuring the implementation of the most cost-effective regulatory controls.

VOCs measured are gaseous aliphatic and aromatic hydrocarbons in ambient air up to C16, including the components of interest at the PAMS program as well as the extra chlorinated compounds covered by Compendium Methods TO-14 (EPA 625/R-96/010b) and TO-15. The data collected at the PAMS sites include measurements of a target list of VOCs including paraffins, olefins, aromatics, and alkynes. Most PAMS sites measure 56 target hydrocarbons listed in the adjacent Table 1.

Additionally, the airmOzone expert system is used by various reference institutes and universities to monitor polycyclic aromatic hydrocarbons (PAHs) in industrial site, tropical forest and on site under decontamination. Volatile PAHs measured in standard are: naphthalene, 2-methyl-naphthalene, 1-methyl-naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene and anthracene.

Configuration

The airmOzone expert system consists in two automatic gas chromatographs (airmoVOC C2-C6 and airmoVOC C6-C16) both equipped with a FID detector, one for light compounds (C2-C6) and the other for heavy compounds (C6-C16). Both TD-GCs are

coupled to a single Quadrupole MS. Extremely sensitive it can automatically identify and quantify VOCs down to ppt levels. Results are obtained every 30 minutes for molecules from 2 to 16 carbon atoms simultaneously. LOQ for Benzene is as low as 1 ppt in automatic.

The equipment is specially designed for field applications with the best performance and flexibility, optimizing the space. It can be placed in one cabinet or in two smaller ones, as showed in the following picture, each one occupying less than one square metre of floor space. The airmOzone expert is a transportable system, thanks to its wheels and the inside is easily accessible thanks to the rack sliders. This miniaturized system is perfect to be installed in mobile laboratories for on-site analysis.

Table 1. Revised PAMS Target Lista

<https://www3.epa.gov/ttnamti1/files/ambient/pams/targetlist.pdf>

Existing Priority Compounds	Optional Compounds
1,2,3 - Trimethylbenzene	1,3 Butadiene
1,2,4 - Trimethylbenzene	1,3,5-Trimethylbenzene
1-Butene	1-Pentene
2,2,4 - Trimethylpentane	2,2-Dimethylbutane
Acetaldehyde ^b	2,3,4- Trimethylpentane
Benzene	2,3-Dimethylbutane
Cis-2-Butene	2,3-Dimethylpentane
Ethane	2,4-Dimethylpentane
Ethylbenzene	2-Methylheptane
Ethylene	2-Methylhexane
Formaldehyde ^b	2-Methylpentane
Isobutane	3-Methylheptane
Isopentane	3-Methylhexane
Isoprene	3-Methylpentane
M/P Xylene	Acetone
M-Ethyltoluene	Acetylene
N-Butane	Alpha Pinede
N-Hexane	Benzaldehyde ^b
N-Pentane	Beta Pinede
O-Ethyltoluene	Cis-2-Pentene
O-Xylene	Carbon Tetrachloride
P-Ethyltoluene	Cyclohexane
Propane	Cyclopentane
Propylene	Ethanol
Styrene	Isopropylbenzene
Toluene	M-Diethylbenzene
Trans-2-Butene	Methylcyclohexane
	Methylcyclopentane
	N-Decane
	N-Heptane
	N-Nonane
	N-Octane
	N-Propylbenzene
	N-Undecane
	P-Diethylbenzene
	Tetrachloroethylene
	Trans-2-Pentene

* This table only includes individual target compounds. Monitoring agencies should continue measuring and reporting total non-methane organic compounds (TNMOC)

^b These compounds are carbonyls and are measured using Method TO-11a



airmOzone expert + DET QMS analyzer in 19" cabinet from 18U to 38U.

The stability and accuracy of the system is checked in automatic every day with the internal calibration system with benzene permeation tube for validation of the complete system and to provide automatic data validation. Both detectors gave an excellent correlation between their response and the concentration ($>R^2=0,999$).

The robustness and long term stability of the complete system allow validating data without frequent calibration need. The results are extremely stable at 10 ppb level with for example on benzene peak area RSD at 3.77% for MS detector and 2.51 for FID detector over more than 120 days without tune or calibration during this period. The concentration are automatically computed using VistaMS software which calculate the compounds concentration analyzed using high intensity on selected ion for each species. It records all data in an embedded computer for full traceability and transfer of all results and information using different data transfer protocols (MODBUS / MGS1 / 4-20mA / 0-10V). The software also allows remote control and setting up threshold alarms.



