

Gas chromatography coupled to tunable pulsed glow discharge time-of-flight mass spectrometry for environmental analysis

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A tuneable microsecond pulsed direct current glow discharge (GD)-time-of-flight mass spectrometer MS(TOF) developed in our laboratory was coupled to a gas chromatograph (GC) to obtain sequential collection of the mass spectra, at different temporal regimes occurring in the GD pulses, during elution of the analytes. The capabilities of this set-up were explored using a mixture of volatile organic compounds of environmental concern: BrClCH, Cl₃CH, Cl₄C, BrCl₂CH, Br₂ClCH, Br₃CH. The experimental parameters of the GC-pulsed GD-MS(TOF) prototype were optimized in order to separate appropriately and analyze the six selected organic compounds, and two GC carrier gases, helium and nitrogen, were evaluated. Mass spectra for all analytes were obtained in the prepeak, plateau and afterpeak temporal regimes of the pulsed GD. Results showed that helium offered the best elemental sensitivity, while nitrogen provided higher signal intensities for fragments and molecular peaks. The analytical performance characteristics were also worked out for each analyte. Absolute detection limits obtained were in the order of ng. In a second step, headspace solid phase microextraction (HS SPME), as sample preparation and preconcentration technique, was evaluated for the quantification of the compounds under study, in order to achieve the required analytical sensitivity for trihalomethanes European Union (EU) environmental legislation. The analytical figures of merit obtained using the proposed methodology showed rather good detection limits (between 2 and 13 µg L⁻¹ depending on the analyte). In fact, the developed methodology met the EU legislation requirements (the maximum level permitted in tap water for the “total trihalomethanes” is set at 100 µg L⁻¹). Real analysis of drinking water and river water were successfully carried out. To our knowledge this is the first application of GC-pulsed GD-MS(TOF) for the analysis of real samples. Its ability to provide elemental, fragments and molecular information of the organic compounds is demonstrated.

Introduction

The need for chemical speciation analysis is well recognized nowadays, because the physico-chemical form of a given element determines its actual toxicity, bioavailability and metabolism within environmental and biological systems.^{1,2} At present, chemical speciation is commonly accomplished by resorting to hyphenated analytical techniques, which include a powerful chromatographic separation technique coupled to a highly sensitive elemental spectrometric detector. Unfortunately, current elemental speciation methods provide limited chemical information, they need additional molecular techniques and are prone to errors in element species quantification.^{3,4} Thus, a reliable, selective and sensitive system capable of providing, simultaneously (or in a rapid sequence but in a single instrument), atomic and molecular information should be desirable.⁵ A possible way out is the use of MS with a single ionization source which is able to work at different modes to produce elemental and molecular ions alike.

It is known that glow discharges (GDs) can be operated in a transient power mode (pulsed-mode) allowing different ionization processes^{6,7} and, so, providing different types of information depending on the time of the GD pulse-regime where the ions are generated: elemental information could be collected detecting ions generated in the first part of the GD pulse (pre-peak), structural information in the plateau of the GD pulse, and molecular ion information in the afterpeak,^{7,8} that is, after the application of power to the discharge chamber is terminated. Thus, in principle, the coupling of such pulsed ion-sources to a time-gated detection mass analyser, such as a MS(TOF), would allow the quasi-simultaneous collection of elemental, structural and molecular ion information. Although “the proof of concept” was already published,⁷⁻¹⁰ actual analytical applications of such an approach are very limited so far, mainly because the analytical performance characteristics of published systems are relatively poor. One possible cause for such overall poor performance could be the design of the discharge chambers and their optimization for gaseous analytes analysis.

The development and optimization of a new microsecond pulsed direct current (µsGD), its coupling to a MS(TOF) detection system and its analytical performance for volatilized analytes examination, was presented in a previous work.¹¹ The GD chamber used, characterized by about 100 mm³ of internal

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volume and two opposite inert gas inlets, was designed in our laboratory,^{12,13} and provided very good electrical stability to the discharge, ensuring a high robustness to the entrance of volatile organic compounds in the microsecond-pulsed plasma (with minimal dilutions of the introduced sample in the GD plasma gas).

As an extension of such work, here we investigate the coupling of a gas chromatograph (GC) with the previously developed plasma-based pulsed GD-MS(TOF) detection system.¹¹ The experimental parameters of such GC- μ GD-MS(TOF) prototype were optimized to separate with good chromatographic resolution, characterise and determine a representative mixture of volatile organic compounds (VOCs).

