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Tutorial Article

Development, optimization and validation of automated volatile organic compound data analysis using an on-line thermal desorption gas chromatograph with dual detection and application to measurements in ambient air

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ABSTRACT

Because of their major role in indoor and outdoor air pollution, even at trace levels, VOCs are of great interest, and their monitoring requires sensitive analytical instruments. Several techniques are commonly used, such as portable sensors, Proton Transfer Reaction Mass Spectrometry (PTR-MS) and Thermal Desorption Gas Chromatography (TD-GC). The latter is widely used off- and on-line with Flame Ionization Detectors (FID) or Mass Spectrometers (MS). Given the large number of molecules detected per chromatogram, the data generated by these monitoring techniques are usually checked and reprocessed manually. This process is extremely time consuming and could result in human error. The challenge is to provide reliable results as quickly as possible.

In this study, the performances of an on-line TD-GC system with dual detection FID and MS were tested. The Method Detection Limits (MDL), linearities and accuracies of 60 VOCs (alkanes, aromatics, oxygenated and halogenated) were calculated both for FID and MS detectors. The MDLs and accuracies ranged from 0.006 to 0.618 ppbv and from 77 % to 100 % for FID, and from 0.018 to 0.760 ppbv and from 80 % to 100 % for MS. Both detectors showed good complementarity and allowed the development of two programs to facilitate data analysis. These algorithms were designed to autonomously select optimal results between FID and MS detectors, and were evaluated for outdoor and indoor measurement conditions. Measuring VOCs in field campaigns is challenging, and it is anticipated that these programs could be extended to other types of dual-detector systems or for the comparison of data from different calibrated instruments.

1. Introduction

Volatile organic compounds (VOCs) are a class of pollutants emitted into the atmosphere both from anthropogenic and biogenic sources [1,2]. VOCs constitute a broad range of compounds, many of which have adverse effects on human health. According to the health agencies, longtime exposure to air polluted areas could lead to long-term diseases [3]. For example, traces of carbonyl and aromatic compounds such as formaldehyde and benzene are implicated in incidences of some cancers and pulmonary issues [4,5].

VOCs also play a major role in global climate change. During daytime, they react mostly with hydroxyl radical (OH) [6,7]. During Nighttime, olefinic and aldehydic VOCs will be oxidized by reaction with nitrate radical (NO_3) [8–10]. Ozone can also oxidize VOCs during day and night [11,12]. All these oxidation processes lead to the formation of secondary organic aerosols and tropospheric ozone, considered to be one of the most important greenhouse gases [13].

While VOC emissions in outdoor air are mainly related to environmental issues, their role in indoor environments are directly linked to human health. Nowadays, people spend the majority of their time indoors (e.g. homes, schools, offices, public transport). As these compounds are widely emitted from building materials, paints, solvents and furniture, indoor air is a major source of human exposure to VOCs. These pollutants, depending on their concentration and exposure time, can have immediate or future adverse health effects [14]. In addition,

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they are generally present at higher concentrations, at ppbv levels indoors compared to pptv in outdoor environments [15].

As each VOC has a specific toxicity [16] and reactivity [17] in the atmosphere, it is important to identify these compounds in order to assess their impact on health and the environment. For these reasons, it is necessary to accurately measure the VOC concentrations in both indoor and outdoor environments. To do so, numerous monitoring techniques exist. Low-cost screening devices have been developed and deployed over the last few years. These instruments are affordable and constantly evolving. Nevertheless, these systems usually suffer from a lack of sensitivity and specificity [18]. On-line near real-time measurement techniques such as Proton Transfer Reaction Mass Spectrometry (PTR-MS) [19], Differential Optical Absorption Spectroscopy (DOAS) [20], and Fourier Transform InfraRed spectroscopy (FTIR) [21] are also widely employed to monitor VOCs in ambient air. Among them, Proton Transfer Reaction Time-of-Flight Mass Spectrometry (PTR-ToF-MS) is commonly used in atmospheric science for monitoring [22]. Another main approach to monitor VOCs in ambient air is the Gas Chromatography (GC) technique [23,24]. Thanks to its high reliability, this technology is used in the EPA Standard method to quantify VOCs in ambient air by off-line sampling of canisters and GC–MS (USEPA, 1999). Major drawbacks of off-line sampling include low temporal resolution and the possibility of losing information during canister transport. Hence, on-line thermal desorption (TD) gas chromatographs are also frequently deployed [25–27].

Recently, the Aerosol, Clouds and Trace Gases Research Infrastructure (ACTRIS) published measurement guidelines for NOx and VOCs [28]. In this report, the TD-GC technique is presented as the method of choice for VOCs monitoring for the reasons of medium cost, high sensitivity and excellent reproducibility. On-line GCs appeared to be good alternatives to deliver accurate and continuous VOC monitoring in ambient air while avoiding storage issues. However, PTR and GC methods remain expensive and require well-trained personnel to operate and analyze the data, which increases their overall costs.

Two major types of detectors are coupled to on-line TD-GC: Flame Ionization Detection (FID) and Mass Spectrometry (MS). It is challenging to identify which detector is the most suitable for ambient air measurement as they both have their specific advantages.

The MS is a very powerful detector for identification and quantification of complex mixtures with potential coeluted compounds but remains less stable and linear than the FID, especially for long-term measurements [29]. However, FID is wholly dependent upon retention time for compound identification, and under real-world conditions where retention times can vary subtly, and where complex sample mixtures lead to coelutions, compound peaks are easily misidentified and/or misinterpreted, especially using automated software approaches.

The complementarity of these detectors has motivated the attempt to couple them after GC separation since 1968 [30–32]. In the field of atmospheric science, off-line TD-GC-FID/MS have been used essentially for laboratory studies [33,34]. Despite the advantages of the dual detection, measurements in parallel of FID and MS generate twice as many data to analyze, representing a significant part of a scientist's work time, especially for concentrations at pptv levels. Hence, there is a need to automatize the data processing as much as possible.

We discussed in a previous study [35] about the development of an automatic TD-GC with dual detection FID and MS for measuring light odorous compounds from certified gas cylinders.

