HAL
open science

Development and validation of on-line and in-field Auto-GC for the analysis of trace-level OVOCs

Fanny Bachelier, Jean-Philippe Amiet, Véronique Daële, Damien Bazin

To cite this version:

Fanny Bachelier, Jean-Philippe Amiet, Véronique Daële, Damien Bazin. Development and validation of on-line and in-field Auto-GC for the analysis of trace-level OVOCs. 1st ACTRIS Science Conference, May 2022, Virtuel, France. hal-03868046

HAL Id: hal-03868046

https://hal.science/hal-03868046v1

Submitted on 23 Nov 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

DEVELOPMENT AND VALIDATION OF ON-LINE AND IN-FIELD AUTO-GC FOR THE ANALYSIS OF TRACE-LEVEL OVOC

F. BACHELIER[1,2], J.P. AMIET[1], V. DAËLE[2] and D. BAZIN[1]

[1]Chromatotec, 15 rue d'Artiguelongue, 33240 Saint-Antoine, France.
[2]ICARE – UPR 3021 – CNRS, 1C, av. De la recherche scientifique CS50060 - 45071 Orléans, France.

Keywords: On-line monitoring, gas chromatography, OVOCs, Mass spectrometry.

INTRODUCTION

Oxygenated Volatile Organic Compounds (OVOCs) are an important fraction of the VOCs and are emitted in the atmosphere from anthropological (solvent, industry, transport) and biogenic sources (Legreid et al., 2007; Placet et al., 2000). Also, oxidation process in the atmosphere can lead to the formation of OVOCs (Atkinson, 2000). Aldehydes and Ketones are generally measured following the ISO 16000-3 method where DNPH cartridges are used to preconcentrate the sample. The method is very sensitive and allows identification and quantification from low ppt to high ppb depending on flow and sampling time (Uchiyama et al., 2004). Nevertheless, this technique is time consuming as it is needed to manually elute the DNPH cartridge before HPLC-UV analysis. Other techniques allow specific quantification of OVOCs such as formaldehyde but cannot quantify all OVOCs (Becker et al., 2019). Therefore, there is a need for automated and continuous measurement of Aldehydes, Ketones and also Alcohols (which are not measured with ISO 16000-3 method). Automated gas chromatograph are widely used for the characterization of VOCs in ambient air (Martin et al., 2012). Nevertheless, OVOCs and particularly light OVOCs are often difficult to measure without interference. In this article, we present a study on the performance and limitation of a dual thermo-desorption gas chromatograph equipped with flame ionisation detector and mass spectrometer for the characterization of OVOCs in ambient air. Also, we will present results on a specific module dedicated to the measurement of light OVOCs.

METHODS

auto-TDGC-FID/MS for C2 to C6 Monitoring

An automatic gas chromatograph (airmoVOC C2-C6, Chromatotec, France) equipped with a flame ionization detector (FID) and mass spectrometer has been used for the monitoring of non-polar molecules containing from 2 to 6 carbon atoms. For each analysis, 107 mL of ambient air was drawn into the system with a flow rate of 12 $mL.min^{-1}$ (air sample is integrated over 10 min). The air 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 Carbopack. The pre-concentrated air sample was thermally desorbed at 220°C for 4 minutes and directly injected in a 25 m Al_2O_3/Na_2SO_4 column (PLOT column, 0.53 mm ID, 10.0 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 15°$C.min^{-1}$ was applied and the temperature reached 202°C. Then the temperature is kept at 202°C for 630s before cooling. C2–C6 hydrocarbons were detected by FID and the detection limit has been determined to be 0.065 $\mu g.m^{-3}$ for N-butane.

auto-TDGC-FID/MS for C6 to C12 Monitoring

For the monitoring of molecules containing from 6 to 12 carbon atoms an automatic gas chromatograph (airmoVOC C6-C12, Chromatotec, France) equipped with FID and mass spectrometer has been used. For each analysis, 440 mL of ambient air was drawn into the system with a flow rate of 20 mL.min-1 (air sample is integrated over 20 min). The compounds were pre-concentrated at room temperature on a trap filled with Carbopack mixture. The pre-concentrated air sample was thermally desorbed at 380°C for 4 minutes and directly injected in a 60 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. C6–C12 compounds were detected by a FID and the detection limit has been determined to be 0.045 µg.m^{-3} for Benzene.

