

Mass spectrometry/gas chromatography–mass spectrometry approach for rapid screening/quantitative determination of perchloroethylene in air

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Abstract

A new mass spectrometry/gas chromatography–mass spectrometry (MS/GC–MS) approach has been developed for the screening and quantitative determination of perchloroethylene (PERC) in workplace and outdoor air samples, which could be extended to the screening and analysis of other analytes and samples. This approach may be rapidly modified in order to be used directly as an MS detector for screening purposes or alternatively as a common GC–MS, for confirmation. The screening alternative by MS is approximately 20 times faster than the quantitative-confirmatory determination by GC–MS. Detection limits of both alternatives are sufficiently low to screen and determine PERC in the above-mentioned matrixes. The advantage of this approach over others previously described is that, in the present case, the sample passes through the chromatographic column only when the confirmatory GC–MS is used. For the MS screening method, the chromatographic column is bypassed by using an appropriate selection valve. In this way, the column lifetime is extended and screening time is considerably shortened.

Keywords: Screening system; Mass spectrometry; GC–MS; Perchloroethylene; Air samples

1. Introduction

Perchloroethylene (PERC), also known as tetrachloroethylene, is a solvent commonly used in dry-cleaning operations. PERC enters the body when breathed in with contaminated air or when consumed with contaminated food or water. Once in the body, PERC can remain stored in fat tissue. This volatile compound is regulated as a hazardous air pollutant due to its toxicity. The OSHA method for determination of PERC in the workplace involves the use of adsorbent tubes for sample collection and GC-FID for sample analysis [1]. In the case of outdoor atmospheric samples, PERC as well as other VOCs are determined by the TO-14 United States Environmental Protection Agency (US-EPA) method [2], which involves sampling in canisters and GC–MS analysis.

The development of rapid screening methods is currently becoming significantly important in analytical chemistry. Conventional methods used in analytical laboratories are usually

not compatible with the highly desirable routine and extensive monitoring. When timely decisions are made, the delivery of rapid analytical information, not necessarily possessing a high level of accuracy and precision, is highly appreciated. It must be stressed that screening approaches are not a substitute for but rather a complement to the reference conventional techniques [3,4].

In recent years, there has been an increasing demand for analysis of samples considering their volatile constituents. Mass spectrometry coupled to gas chromatography (GC–MS) has been the most widely used technique to study this type of pollution [5–8] but, as stated above, the development of nonseparative methods for the resolution and determination of different analytes is of great interest owing to their speed. Consequently, the direct coupling of mass spectrometry with methods such as solid-phase microextraction (SPME-MS) [9], or headspace (HS-MS) [10–15], has been developed for the analysis of raw materials and foods in the agrofood industry. These techniques provide “fingerprints” of the products under analysis, and the information, suitably processed by applying chemometric data treatment (such as hierarchical cluster analysis (HCA), linear discriminant analysis (LDA) and soft independent modeling class analogy (SIMCA)), can be used to differentiate such products.

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In the same context, a mass spectrometer coupled to a gas chromatograph can also be directly used as a screening system by keeping the column temperature at a level high enough to avoid chromatographic resolution of the target analytes [4]. Under these conditions, the MS provides a global signal, which can be differentiated on the basis of chemometric data treatment. This system provides the additional advantage that samples containing the analyte near an imposed threshold, or samples in which the presence of the analyte is doubtful, can be subjected in the same system to conventional gas chromatographic mass spectrometry detection for confirmatory purposes.

The aim of this study was to assess a new mass spectrometry/gas chromatography–mass spectrometry (MS/GC–MS) approach for the screening and quantitative determination of PERC and eventually other VOCs in air samples. In the present case, the sample passes through the chromatographic column only when the confirmatory GC–MS is used. For the MS screening method, the chromatographic column is bypassed by using an appropriate selection valve.

2. Experimental

2.1. Reagents

Perchloroethylene 99.9% (Supelco, Bellefonte, PA, USA, 48571) was used for calibration purposes in the determination of PERC in workplace samples. Working standards in the interval 1–100 ppm_v were prepared by dilution of this standard with helium in Tedlar bags (Supelco, Bellefonte, PA, USA, 24633).