Accordingly, we present the optimization of this on-line TD-GC-FID/MS for the monitoring of a wider range of ambient VOCs (between 2 and 16 carbon atoms), in field campaigns and the performance studies of the instrument for FID and MS detectors to demonstrate their complementarity. We describe the development and optimization of a comparison algorithm made to improve data reprocessing automation. Its objective is to automatically select for each compound the FID or MS data in order to quickly provide an accurate validated result.

To illustrate the performance of this newly developed algorithm, it was applied two indoor and outdoor measurement campaigns and tested against a manual data analysis.

2. Materials and methods

2.1. Auto-TD-GCs for C_2 to C_{16} VOC monitoring

An automatic dual thermo-desorption gas chromatograph equipped with Flame Ionization Detector and Mass Spectrometer presented in Fig. 1, was used to monitor VOCs in ambient air during indoor and outdoor measurement campaigns.

This system was composed of two independent modules made to separate and detect lighter VOCs containing 2 to 6 carbon atoms (airmoVOC C2-C6, Chromatotec®, France) and heavier VOCs containing 6

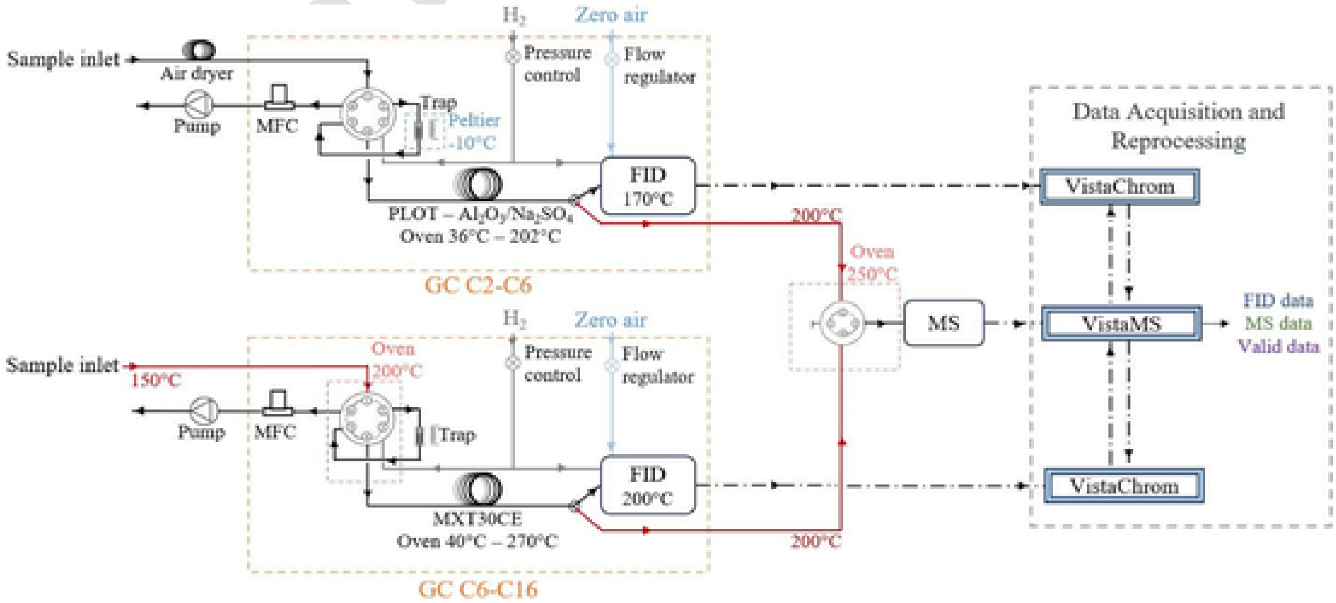

Fig. 1. Schematic of the Auto-TD-GC(C2C16)-FID/MS system for online VOC measurements.

to 16 carbon atoms (airmoVOC C6-C16, Chromatotec®, France). The cabinet was also equipped with zero air (dew point < −10 °C, TVOCs < 5 ng) and ultra-pure hydrogen (99.9999 %) generators (airmopure and hydroxychrom, Chromatotec®, France), calibration system (airmoCal, Chromatotec®, France) and a mass spectrometer (DET QMS, Chromatotec®, France). Samples were collected through a heated sampling line (150 °C) every ten minutes for 30 min under a flow rate of 50 mL.min^{-1} using a diaphragm pump and mass flow controller.

In the C2–C6 module, 110 mL of air sample was drawn with a flow rate of 12 mL.min^{-1}. Firstly, the sample passed through a permeation dryer (airmoDry, Chromatotec®, France) to remove the humidity and was then pre-concentrated using a cryotrap filled with a mixture of Carboxen and Carbopack, held at −10 °C using a Peltier cooler. Secondly, the pre-concentrated sample was desorbed at 220 °C for 4 min and directly injected in an Al_2O_3/Na_2SO_4 PLOT column (25 m × 0.53 mm × 10 µm). Within the first minute, the temperature of the oven rose from 36 °C to 38 °C. In a second stage, a constant heating rate of 10 °C.min^{-1} was applied up to 202 °C, and held for 10 min before cooling. Finally, the air sample reached the first FID detector heated at 170 °C.

In the C6–C16 module, 1150 mL of ambient air sample was drawn into the system at 38 mL.min^{-1}. The sample was then pre-concentrated at ambient temperature on a trap filled with Carbopack. Then, it was desorbed at 380 °C for 4 min and injected into a MXT30CE column (30 m × 0.28 mm × 1.0 µm). During the first 7 min of the analytical procedure, the oven temperature was set from 40 °C to 50 °C. Afterwards, a heating rate of 10 °C.min^{-1} was applied for 3 min followed by heating rates of 15 °C.min^{-1} for 8 min, 2 °C.min^{-1} for 5 min and 9 °C.min^{-1} for 4 min up to 270 °C. Then, the temperature was kept at 270 °C for 3 min before cooling. Finally, the air sample reached the second FID detector at 200 °C.

A single quadrupole mass spectrometer equipped with a heated multiplexing system for C2-C6 and C6-C16 streams (250 °C) was connected in parallel with a heated transfer line (200 °C) to the C6C16 module. Electron impact spectra were obtained at 70 eV and the source temperature was set at 150 °C. Full-scan mode acquired all mass-to-charge ratios between 35 and 170 amu.