Mass spectrometer for C2-C12 monitoring

Low-resolution mass spectra (MS) were recorded in the electron impact mode (EI, 70 eV) with a single quadrupole mass spectrometer (DET QMS, Chromatotec, France). The system is equipped with a heated multiplexing system for two streams (200°C) and two heated transfer lines (200°C). The measured intensities were computed using VistaMS software and concentration calculations were performed using hight intensity on selected ion for each species. The determination of validated results was performed with VistaMS. The tuning of the mass spectrometer was performed using Perfluorotributylamine (PFTBA) from Sigma-Aldrich. All electronic parameters were saved and used for the whole time of the experiment.

auto-TDGC-FID with methanizer for light OVOCs

The monitoring of formaldehyde, acetaldehyde and methanol was performed using automatic gas chromatograph equipped with a hydrogenating reactor to convert all OVOCs to methane before quantification using FID. The OVOCs were pre-concentrated at room temperature on a trap filled with Carbopack. The pre-concentrated air sample was thermally desorbed at 380°C for 4 minutes and directly injected in a two-dimensional columns system (polar and apolar capillary columns) located inside the heated oven of the GC. The first column is used for separation of light compounds according to their molecular mass. The polar column separates polar from non-polar compounds before identification and quantification.

Gas supply

Air generators (airmopure, Chromatotec, France) and Hydrogen generators 99.9999% with dew point below -15°C (Hydroxychrom, Chromatotec, France) were used for the flames of FIDs, valve actuations of the auto-TDGC-FIDs and drying of samples for C2 to C6 analysis. The VOCs content of gas generated by both generators was verified experimentally using auto-TDGC-FID and Non-Methanic Hydrocarbon Concentration (NMTHC) for both analysers was below 0.1 µg.m-3.

Standards used for calibration

Quality controls of the instruments were performed using NIST certified cylinders. TO15 (64 compounds) and PAMS 58 (Takachiho, Japan) were used for the calibration of instruments and response factor calculations.

Calibration setup

For the calibration of OVOCs, a certified gas mixture of TO15 compounds was used at different concentrations in the range 0.5 – 10 ppb$_v$. The concentration of each compound in the cylinder is 100 ppb$_v$ ± 10%. To perform the dilution of the cylinder with zero air, 2 mass flow controllers (MFC) from Bronkhorst were used. The flow range of the Cylinder MFC was 0-10 mL.min^{-1} and the flow range of Dilution MFC was 0-1 L.min^{-1}. The sample flow rate was 30 mL.min^{-1}. Calibration curves were performed with 6 different

concentrations with 10 replicates for the first calibration point and 6 replicates for the others. Precision and accuracy were evaluated at 4 ppb_v.

CONCLUSIONS

The aim of this study was to analyse specifically oxygenated VOCs in ambient air, using an on-line system including 2 automatic TDGC-FID coupled to a mass spectrometer, and an auto-TDGC-FID with a methanizer.

C2 to C6 measurement

Light non-polar VOCs containing 2 to 6 carbons were analysed using the first on-line auto-TDGC-FID/MS equipped with an Al_2O_3/Na_2SO_4 PLOT column. The system can analyse all light compounds from PAMS 58 cylinder and some of the molecules included in the TO15 cylinder such as freons, chlorinated compounds and carbon disulphide. Nevertheless, light OVOCs such as Methanol, Ethanol, Formaldehyde and Acetaldehyde cannot be analysed with the analyser because they cannot be eluted from Al_2O_3/Na_2SO_4 PLOT column.

C6 to C12 measurement and performance studies

The second on-line auto-TDGC-FID-MS equipped with an MXT-1 column is designed to analyse molecules containing 6 to 12 carbons and was used for the measurement of OVOCs heavier than Acetaldehyde.

	VOCs
1	Ethanol
2	Acrolein
3	Acetone
4	Isopropyl alcohol
5	Methyl *tert*-butyl ether
6	Vinyl acetate
7	Methyl ethyl ketone
8	Ethyl acetate
9	1,4-Dioxane
10	Methyl methacrylate
11	Methyl isobutyl ketone
12	Methyl butyl ketone

Table 1: List of OVOCs in TO15 standard gas mixture

The TO15 gas mixture (64 compounds) contains 12 OVOCs that are listed in Table 1. Among these 12 compounds only ethanol is not retained enough by the trap to be detected. The FID chromatogram of TO15 standard mix at 4ppb is showed in Fig. 1. The 11 OVOCs detected were identified with their retention times. To confirm identifications, mass spectrometry detection and NIST database were used.