A TO-14 standard (Supelco Bellefonte, PA, USA, 4-1902) was used directly as a quality control standard of workplace determinations. The same standard was used for calibration in the determination of VOCs in outdoor samples. Working standards in the interval 0.1–320 ppb_v were prepared by dilution of the TO-14 standard with helium in canisters.

Helium 5.0 UHP (AGA, Chile) was used as a diluting gas, as a carrier gas and also for the canister cleaning process.

Liquid nitrogen (AGA, Chile) was used for cold-trap preconcentration in outdoor sample analysis.

2.2. Instruments and apparatus

An autosampler (model 7016, Entech Instruments Inc., CA, USA) and a gastight syringe (Hamilton, Reno, NV, USA, 80600) were, respectively, used to inject the outdoor and workplace samples.

An air preconcentrator (model 7000, Entech Instruments Inc., CA, USA) was used in the analysis of outdoor samples.

Three-liter stainless steel canisters (Entech Instruments Inc., CA, USA) were used for sample collection and preparation of working standards starting from a TO-14 standard. The vacuum or pressure inside the canister during sampling was measured with a high-quality gauge on the canister (CS-1100, Entech Instruments Inc., CA, USA).

Analyses were conducted using a gas chromatograph Hewlett-Packard model 6890 HRGC coupled to a 5973 MSD, equipped with a 60 m DB-1 column (1 μm film thickness, 250 μm I.D., J&W Scientific Inc., CA, USA).

A 6-port selecting valve (Valco, Houston, TX, USA) was assembled in the upper part of the chromatograph (Fig. 1) in order to select subjecting the sample directly to MS (position 1) or to GC–MS (position 2). The transfer line connected to the 6-position valve was a 5 m fused silica capillary (250 μm I.D.).

2.3. Sampling

Workplace samples were taken inside 19 dry-cleaning shops located in the following sectors in eastern Santiago city: Lo Barnechea, Las Condes, Vitacura, Providencia, La Reina, Peñalolén, Ñuñoa, Macul, La Florida and Puente Alto. Two kinds of integrated samples were taken inside the 19 dry-cleaning shops:

- (a) full period single sample measurement (one 8-h sample), and

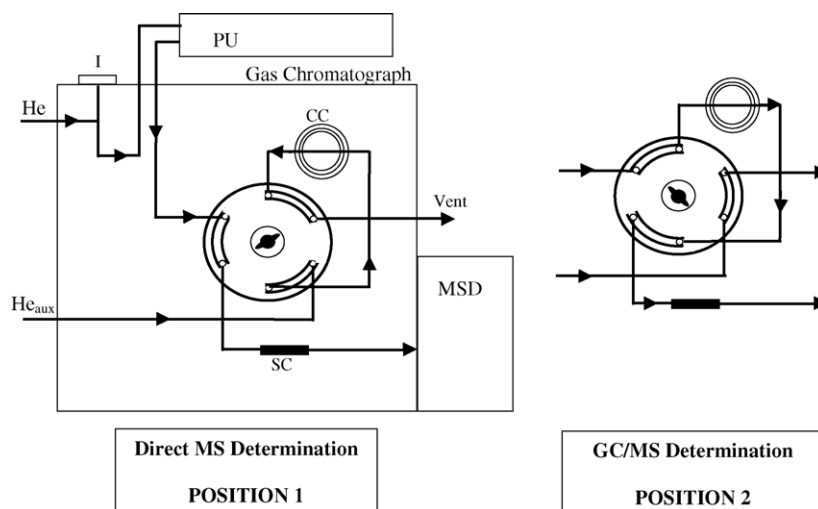


Fig. 1. Manifold for implementation of the method. PU, preconcentration unit; I, injector; CC, chromatographic column; He_{aux}, auxiliary helium gas; SC, silica capillary; MSD, mass selective detector.

(b) fifteen-minutes sampling period considering the maximum exposure concentration in a working day.

Both kinds of samples were taken in three-liter canisters by using a mass flow controller, which allowed to fill the canister with the air sample in 8 h or 15 min, respectively.

One grab air samples were collected immediately outside (outdoor samples) some of the monitored dry-cleaning shops. In all cases, the vacuum or pressure inside the canister during sampling was measured with a high-quality gauge on the canister.