In this study, the molecules separated with the C6-C16 module were detected in parallel with the FID and the MS, meaning that the results of each detector could be compared with one another.

2.2. *Experimental setup for VOC calibration*

Calibrations of the system were performed using two certified gas cylinders. PAMS 58 (Takachiho®, Japan) containing a mixture of 58 hydrocarbons and TO-15 (Takachiho®, Japan) containing a mixture of 68 oxygenated VOCs and halogenated compounds were used to calibrate the VOCs. The calibrations were performed by dilutions of PAMS and TO-15 cylinders containing 100 ± 1 % ppbv of each molecule. To do so, Mass Flow Controllers (MFC) (Chromatotec®, France) were used to adjust zero air and cylinders flows (accuracy ± 1 % reading on range 5 % - 100 %). Six points calibration curves were performed in the range 0.5–10 ppbv with 10 and 6 replicates for the first and the next calibration points respectively.

2.3. *Performances evaluations*

Method Detection Limits (MDL) and accuracies of each detector were calculated according to the Chinese standard for ambient air measurement [36]. MDL were calculated using the following formula:

$$MDL_{(ppbv)} = t_{(n-1,\ 0.99)} \times S$$

Where, $t_{(n\text{-}1,\ 0.99)}$ corresponds to the Student's t-value for a single-tailed 99th percentile *t* statistic and with n-1 degrees of freedom, and S is the standard deviation of 10 replicates of the first concentration level.

The equation to evaluate the accuracy of *i* compounds at 4 ppbv was:

$$\%recovery_i = 100 - \left(\frac{|Ccalc_i - Cinj_i| \times 100}{Cinj_i} \right)$$

Where, C_{calc} is the concentration calculated with calibration curve, and C_{inj} is the injected concentration determined with the dilution of the certified gas cylinder.

2.4. *Data acquisition and automatic reprocessing*

As shown in Fig. 1, VistaChrom and VistaMS were the software programs used to acquire and process the data coming from FID and MS detectors respectively. Both programs were fed by databases of known VOCs in ambient air called the substance tables.

As the FID detector is able to detect any burned organic molecule giving a signal that is approximately proportional to the carbon content of a molecule, it is possible to quantify these molecules depending on the response of the detector according to a reference substance. This semi-quantitative technique was used when the molecule could not be calibrated using certified gas cylinders.

The mass spectrometer was scanned from *m/z* 35 to *m/z* 170. Therefore, for each compound in the database, a quantifier ion within this range was selected to calculate its concentration. The aim was to select the more specific ion to avoid interferences between any coeluted molecules detected.

To allow automatic identification, a period covering the theoretical retention time of each compound was entered in both substance tables. For the MS detector, as a specific ion was assigned to a molecule, the period time could be longer in the Mass Spectrometer substance table (≈20 s) than in the FID one (≈10 s).

2.5. *Measurement campaigns*

To test and compare the newly developed algorithm's efficiencies, data sets from two measurement campaigns were used. The data from an outdoor measurement campaign located in a suburban Parisian forest during summer 2022 [37] were collected and analyzed. In this dataset, emissions of biogenic compounds such as oxygenated VOCs (OVOCs) and terpenes were expected. As the forest was located close to a large urban area, aromatic compounds could be detected as well. In this dataset, VOCs at tens to hundreds of pptv were observed.

Another set of data coming from an indoor workplace was also used. This environment was composed of offices and a quality control laboratory. During this campaign, higher concentrations of VOCs were expected, closer to ppbv levels.

The objective of these different locations and conditions was to challenge the algorithm on a large range of VOC concentrations and conditions.

3. Algorithm development

After automatic peak matching of the compounds (as described in Section 2.4) detected by the FID and MS detectors on VistaChrom and VistaMS, the data were submitted to the comparison algorithms.

A first version (V1), was developed in the VistaMS software to select, for each compound, a result between FID and MS detectors. To make the comparison, VistaMS communicated with VistaChrom to import its data (Fig. 1). The flowchart of this algorithm is shown in Fig. S1. Its two stages aimed to compare the difference between the FID and MS values to select one of them and provide a validated measurement. The FID value will be chosen if one of the conditions is true. When both stages are false, the FID value is considered significantly different from the MS value. As the typical problems encountered with FID detection are coelutions and misidentifications, MS is selected in this case.

Concentration gap values (C_Gap) and percentage gap values (%_Gap) were predefined by the manufacturer and can be modified in VistaMS whether the FID or MS is preferred. When the compound is usually not coeluted, the values are large enough to favor FID as it is the more stable and linear detector. Table 1 shows an example of the values chosen depending the detector preferred.

To develop a second algorithm, MATLAB version 9.13.0.2105380 (R2022b) (The Mathworks, Inc, Natick, MA) was used. The FID and MS data were exported in .csv format from VistaMS and were submitted to the newly optimized algorithm (V2) presented in Fig. 2.

This optimization aimed to account for the performances of each detector, i.e. the MDL and the accuracy (%recovery) for each compound. The flowchart can be divided into 3 sections, namely S1 (comparison to the MDLs of each detector), S2 (comparison of the compounds calibrated with a certified gas cylinder) and S3 (comparison of the compounds not calibrated with a certified gas cylinder). Depending on the stage where the value is output, the FID or MS value will be considered as the validated data.

3.1. S1: comparison to the MDLs of each detector

The first section was to determine if the values have to be considered. To do so, 3 stages are made to compare the FID and MS values with the detection limits (Fig. 2). When both FID and MS values are under their respective MDLs, the value is not considered and is output as “Not detected”. When the MS value is above MDL_{MS} but the FID value is under MDL_{FID}, the MS result is selected. In the opposite case, a stage to compare the FID value to the MDL_{MS} is added. Its goal is to avoid misidentifications from the FID. Indeed, if the “FID value” is higher than the MDL_{MS} a peak should be detected with the specific ion on the Mass Spectrometer. As this is not the case, the output is “Not detected”. Otherwise, the FID result is selected. Finally, when both FID and MS values are above their MDLs, they continue on to the next section depending on whether the compound was calibrated with a certified gas cylinder or not. It should be noted that for a compound that was not calibrated with a certified cylinder, the MDL was set to zero and could be modified manually.

Table 1
Values of C_Gap and%_Gap defined in V1 algorithm.