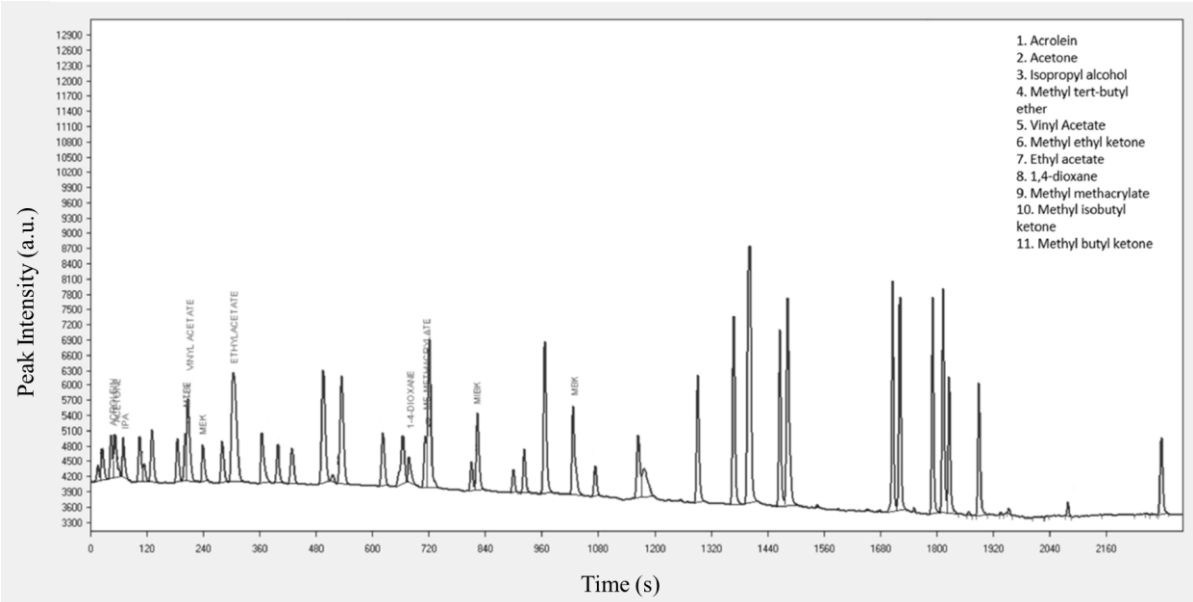

Figure 1: FID chromatogram of 4 ppb of 11 OVOCs contained in TO15 standard mix

It is noticeable that coelutions occur between some OVOCs and the other compounds of the cylinder. As shown in Fig. 1, MTBE and Vinyl acetate are co-eluted, Ethyl acetate is co-eluted with Chloroform and Methyl methacrylate with N-heptane. Fortunately, we can avoid these coelutions with MS detection by selected the specific ion for each compound.

Calibration curves for each OVOCs were performed with six different concentrations of standard mixture. The range of concentrations is 0.5 to 10 ppb. The linearity of calibration curves was determined with determination coefficient (R^2) for FID and MS detection. As reported in Table 2, the determination coefficients varied between 0.9829 and 0.9992 for FID and 0.9871 and 0.9995 for MS showing linear calibration curves for every compounds.

The limits of detection (LOD) of the systems were calculated according to the Chinese standard norm for ambient air measurement (HJ 1010-2018, 2019). Thus, the LODs were determined with the standard deviation of 10 replicates of the standard gas at 0.5 ppb (Table 2). The detection limits ranged from 0.065 to 0.325 ppb and 0.068 to 2.110 ppb for FID and MS respectively. Except for MEK and MBK, all detection limits are at least 50% higher with MS detection.

The precision and accuracy were calculated at 4 ppb according to the Chinese standard method. The majority of the compounds presented relative standard deviations below 10%, but the non-gaussian peak shape of oxygenated compounds could be responsible of accuracies over 10% (Table 2). In comparison, Benzene accuracies are 0.68% and 3.00 % for FID and MS respectively.