2.4. Analytical procedure

2.4.1. Determination of PERC in workplace samples

Workplace samples were diluted in the canister with helium to reach a pressure of 1 atm. By using a gastight syringe, a volume of 40 μ l of the diluted sample was injected directly to a GC-MS instrument. The selecting valve allows to carry the sample directly to the MS detector through a silica capillary (Fig. 1). This mode prevents the sample from passing through the

chromatographic column. Injector, valve and chromatographic oven were kept at 150 °C. Flow rate of the carrier gas (He) was 2 ml/min. The MS transfer line was held at 280 °C. Determination of PERC was carried out by using the single ion monitoring (SIM) mode (target ion 166 m/z ; qualifier ion 164 m/z); thus, it was possible to screen PERC quickly in the presence of other VOCs.

2.4.2. Determination of PERC and other VOCs in outdoor samples

Outdoor atmospheric samples were collected in the canisters by air aspiration to reach atmospheric pressure. A volume of 250 ml of sample was cryogenically preconcentrated in a Tenax trap at -50 °C, in a cryogenic preconcentration system. After the preconcentration, the retained compounds were thermally desorbed and carried online to the mass spectrometer through position 1 of the valve (Fig. 1). Then PERC was determined following the same procedure as described for workplace PERC determination. The same approach was also valid to screen benzene by using a target ion of m/z 78.

Table 1
Analytical features of the GC-MS method

VOC	RTW	Retention time. min	Ion mass		Analytical features	
			Target	Qualifier	LOD ppt _v	RSD % (n=6)
Freon12		4.86	85.0	87.0	6.69	0.63
Chloromethane		5.09	50.1	52.0	22.97	0.82
Freon114		5.23	85.0	135.0	6.15	0.69
Vinyl Chloride		5.39	62.1	64.0	6.16	0.83
Methylbromide		5.91	94.0	96.0	7.27	0.66
Ethylchloride		6.11	64.1	66.1	7.51	0.67
Freon11		6.96	101.0	102.9	6.82	0.64
1,1-dichloroethylene		7.65	61.0	96.0	7.19	1.05
Dichloromethane		7.74	84.0	86.0	11.46	1.07
Freon113		8.04	101.0	150.9	6.20	0.65
1,1-dichloroethane		9.03	63.1	65.0	7.74	1.91
1,2-dichloroethylene		10.00	61.0	96.0	7.04	3.24
Chloroform		10.36	83.0	85.0	8.25	3.62
1,2-dichloroethane		11.35	62.1	64.0	9.07	3.53
1,1,1-trichloroethane		11.74	97.0	99.0	6.93	0.85
Benzene		12.42	78.1	77.1	10.40	2.88
Carbontetrachloride		12.65	116.9	118.9	6.87	0.90
1,2-dichloropropane		13.74	63.1	62.1	10.25	3.12
Trichloroethylene		14.15	129.9	95.0	8.17	3.50
cis-1,3-dichloropropene		15.88	75.0	77.0	11.50	2.94
trans-1,3-dichloropropene		17.01	75.0	77.0	11.85	3.41
1,1,2-trichloroethane		17.44	97.0	83.0	13.36	6.41
Toluene		18.12	91.1	92.1	10.24	5.29
1,2-dibromoethane		19.59	107.0	109.0	13.91	3.26
Perchloroethylene		20.64	165.9	163.9	11.03	3.80
Chlorobenzene		22.14	112.0	77.1	14.51	6.97
Ethylbenzene		23.05	91.1	106.1	a	a
m,p-xylene		23.52	91.1	106.1	a	a
Styrene		24.00	104.1	103.1	18.90	5.33
1,1,2,2-tetrachloroethane		24.15	83.0	85.0	6.90	0.77
o-xylene		24.24	91.1	106.1	a	a
1,3,5-trimethylbenzene		26.49	105.1	120.1	8.02	0.52
1,2,4-trimethylbenzene		27.14	105.1	120.1	8.95	0.60
m-dichlorobenzene		27.37	146.0	148.0	8.46	3.18
p-dichlorobenzene		27.48	146.0	148.0	9.26	4.25
o-dichlorobenzene		28.02	146.0	148.0	7.23	1.52
1,2,4-trichlorobenzene		31.16	180.0	182.0	6.46	0.94
Hexachloro-1,3-butadiene		32.19	225.0	227.0	6.95	0.44

a: Determination was not carried out.