	FID preferred	MS preferred
C_Gap (ppbv)	0.5	0.01
%_Gap (%)	20	1

3.2. S2: comparison of the compounds calibrated with a certified gas cylinder

If the compound was calibrated with a certified gas cylinder as described in Section 2.3, this section of the algorithm was selected. It consists of two steps. The first aims to avoid coelutions or misidentifications from the FID. This is performed by checking whether the FID and MS values are equal to ± 50 %. If this is the case, the second stage compares the recovery percentages at 4 ppbv calculated during the calibrations tests to determine the most suitable detector.

The addition of this section allowed the instrument-dependent performances to be taken into account.

3.3. S3: comparison of the compounds not calibrated with a certified gas cylinder

In case where the compound wasn't calibrated with a certified gas cylinder, the algorithm proceeds to Section 3. This section is present in the newly developed algorithm to be able to quantify molecules without gas standards, that are sometimes difficult to find, but chemically close to a calibrated compound, or semi-quantified with the FID thanks to the equivalent carbon number [38]. It therefore allows the user to manually modify the “C_Gap value” if necessary. Its only stage corresponds to the V1 version implemented in VistaMS software, i.e. selec-

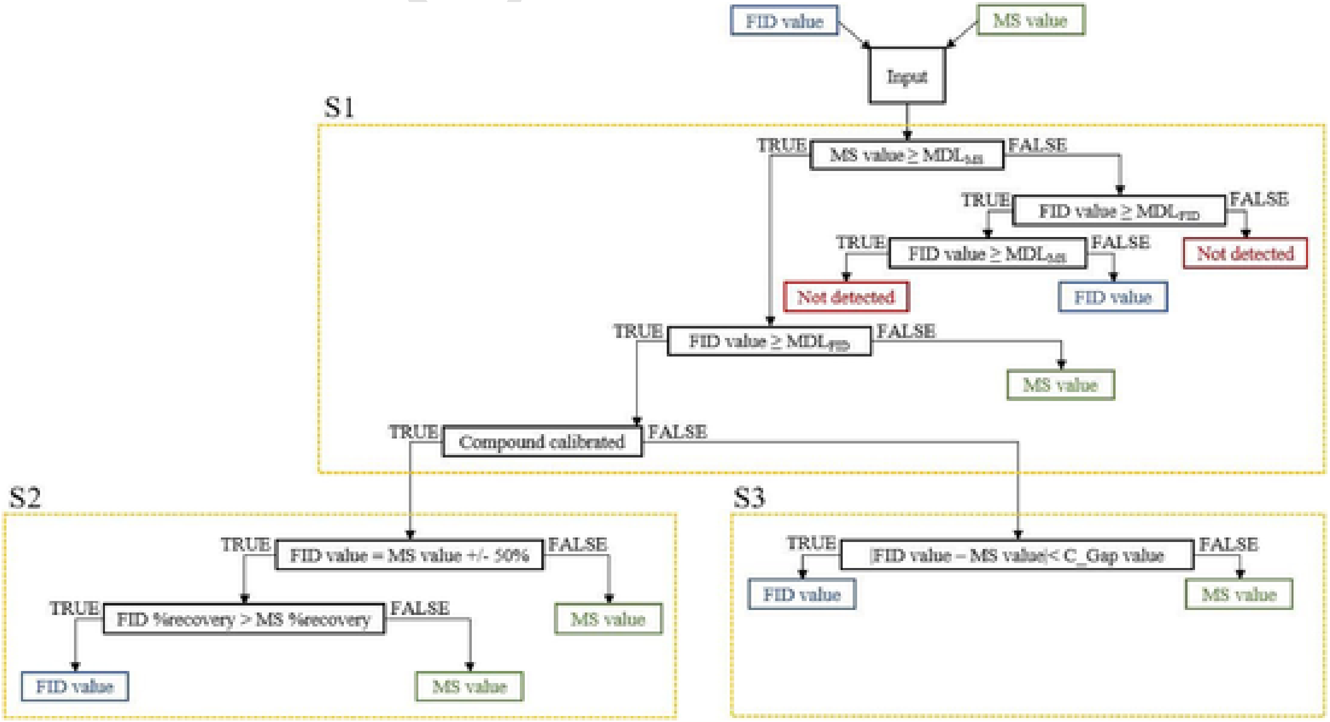

Fig. 2. FlowChart of the newly developed comparison algorithm to select FID or MS result (V2).

tion of the FID value if the difference with MS value is under a C_Gap value chosen by the user.

4. Results and discussion

4.1. Results and comparison of the performance studies

In order to evaluate the suitability of the auto TD-GC-FID/MS to quantify VOCs in ambient air, the performance studies were calculated for 60 compounds. For this purpose, two certified standard mixtures were used: PAMS 58 for alkanes and aromatic hydrocarbons, and TO-15 for OVOCs and halogenated compounds. Calibrations were performed with six concentrations of standard gas, ranging from 0.5 to 10 ppbv. The first concentration point at 0.5 ppbv was repeated 10 times for the calculation of the MDLs and six replicates were done for the other points to assess repeatability. Calibration curves of the detector responses versus the corresponding injected concentrations were plotted for each compound. Linearities, LODs and accuracies for FID and MS are given in Table 2 for the 4 families. Only the most common VOCs are presented, but the performance result ranges of all 60 VOCs are reported on the family rows (in bold).

The calibration curves were overall linear for both FID and MS in the concentration range as the determination coefficients R^2 varied from 0.9825 to 0.9999 for FID and 0.9850 and 0.9998 for MS. Three calibration curves of α-pinene, benzene and methyl ethyl ketone (MEK) are shown in Fig. S2 for FID and MS detectors. Linearities of α-pinene and benzene were good both for FID and MS. It is important to note that, except for the isopropyl alcohol which is a challenging compound for GCs, the lowest R^2 of one detector can be compensated by the other. For example, the R^2 of methyl ethyl ketone was 0.9899 for MS but was 0.9958 for FID. MDL and accuracy calculations were presented in Section 2.3.