Ambient air monitoring for Research National Institute

Analytical performance

The performance of the system was studied using permeation tubes and certified cylinders containing VOC mixtures (PAMS, TO14 and TO15) and a dilution system equipped with two mass flow controllers and a dilution chamber. With this system, concentrations ranging from 0 ppb up to 40 ppb were generated.

Solving coelutions in ambient air samples

Compounds taking part in a coelution can be identified by FID coupled to MS detection. When a single FID detector is used, interferences may occur (e.g. acetylene and 2-me-pentane with N-Butane and 3-me-pentane respectively) but the additional MS can identify individual components of a peak by choosing the compound with the best matching mass spectra pattern available in the NIST library. Like this, the peak at 680 s identified as only N-Octane in Figure 1a could be deconvoluted into N-Octane and tetrachloroethene in Figure 1b.

Validation of the results

The determination of validated results by the automatic intercomparison of FID and MS results was performed automatically by VistaMS software following an algorithm that privileges the result obtained by FID because it is a very accurate and sensitive detector. In case of coelution, validated results are considered those obtained using the MS detector, due to its ability to identify individual compounds.

Thus, dual-detection allowed improving the accuracy of the

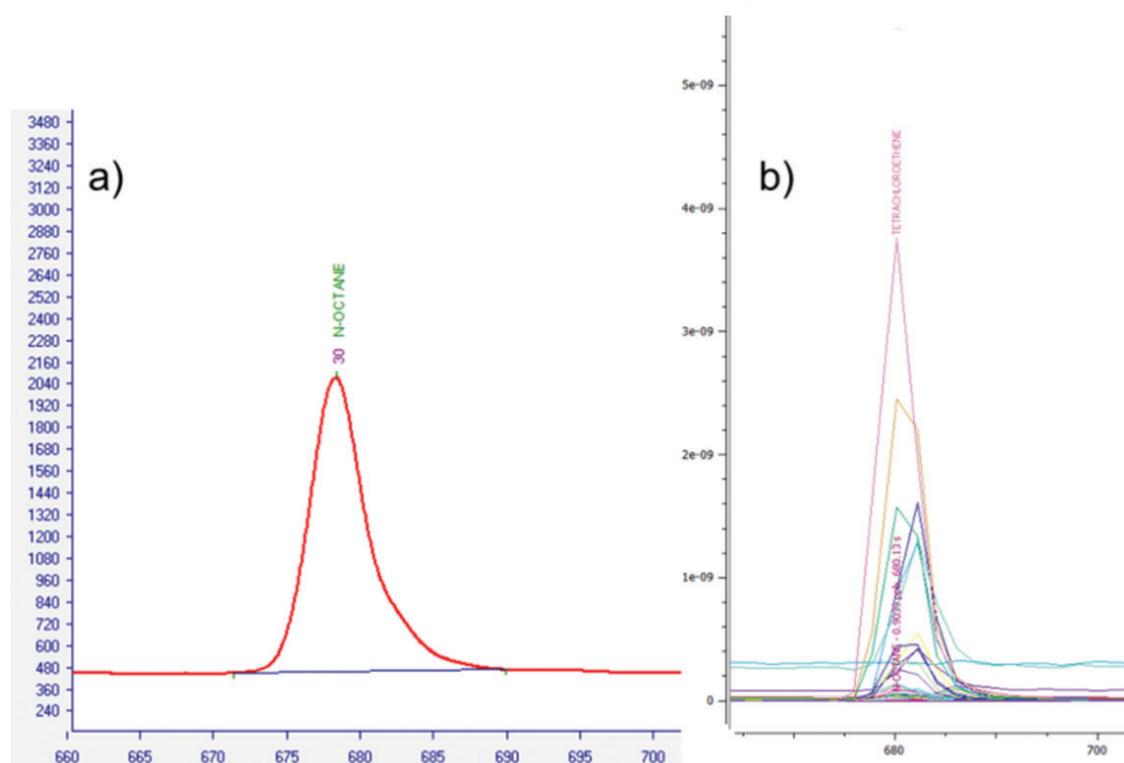


Figure 1. Chromatograms, intensity of the signal [A] vs. retention time (s), of the N-Octane and tetrachloroethene coelution observed by FID detection (a) solved with the MS (b) for C6-C16 analysis.