If accurate and confirmatory determination of PERC and other VOCs present in the sample is required, the selecting valve is switched to position 2 (Fig. 1) in order to allow the sample volume to be fed into the chromatographic column before mass spectrometry detection. VOCs determination by GC–MS was carried out according to the following parameters:

Carrier gas: Helium (1 ml/min, constant flow)

Temperature programme: 40 °C (0 min), 40–80 °C (3.5 °C/min), 80 °C (4 min), 80–120 °C (6 °C/min), 120 °C (0 min), 120–200 °C (15 °C/min), 200 °C (20 min).

By using this temperature programme, it is possible to resolve the 39 VOCs mixture present in the TO-14 standard.

The quadrupole and MS transfer line were held at 150 and 280 °C, respectively. Determination and confirmation of the 39 VOCs present in the TO-14 standard was carried out by using the SIM mode. The identification of target VOCs was carried out by searching in the appropriate retention time windows (RTWs) (Table 1).

3. Results and discussion

3.1. Determination of PERC in workplace by MS

It was observed that the transient signal obtained directly by MS depends on the variables temperature of the chromatographic oven, injection volume and flow rate of the carrier gas. Although in this mode, the sample does not pass through the chromatographic column, oven temperature is an important factor to maintain the analyte in the gas phase thus preventing any condensation whatsoever while it is carried from the injector to the MS interface. The sensitivity of the signal increases in the 75–175 °C range, remaining constant from 150 °C up. This effect is consequent with the boiling point of PERC (121 °C). A temperature value of 150 °C was selected for further studies. The sensitivity of the signal also increases with injection volume in the interval 10–80 μ l. Even though sensitivity increased with increasing injection volumes, repeatability of the signal decreased concomitantly. Consequently, a volume of 40 μ l was selected as a compromise between both analytical features.

On the other hand, flow rate was studied between 1 and 3.5 ml/min. Increasing flow rate favored the sample throughput. However, a selected flow rate of 2 ml/min was considered because above this value, the repeatability of the signal decreased reaching relative standard deviation values higher than 10%.

3.2. Analytical features of the direct MS method

The method precision was assessed by injecting ($n = 10$) standard samples of PERC at two different concentration levels. Precision, expressed as relative standard deviation, was of 3.5% at 1 ppm_v level and 2.7% at 100 ppm_v. Detection (LOD) and quantitation (LOQ) limits were determined considering a 3 and 10 signal-to-noise ratio, respectively. LOD and LOQ were found to be 0.11 and 0.37 ppm_v, respectively. These values of LOD

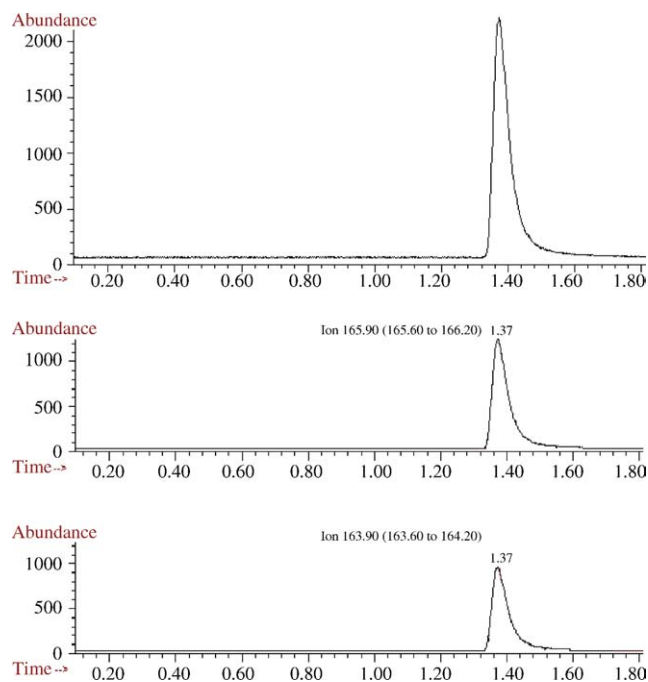


Fig. 2. (a) Total ion SIM integrated signal for PERC in presence of other VOCs obtained by direct MS method. (b) Single ion monitoring signals (at m/z 166 and 164) obtained for PERC by direct MS method.

and LOQ are sufficiently low to determine PERC directly in the workplace by MS, considering that the most rigorous exposure limits are 40 ppm_v [1]. The selectivity of this direct method was assessed by analyzing a certified TO-14 standard (Supelco), which contains PERC together with other 38 volatile organic compounds, all at a concentration of 1 ppm_v. Recovery for PERC was $102 \pm 3\%$ and it was observed that none of the standard components interferes in the direct determination of PERC by MS. Fig. 2 shows the signal obtained for PERC in presence of other 38 VOCs under the selected conditions. As can be seen, a sharp transient signal is obtained at about 1.4 min after injection of the sample. In this context, one of the main advantages of the present method is its rapidity. The sample throughput was 30 samples per hour.