Detection limits were overall lower for FID (values between 0.006 and 0.618 ppbv and 58 % of them under 0.1 ppbv) than MS (0.032–0.760 ppbv and 41 % under 0.1 ppbv), especially for alkanes and aromatic hydrocarbons. The families with the highest limit of detections were OVOCs and halogenated compounds both for FID and MS, due to their poorer responses than alkanes and aromatics. Some oxygenated compounds have an asymmetrical peak shape with these types of column leading to less intense signals with lower signal to noise ratios. For example, the tailing factor of isopropyl alcohol and 1,4-dioxane were 1.6 and 1.8, respectively (from 1 to 1.5 for gaussian peaks).

Finally, accuracy was studied at 4 ppbv. The% recovery was considered acceptable when above 90 %. The FID was highly accurate for non-coeluted alkanes and aromatic hydrocarbons as all of them were over 90 % recovery. For the OVOCs and halogenated compounds, 56 % and 85 % were above this limit, respectively. The poorest accuracy was of 76.56 % for tetrachloromethane, a compound having a low response with this detector, and a poor separation with benzene. For the MS, 85 % of the compounds had an accuracy above 90 %. The most challenging compounds remained the OVOCs as 25 % of them were under this limit.

The study of the performances of each detector showed their ability and complementarity to monitor these VOCs in ambient air.

4.2. Test of automatic data analysis for calibration data

In order to verify the ability of the two versions of comparison algorithms, they were first tested with calibration data at 4 ppbv. The objec-

Table 2
FID and MS determination coefficients, detection limits (ppbv), and accuracies at 4 ppbv of 4 families of VOCs.

VOCs	FID Detection			MS detection		
	Determination coefficient (R^2)	LOD (ppbv)	Accuracy at 4 ppbv ($\%_{recovery}$)	Determination coefficient (R^2)	LOD (ppbv)	Accuracy at 4 ppbv ($\%_{recovery}$)
Alkanes	**0.9955 - 0.9999**	**0.012 - 0.053**	**95.76 - 99.99**	**0.9925 - 0.9997**	**0.032 - 0.197**	**84.25 - 99.75**
cyclohexane	0.9997	0.024	98.01	0.9977	0.197	98.25
n-heptane	0.9995	0.053	98.42	0.9973	0.04	84.25
n-octane	*Coeluted*	-	-	0.9989	0.117	98.01
α-pinene	0.9996	0.023	96.51	0.9996	0.032	98.25
n-decane	0.9998	0.012	99.99	0.998	0.086	98.25
Aromatic hydrocarbons	**0.9838 - 0.9999**	**0.006 - 0.124**	**91.27 - 99.75**	**0.9924 - 0.9995**	**0.018 - 0.092**	**91.27 - 99.99**
benzene	0.9998	0.019	99	0.9991	0.018	95.26
toluene	0.9981	0.018	99.75	0.9924	0.026	98.75
ethyl-benzene	0.9999	0.012	98.5	0.999	0.043	99.75
m&p-xylenes	0.9999	0.017	98.63	0.9906	0.057	93.25
styrene	0.9999	0.006	99	0.9991	0.092	98.25
o-xylene	0.9997	0.054	99.02	0.9995	0.054	92.77
1,3,5-timethylbenzene	0.9981	0.016	95.26	0.9962	0.082	92.02
1,2,4-trimethylbenzene	0.9999	0.029	98.75	0.9982	0.04	91.27
1,2,3-trimethylbenzene	0.9838	0.104	91.27	0.9941	0.046	94.76
OVOCs	**0.9834 - 0.9999**	**0.065 - 0.325**	**84.71 - 97.51**	**0.9871 - 0.9995**	**0.068 - 0.760**	**80.23 - 99.27**
acrolein	0.9992	0.093	97.51	0.999	0.277	98.25
acetone	0.996	0.065	91.77	0.9995	0.153	97.76
isopropyl alcohol	0.9834	0.13	85.04	0.9871	0.404	92.13
methyl *tert*-butyl ether	*Coeluted*	-	-	0.9994	0.216	97.91
vinyl acetate	*Coeluted*	-	-	0.9993	0.431	99.27
methyl ethyl ketone	0.9958	0.124	86.28	0.9899	0.068	80.23
Halogenated compounds	**0.9825 - 0.9999**	**0.080 - 0.618**	**76.56 - 99.69**	**0.9850 - 0.9998**	**0.098 - 0.345**	**81.39 - 99.99**
dichloromethane	0.9997	0.114	93.52	0.9992	0.153	95.76
1,1-dichloroethane	*Coeluted*	-	-	0.9992	0.098	96.51
chloroforme	*Coeluted*	-	-	0.9965	0.108	96.01
1,2-dichloroethane	0.9998	0.148	96.51	0.9995	0.157	95.51
1,1,1-trichloroethane	0.9991	0.08	95.01	0.9923	0.237	91.52
tetrachloromethane	0.9825	0.618	76.56	0.9973	0.345	95.51
tetrachloroethene	*Coeluted*	-	-	0.992	0.258	91.64
1,2-dichlorobenzene	0.9999	0.277	96.52	0.9991	0.323	93.52

tive was to study their capability to deliver the most accurate validated data between FID and MS detections. To do so, these data were fed into the VistaMS algorithm (V1) and the Matlab algorithm (V2) described in Section 3. The validated data corresponding to the selected value of FID or MS, were then compared with the injected concentrations. As an example,

Table 3 shows the results of benzene, α-pinene, methyl *tert*-butyl ether (MTBE) and tetrachloromethane given by FID, MS, V1 and V2. For benzene and tetrachloromethane, by selecting FID and MS respectively, both V1 and V2 algorithms chose the result closest to the injected concentration. As MTBE was a coeluted compound in FID, the algorithms succeeded in selecting the MS value as validated data. However, V1 and V2 did not obtain the same result for α-pinene. The difference is that V1 only studies the difference between FID and MS (lower than C_Gap or%_Gap values here, so FID value was selected) whereas V2 is designed to select the validated data from the calibration results, i.e. MS. In both cases, the concentrations selected were acceptable as they are included in the measurement uncertainties.

Fig. 3a shows the average percent recoveries calculated with FID, MS, V1 and V2 results for different families of VOCs. As shown in the figure, the FID alone suffers from certain coelutions leading to a lower recovery. The percent recoveries of V1 and V2 algorithms showed their ability to deliver reliable results. Both algorithms selected nearly equal proportions of FID and MS (Fig. 3b). However, V2 benefits from its improved capacity to select the more accurate detector.