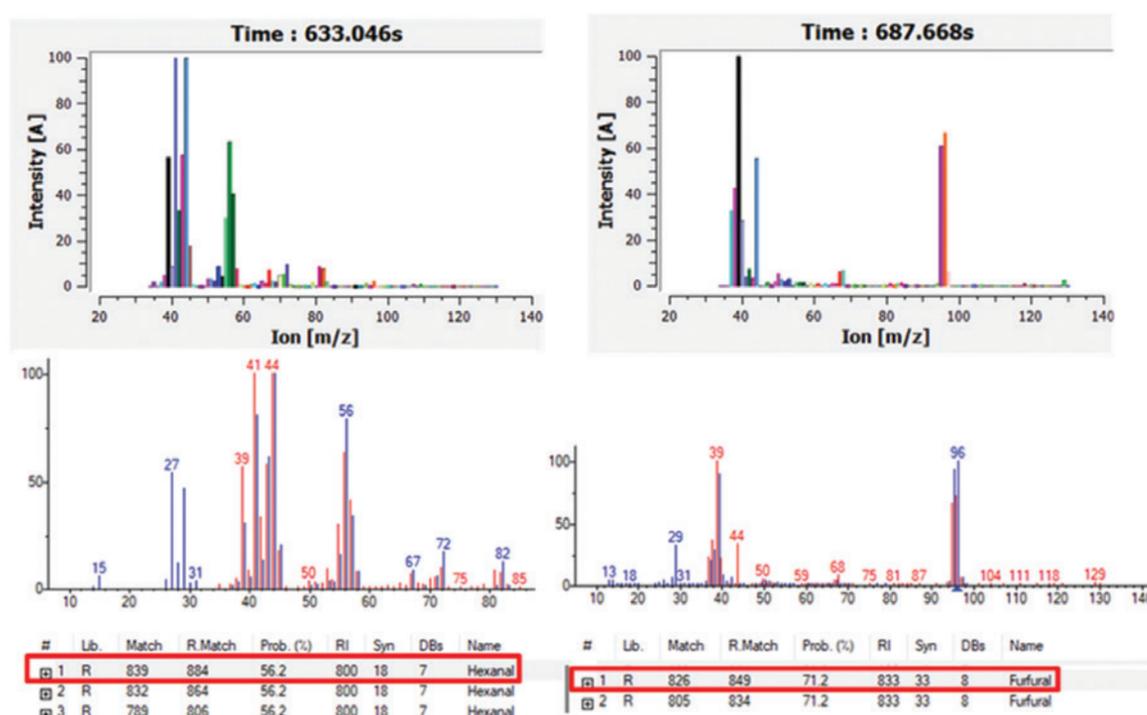


Figure 2. Automatic comparison between mass spectra obtained (top) and reference (bottom).

identification and quantification of the compounds in ambient air by 14%, with precision values expressed as RSD better than 5%.

Identification of unknown compounds

Two unidentified peaks of less than 1 ppb were found in the GC-MS data. Compound identification was performed by comparison of the mass spectrum (m/z values and the relative intensities) obtained with those from the NIST Library. Figure 2 shows the excellent spectral match obtained for Hexanal and Furfural by C6-C16 analysis.

Thus, in case of identifying additional compounds during data collection, which were not included by default in the list provided with the system they can be easily added to the target substance tables. The parameter list is not limited to the measurement of the SVOCs, VOCs and PAHs from 2 to 16 carbon molecules in standard. Instead, it can be adapted according to the needs of the measurement campaign (for example, depending on the geographical area) or if the requirements of the PAMS, TO14 and TO15 methods change.

Conclusion and main features

- The system measures from C2 to at least C16 range. Recently, linear alkanes have been measured up to C20.
- Complete autonomy: The FID can be operated continuously using hydrogen and zero air generators. No cylinders are required.

- On-field analysis with laboratory quality results with this fully automatic, intrinsically linear, and precise down to ppt levels and very stable system.
- Potentially coeluted compounds are identified and validated by VistaMS software thanks to the intercomparison of FID and MS results.
- Every unexpected or unknown compounds are automatically identified thanks to the internal NIST library linked to VistaMS in the internal computer of the GCMS system.
- Saves space: the complete system in 1 or two small rack mounted units for convenient use in a monitoring station.
- Transportable: it can be installed in an analyzer shelter on-site as well as in a mobile van.
- Enhanced ease of use: The measurement system performance evaluation is completed with internal calibration using NIST traceable permeation tube technology to provide automatic data validation to access expertise level results. This fully automatic, user-friendly system is capable of operating in an unattended mode over extended periods of time.
- All data collected are stored to assure their full traceability and availability.

Chromatotec will exhibit at Pittcon Booth #1637 and Analytica – French Pavilion

Author Contact Details

Franck Amiet – President and CEO, Chromatotec • 15 rue d'Artiguelongue, – Saint-Antoine, 33240 Val de Virvée France
• Tel +33 5 57 94 06 22 • Email: info@chromatotec.com • Web: www.chromatotec.com



Read, Print, Share or Comment on this Article at: envirotech-online.com/article