3.3. Dry-cleaning shop monitoring

Workplace samples were taken from inside 19 dry-cleaning shops located in different sectors in eastern Santiago city. In all dry-cleaning shops, 8-h samples were taken and in some of them 15-min samples were also taken considering the maximum exposure concentration in a working day. Table 2 shows the results obtained in the determination of PERC. According to the determined concentrations, it can be stated that all the monitored dry-cleaning shops fulfill the present Chilean regulation (Decreto 594), which establishes maximum values of 40 ppm_v (for full period single sample measurement one 8-h sample), and 200 ppm_v (15-min sampling period considering the maximum exposure concentration in a working day). These Chilean standards are, respectively, equivalent to the time weighed average (TWA-8h) exposure limit and the short term exposure limit (STEL) used in the standard industrial hygiene terminology.

Table 2
Determination of PERC in workplace samples

Dry-cleaning shop (Sectors)	PERC concentration (ppm _v)	
	8-h Monitoring	15-min Monitoring
Fast Clean (Lo Barnechea)	23.0	a
Donde Simón (Ñuñoa)	4.5	31
5 ^a Sec. (La Florida)	3.4	a
Sandrico (Lo Barnechea)	3.2	18
Lavamatic (Peñalolén)	3.0	a
5 ^a Sec Apumanque (Las Condes)	2.9	a
Los Leones Ltda. (Vitacura)	2.4	a
Salerno (Las Condes)	1.6	a
La Florida (La Florida)	1.6	a
Lavaseco Manquehue (Vitacura)	1.2	a
Plaza (PuenteAlto)	1.1	a
Grecia Ltda. (Ñuñoa)	1.2	4.6
Quilín (Macul)	1.1	12
El Rey (La Reina)	0.9	13
San Cristobal (Providencia)	0.75	a
Sandrico Lider (La Reina)	0.75	4.0
Maestrelli (Puente Alto)	0.75	a
Lavatutti (Providencia)	0.60	a
Nina (Macul)	0.45	a

a: Determination was not carried out.

On the other hand, the sample taken in the dry-cleaning shop “Donde Simón” in Ñuñoa (8-h sample) was also evaluated by GC–MS for confirmation giving a concentration value of 4.6 ± 0.2 ppm_v. Consequently, it is possible to establish that PERC can be determined directly by MS in workplace air samples, without interference of other VOCs. The sample throughput of the GC–MS confirmation method is 1.2 samples per hour.

3.4. Determination of PERC in outdoor samples by direct MS and GC–MS methods

Taking into account the considerably lower concentration level observed in atmospheric samples, the determination of PERC, in this case, requires the use of a preconcentration system. Consequently, a volume of 250 ml of sampled air was cryogenically preconcentrated in a Tenax trap at different temperatures of the first cryogenic trap, ranging from -20 to -150 °C. Fig. 3 shows the calibration graphs obtained at different preconcentra-

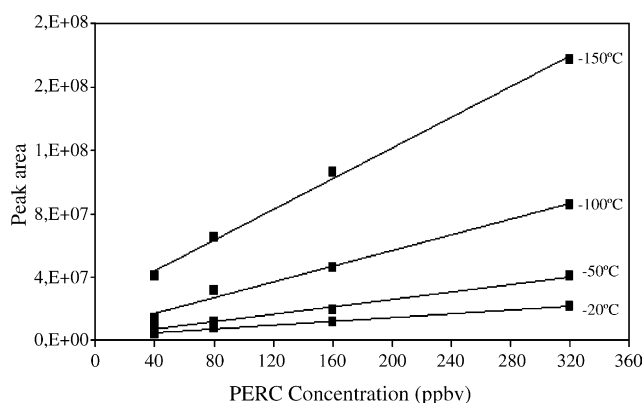


Fig. 3. Effect of preconcentration temperature of the first cryogenic trap on the slope of the calibration graph for PERC.