Table 3
Results of 4 VOCs quantification using FID and MS detections and V1 and V2 validated data compared to the injected concentration.

	Injected concentration (ppbv)	FID value (ppbv)	MS value (ppbv)	**V1 (ppbv)**	**V2 (ppbv)**
benzene	4.0 ± 0.4	**4.0**	3.8	**4.0**	**4.0**
α-pinene	4.0 ± 0.4	4.2	**4.1**	4.2	**4.1**
methyl *tert*-butyl ether	4.0 ± 0.4	*Not detected*	**3.9**	**3.9**	**3.9**
tetrachloromethane	4.0 ± 0.4	3.1	**3.8**	**3.8**	**3.8**

4.3. Automatic data analysis of indoor air monitoring

Indoor VOC measurements were used to challenge the V1 and V2 algorithms at levels close to calibration tests. In Fig. 4a, the higher concentrations of VOCs obtained during 24 h are plotted. Different families were analyzed at significant levels such as terpenes, OVOCs and aromatics. The main compound was α-pinene with an average concentration of 3 ppbv. As shown in the Fig. 4a, V1 and V2 selected broadly the same concentrations for the major compounds.

Only the results for α-pinene differ significantly. The FID was selected by V1 as they were considered close enough by the algorithm. For V2, it was the MS that was selected based on the accuracy tests during calibration (Table 2). The relative deviation between V1 and V2 for this compound averaged <10 %, meaning both results were acceptable.

For the main compounds, whose concentrations are those typically found in indoor air, both V1 and V2 algorithms were able to automatically deliver reliable concentrations. Nevertheless, between all the compounds selected by V1 and V2, the total VOCs concentration is 12 % lower for the latter. This variation was due to all the compounds under the limit of detection not selected by V2.

4.4. Automatic data analysis of outdoor air monitoring

Next, the algorithms were tested against data from an outdoor measurement campaign (as described in Section 2.5) where VOCs were present at lower levels (low ppbvs to pptvs). The results of the main compounds detected by the system and selected by the algorithms are presented in Fig. 4b. As expected, biogenic VOCs such as monoterpenes (α-pinene, β-pinene) and OVOCs (acetone, methyl vinyl ketone) were identified and quantified, as well as aromatic hydrocarbons (benzene and toluene) from urban plumes. Low levels of VOCs were detected and the concentrations of the main compounds obtained with the first and second versions of automatic reprocessing differed by <10 %. However, the α-pinene profile appeared to vary slightly between V1 and V2 validated data. The variation was due to the difference in the choice of detector, FID for V1 and MS for V2. Although this variation does not have a significant impact on the quantification of α-pinene, V2 is more ap-

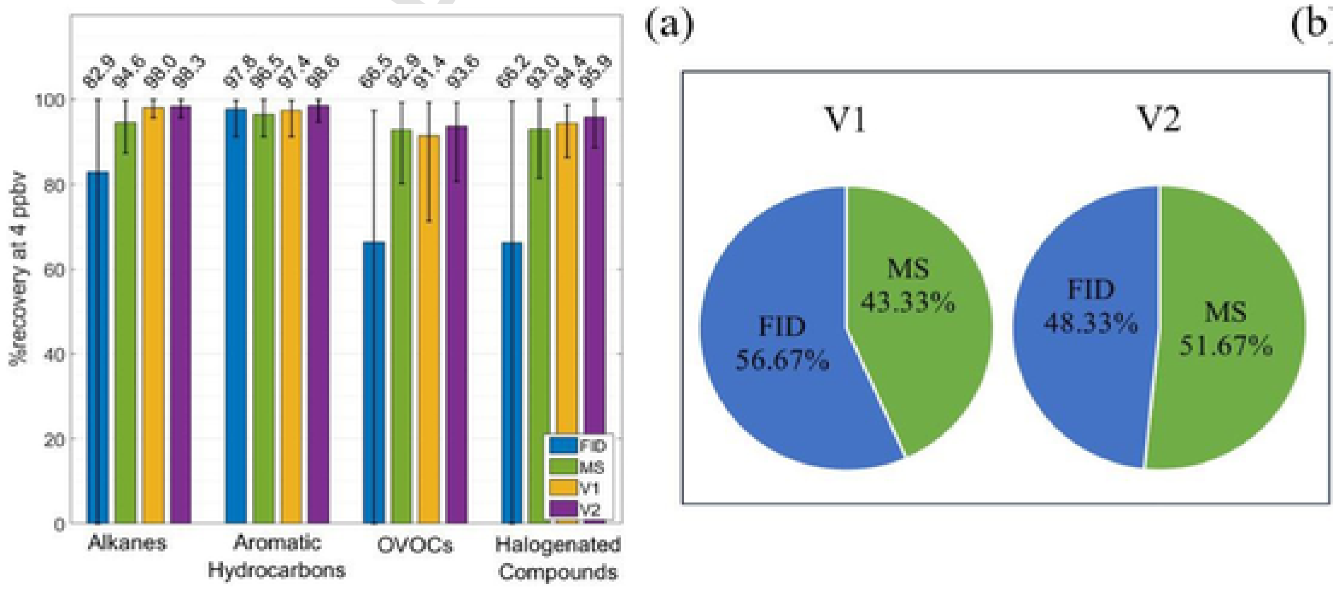

Fig. 3. Mean percent recoveries of FID, MS, V1 and V2 for different VOC families (a), and proportions of FID and MS selected by V1 and V2 (b) during calibration at 4 ppbv. Error bars represent the%recoveries minimum and maximum (0 % corresponds to not-detected compounds).