OVOCs	FID Detection				MS detection			
	Determination coefficient (R^2)	LOD (ppb_v)	Precision at 4 ppb_v (%RSD)	Accuracy at 4 ppb_v (%)	Determination coefficient (R^2)	LOD (ppb_v)	Precision at 4 ppb_v (%RSD)	Accuracy at 4 ppb_v (%)
Methanol	*ND*	-	-	-	-	-	-	-
Ethanol	*ND*	-	-	-	-	-	-	-
Formaldehyde	*ND*	-	-	-	-	-	-	-
Acetaldehyde	*ND*	-	-	-	-	-	-	-
Acrolein	0.9992	0.093	2.04	2.62	0.9990	0.277	10.6	1.67
Acetone	0.9960	0.065	5.79	8.27	0.9995	0.253	5.45	2.22
Isopropyl alcohol (IPA)	0.9829	0.130	1.12	13.6	0.9871	0.404	7.76	7.87
Methyl *tert*-butyl ether (MTBE)	*Coeluted*	-	-	-	0.9995	0.216	2.78	2.09
Vinyl acetate	*Coeluted*	-	-	-	0.9992	0.431	7.49	0.73
Methyl ethyl ketone (MEK)	0.9960	0.124	2.52	14.2	0.9899	0.068	4.37	19.8
Ethyl acetate	*Coeluted*	-	-	-	0.9928	0.179	6.79	19.28
1,4-Dioxane	0.9894	0.150	2.44	29.2	0.9978	0.285	7.29	14.9
Methyl methacrylate	*Coeluted*	-	-	-	0.9984	0.273	3.43	5.92
Methyl isobutyl ketone (MIBK)	0.9986	0.325	1.46	7.36	0.9979	0.760	8.12	2.34
Methyl butyl ketone (MBK)	0.9970	0.270	2.77	7.68	0.9988	0.159	7.79	2.47

Table 2: Determination coefficients, detection limits, precision and accuracy of OVOCs using FID and MS detection

As shown in Table 2, although the LOD and repeatability are overall better for FID than MS, FID detection could not provide analysis of MTBE, Vinyl acetate, Ethyl acetate and 1.4-Dioxane due to the coelutions. However, by selecting a specific ion for each species, MS detection allows accurate quantification of these compounds.

Specific gas chromatograph for light OVOC

As shown previously, methanol, ethanol, formaldehyde and acetaldehyde cannot be quantified using the C2-C12 FID/MS system. Therefore, a specific analyser has been designed for the separation and quantification of these molecules. The three main challenges for this application are: preconcentration, separation and capability to measure these molecules with very low response on FID. Analytical solutions have been found for all three challenges and we have shown that the system is perfectly suited for the measurement methanol, ethanol, formaldehyde and acetaldehyde (Mascles et al., 2021).

In this work, the performances and limitations of detection of OVOCs in ambient air by dual thermo-desorption gas chromatograph equipped with flame ionisation detector and mass spectrometer were described. Using a TO15 standard gas mixture, 11 OVOCs from acrolein to methyl butyl ketone were identified and accurately quantified on the C6C12 system with MS detection. However, for the detection of light OVOCs such as Methanol, Ethanol, Formaldehyde and Acetaldehyde a specific module dedicated to the measurement of these compounds is required.

ACKNOWLEDGEMENTS

This work was carried out as part of a thesis with a CIFRE agreement from the National Association for Technical Research (ANRT)

REFERENCES

Atkinson, R. (2000). Atmospheric chemistry of VOCs and NOx. Atmospheric Environment *34*, 2063–2101.

Becker, A., Andrikopoulou, C., Bernhardt, P., Ocampo-Torres, R., Trocquet, C., and Le Calvé, S. (2019). Development and Optimization of an Airborne Formaldehyde Microfluidic Analytical Device Based on Passive Uptake through a Microporous Tube. Micromachines *10*, 807.

HJ 1010-2018 (2019). Specifications and Test Procedures for Ambient Air Quality Continuous Monitoring System with Gas Chromatography for Volatile Organic Compounds.

Legreid, G., Lööv, J.B., Staehelin, J., Hueglin, C., Hill, M., Buchmann, B., Prevot, A.S.H., and Reimann, S. (2007). Oxygenated volatile organic compounds (OVOCs) at an urban background site in Zürich (Europe): Seasonal variation and source allocation. Atmospheric Environment *41*, 8409–8423.

Martin, N.A., Jarvis, S.D., White, S., Helmore, J.J., and Bevan, O.J. (2012). airmoVOC C6-C12 - MCERTS Performance Standards for Continuous Ambient Air Quality Monitoring Systems (London).

Mascles, M., Grandjean, A., Le Calvé, S., Bazin, D., and Amiet, F. (2021). Development and comparison of three analytical systems for detection and quantification of formaldehyde and other aldehydes for process, indoor and ambient air emissions.

Placet, M., Mann, C.O., Gilbert, R.O., and Niefer, M.J. (2000). Emissions of ozone precursors from stationary sources:: a critical review. Atmospheric Environment *34*, 2183–2204.

Uchiyama, S., Matsushima, E., Aoyagi, S., and Ando, M. (2004). Simultaneous Determination of C1−C4 Carboxylic Acids and Aldehydes Using 2,4-Dinitrophenylhydrazine-Impregnated Silica Gel and High-Performance Liquid Chromatography. Anal. Chem. *76*, 5849–5854.