Table 3
Determination of PERC in outdoor samples

Dry-cleaning shop (Sector)	Concentration (ppb _v)			
	Perchloroethylene		Benzene	
	MS	GC–MS	MS	GC–MS
Quilín (Macul)	0.5	0.4	1.8	1.7
Donde Simón (Ñuñoa)	35	35.3	4.3	5.4
Grecia Ltda. (Ñuñoa)	17	19	0.9	0.73
El Rey (La Reina)	73	a	1.1	a
Nina (Macul)	0.3	a	1.8	a

a: Determination was not carried out.

tion temperatures in the interval from 40 to 320 ppb_v. As can be seen, the preconcentration factor increased considerably as the temperature decreased. However, this increment was associated with considerable increments in the time required to reach the programmed temperature in the Tenax trap (10 min at -50 °C to 30 min at -150 °C) and with increased spending on liquid nitrogen. Consequently, a temperature of -50 °C was selected for further studies, for both direct MS and GC–MS.

In these conditions, the precision and detection limits were determined for PERC. The precision of the method, expressed as relative standard deviation ($n = 11$), was 3.8 and 2.9%, at concentration levels of 0.1 and 10 ppb_v. Detection and quantitation limits were 0.011 and 0.038 ppb_v, respectively. Considering that in this case, analyte preconcentration is mandatory, the sample throughput of the direct MS approach decreased to five samples per hour.

In the case of GC–MS, Table 1 shows the analytical features of the chromatographic method. In the case of ethylbenzene and xylenes, the analytical features could not be determined because the analytical manifold presents some undetermined contamination with these compounds.

By analyzing the mass spectra of the different VOCs present in the TO-14 standard, it can be observed that not only PERC but also benzene (m/z 78) provide selective ions to be monitored directly by MS. Table 3 shows the results of the environmental monitoring for PERC and benzene outside some dry-cleaning shops located in eastern Santiago.

Some of these samples were processed by GC–MS (SIM mode) by switching the selecting valve of the manifold so that a new volume of sample could be fed into the chromatographic column previous to MS detection. The results are also shown in Table 3. As can be observed, the MS direct method provides an excellent estimation of PERC and benzene concentration. Other VOCs could be determined directly by mass spectrometry but using a chemometric data treatment [4,10–15]. However, the sum of toluene and ethylbenzene and the sum of trimethylbenzenes also correlate when the values determined by MS are compared with those obtained by GC–MS.

4. Conclusions

A new mass spectrometry/gas chromatography–mass spectrometry (MS/GC–MS) approach has been developed for the

screening and quantitative determination of PERC and other VOCs in air samples.

The analytical system proposed may be rapidly modified in order to be used directly as an MS detector or alternatively as a common GC-MS. In this way, it is possible to screen different VOCs rapidly by MS in air samples which can be confirmed by GC-MS if required.

The advantage of this approach over others previously described [4] is that in the present case, the sample passes through the chromatographic column only when the confirmatory GC-MS is used. The MS screening method prevents the sample from passing through the chromatographic column. Thus, the lifetime of the column could be extended and screening time is considerably shortened.

The precision (RSD) of the direct MS method for PERC in workplace samples was less than 3.5%. The detection limit was found to be 0.11 ppm_v. This value is sufficiently low to determine PERC directly in the workplace by MS, considering that the most rigorous exposure standards are 40 ppm_v [1]. The accuracy of this direct method was assessed by analyzing a certified TO-14 standard (Supelco). Recovery for PERC was 102 ± 3% and it was observed that none of the components of the TO-14 standard interferes in PERC direct determination by MS. One of the main advantages of the present method is its rapidity. The sample throughput was 30 samples per hour.

The determination of PERC in outdoor air samples required the use of a preconcentration system. In these conditions, the precision of the method, expressed as relative standard deviation, was less than 3.8% and the detection limit was 0.011 ppb_v. Considering that in this case, analyte preconcentration is mandatory, the sampling throughput of the direct MS approach decreased to five samples per hour. The MS direct method provided an excellent estimation of PERC and benzene concentration in outdoor samples. Other VOCs could be determined directly by MS but

in this case, a chemometric data treatment would be required [4,10–15].

Acknowledgements

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