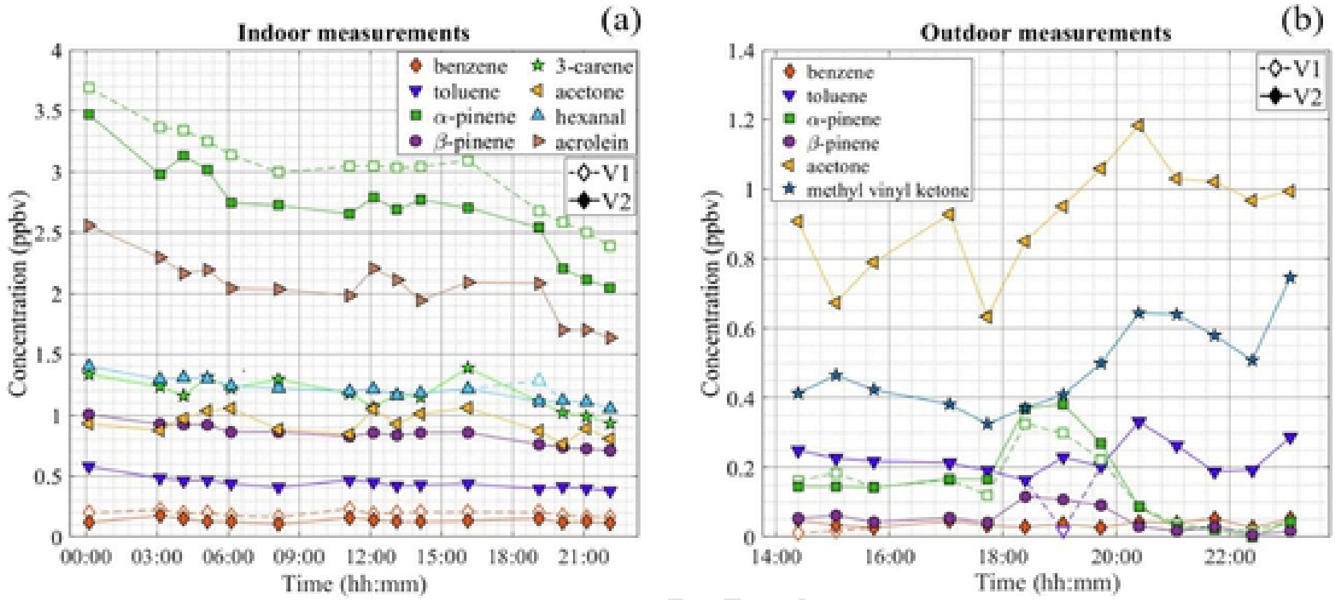

Fig. 4. Diurnal concentration profiles of the major VOCs detected during indoor (a) and outdoor (b) measurement campaigns. Dashed lines and open markers are the results selected by V1 and solid lines and filled marker by V2.

propriate as the MS values are more accurate for this compound (see Table 2).

As shown in Fig. 4b, the toluene concentration at 19:00 UTC between V1 and V2 reveals a significant disagreement, highlighting that the algorithms did not select the same detector. In Fig. 5, the FID, MS and the resulting validated data of toluene profile are presented for V1 and V2. This figure shows that V1 only selected the FID whereas V2 opted for the MS for this result. As the campaign site was located in a suburban forest affected by urban air masses passing through the field throughout the day, toluene is going to be observed in the surrounding area. It is therefore difficult to perceive of a meteorological or chemical mechanism by which its concentration could be suddenly reduced to close to zero ppb as depicted in the V1 analysis. To explain this disagreement, FID and MS chromatograms of toluene at 19:00 UTC are shown in Fig. S3. The FID misidentified the compound because an issue with the baseline occurred. As the V2 algorithm is designed to verify if the FID and MS results are close enough to be compared, it was able to identify that FID result was wrong in this specific case. This problem occurred in 93 out to 900 chromatograms during this outdoor campaign, where the ambient conditions varied considerably.

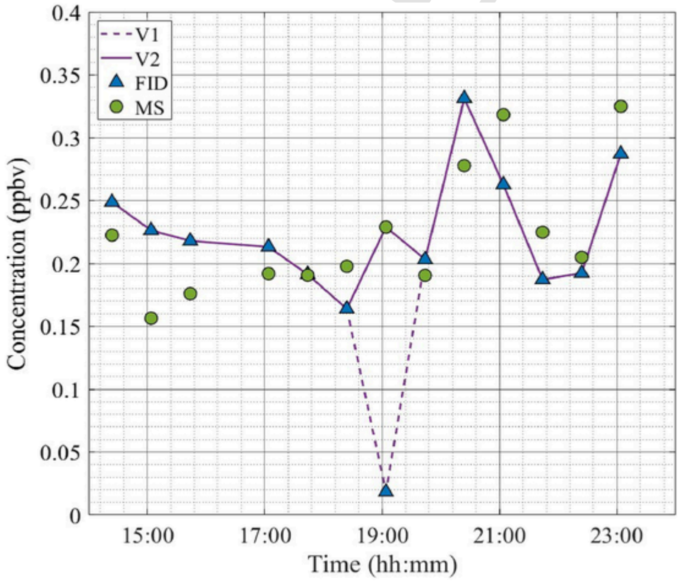

Fig. 5. Selection MS and FID value that V1 and V2 made for the toluene throughout the day. MS result is represented in green circles, FID in blue triangles and V1 and V2 in violet dashed and solid lines respectively.

4.5. *Comparison between manual and automatic reprocessing*

To evaluate the robustness of each algorithm, the average automatic results of 24 h indoor and outdoor measurements were compared with manual treatment. Manual reprocessing, requires experience and training and may introduce significant human error into this analytical step if done by an inexperienced operator. Furthermore, manual treatment is a time consuming process. For example, data reprocessing of a monthly campaign could take at least two weeks of work.

As shown in Fig. 6, both automatic algorithms were overall in good agreement with manual data processing. Nevertheless, the V1 automatic data treatment (Fig. 6a and c) showed poorer correlation than V2 (Fig. 6b and d) with correlation coefficients (R^2) of 0.8914 and 0.9686 for outdoor and indoor campaigns respectively whereas R^2 exceeds 0.99 for V2. This can be explained by the fact that V1 does not take into account the MDL of the compounds. Therefore, the noise was wrongly integrated and identified as a compound, especially for halogenated compounds. For both algorithms, low VOC concentrations presented the biggest challenge, with V1 outdoor and indoor integrations showing significantly more disagreement than V2 (see Fig. 6a). These plots show that, although both V1 and V2 were suitable to automatically analyze compounds with concentrations over 0.5 ppb, for the misidentifications of substances under 0.1 ppbv, the first section of V2 algorithm comparing the detections limits was essential to increase its reliability.

5. Conclusion

In this work, an on-line auto TD-GC with dual detection FID and MS for the monitoring of VOCs was evaluated. The performance studies of both detectors for the quantification of 60 VOCs showed linear regres-

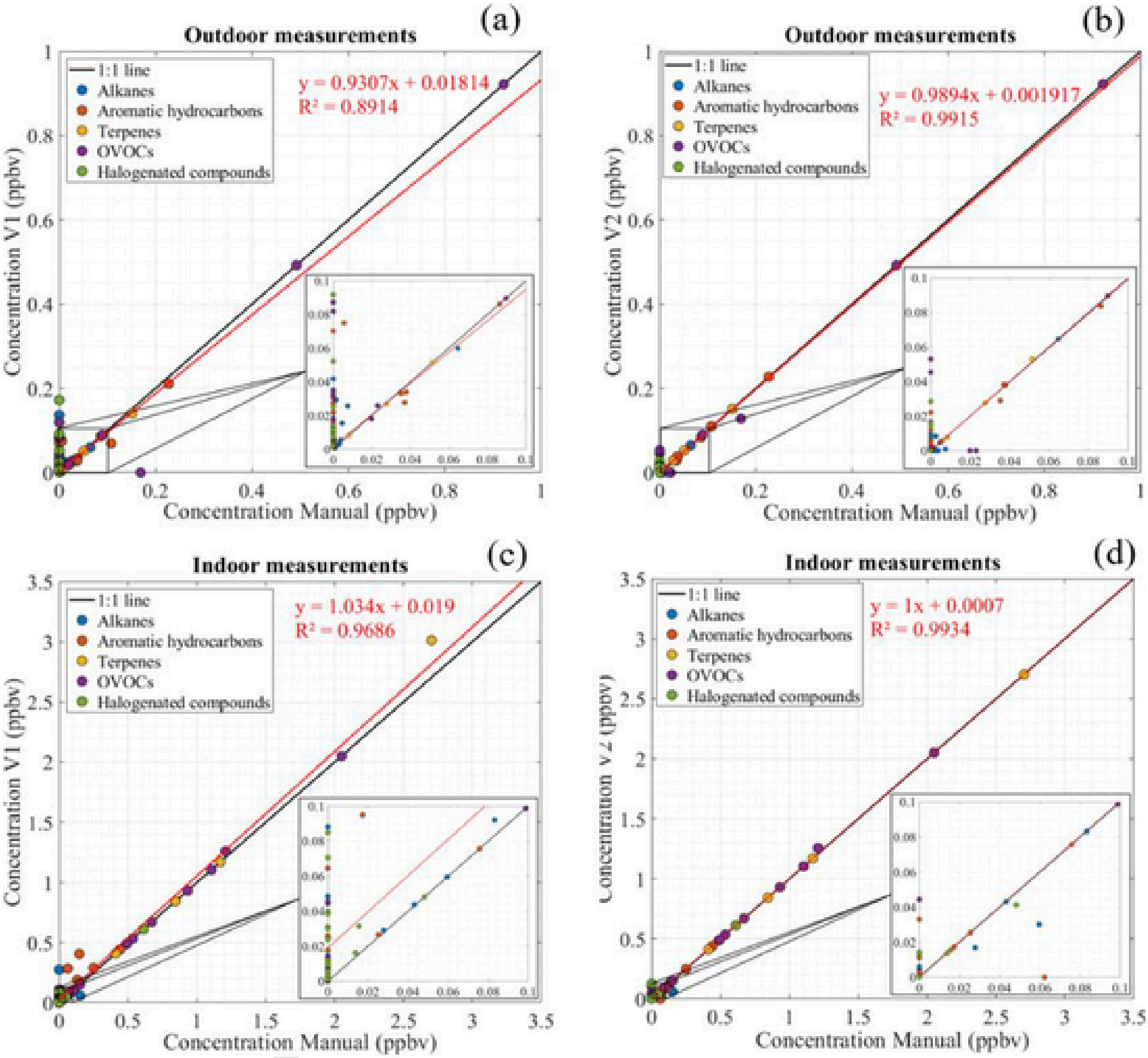

Fig. 6. Scatter plots of V1 and V2 automatic reprocessing versus manual treatment of outdoor (a and b) and indoor (c and d) day measurements. Each circle represents the averaged concentration of each compound detected and are classed by color depending on their family. The red lines correspond to the linear regression fits of the data and the black line the 1:1 relationship.

sions, with 55 % of method detection limits under 0.1 ppbv (FID and MS) and acceptable accuracies (between 77 % and 100 %). The complementarity of each detector was also highlighted, demonstrating the benefits of dual detection.

To save time during data analysis, two different algorithms were developed to select automatically between the FID and MS results. As robustness and reproducibility of data analysis is often one of the major challenges in the field, two measurement campaigns with different measured concentration levels (in indoor and outdoor air) were used to evaluate the effectiveness of each algorithm during real case scenarios. The V1 algorithm, proved sufficient to analyze data at ppbv levels but was limited under 0.5 ppbv. As the second version V2 takes into account the method detection limits of each detector, it was found to be more suitable to analyze the low concentration levels often encountered under field conditions. Moreover, this algorithm is fed by the performance studies of the calibrated compounds, which enhanced its reliability. Furthermore, V1 used two parameters (C_Gap values and%_Gap values) chosen by the user which could also lead to added inaccuracies.

Version 2 of the algorithm is a significant improvement in automatic data processing, particularly for field campaigns where >1000 chromatograms are acquired per month. An extension of this work will focus on the automatic evaluation of the uncertainties associated with the sections of the algorithm.

Finally, a lot of challenges are encountered when measuring VOCs under field conditions, particularly data processing time, and it is anticipated that algorithms of this type that exploit the complementarity of multi-analytical methods will be of utility in other dual-detector systems or, more widely, for a campaign deploying different instruments where they are sufficiently calibrated.

CRediT authorship contribution statement

Fanny Bachelier: Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Mathilde Mascles:** Writing – review & editing, Formal analysis, Conceptualization. **Max R. McGillen:** Writing – review & editing. **Jean-Philippe Amiet:** Funding acquisition. **Benoit Grosselin:** Writing – review & editing. **Damien Bazin:** Writing – review & editing, Supervision, Project administration, Methodology, Investigation. **Véronique Daële:** Writing – review & editing, Supervision, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2024.465327.

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