VOCs are present in water as a consequence of disinfection processes using chlorine or its derivatives in drinking water treatment plants, urban discharges or farming and industrial activities.^{14,15} VOCs have adverse effects on human health, even at very low concentrations, as they have toxic, carcinogenic or mutagenic properties.¹⁶ Therefore, regulatory values of some VOCs in drinking water were established by a European Directive of 1998 in the European Union (EU)¹⁷ and in Spain.¹⁸ Trihalomethanes (THMs) are the main class of VOCs (with a general formula: CHX_3 , where X may be Cl, Br or their combinations) present in drinking waters.¹⁹ The maximum level for "total THMs" permitted in drinking water has been set at $100 \mu\text{g L}^{-1}$ in the EU.

Thus, the aim of this work was to assess the analytical potential of GC - μ GD - MS(TOF) for the simultaneous speciation and determination of VOCs in waters as required by EU legislation. In order to achieve the needed sensitivity for the quantification of the analytes under study, headspace solid phase microextraction (HS SPME) was selected as sample preparation and preconcentration technique.^{20,21} SPME has proved to be a simple, fast, inexpensive, solvent-free sample introduction tool for GC-MS.^{22,23}

Experimental

Chemicals and samples

Four bromine hydrocarbons (bromochloromethane, bromodichloromethane, dibromochloromethane, tribromomethane) were obtained from Sigma Aldrich (Steinheim, German), while carbon tetrachloride and chloroform were from Prolabo (Fontenay sous Boix, France). All the chemicals were of analytical reagent grade and used as received, without any further purification. Stock standard solutions of each VOC at a concentration of 10 g L^{-1} and a mixture of them at a concentration of 100 mg L^{-1} were prepared in methyl *tert*-butyl ether (MTBE) and stored at $-20 \text{ }^\circ\text{C}$. These solutions were used for the preparation of daily working standard mixtures of the six VOCs in MTBE (for further GC-MS and GC- μ GD-MS(TOF) analysis) and in water (HS SPME-GC-MS and HS SPME-GC- μ GD-MS(TOF) analysis). MTBE (purity $\geq 99.0\%$) was obtained from Fluka (Buchs SG, Switzerland). Ultrapure water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA).

A NIST certified reference material (SRM 1639) containing a mixture of halocarbons in methanol at different concentration levels (CHCl_3 6235 ng mL^{-1} , CHBrCl_2 389.9 ng mL^{-1} , CHBr_2Cl

124.6 ng mL^{-1} , CHBr_3 86.5 ng mL^{-1} , CCl_4 157.0 ng mL^{-1} , $\text{CHCl}=\text{CCl}_2$ 85.8 ng mL^{-1} , and $\text{CCl}_2=\text{CCl}_2$ 40.6 ng mL^{-1}) was obtained from LGC Promochem (Teddington, Middlesex, United Kingdom).

Amber glass vials of 15 mL with silicone/PTFE-lined screw caps were used for drinking water sampling. All the glass material was cleaned with detergent, rinsed with Milli-Q water and oven dried at $80 \text{ }^\circ\text{C}$ for at least 1 h. Before its use, glass material was brought to room temperature. Samples were collected in duplicate from different places in the north of Spain without any pretreatment and stored in amber vials. This container should be filled up to avoid headspace. Then the samples were cooled down to $4 \text{ }^\circ\text{C}$ till their analysis.

GC-MS instrumentation and experimental conditions

For comparative purposes, classic GC-MS analysis was performed using an Agilent 6890 Network gas chromatograph (Agilent Technologies, Waldbronn, Germany) equipped with a mass spectrometric detector (Model Agilent 5973 Network) operated in electron impact (EI) ionisation mode. A $30 \text{ m} \times 0.25 \text{ mm}$ id, $0.25 \mu\text{m}$ film thickness, HP-5MS (5% phenyl/methylsiloxane) fused-silica column was used. Helium from Air Liquide (Oviedo, Spain) of 99.999% purity was employed as carrier gas with a constant flow of 0.8 mL min^{-1} . The initial temperature was $30 \text{ }^\circ\text{C}$, held for 5 min; ramped at $10 \text{ }^\circ\text{C min}^{-1}$ up to $50 \text{ }^\circ\text{C}$; a second rate at $50 \text{ }^\circ\text{C min}^{-1}$ up to $200 \text{ }^\circ\text{C}$ and then held for 5 min.

Electron-impact ionisation was performed at an electron energy of 70 eV. A mass range from m/z 40–350 was recorded in the full-scan mode. The mass spectrometer was programmed in its single-ion monitoring (SIM) mode to respond to the 6 analytes at their corresponding gas chromatographic retention times. The analytes elution order and quantification mass/charge ratios (given in parentheses) for the selected method were: CHBrCl (98, 128, 130), CHCl_3 (83, 85), CCl_4 (117, 119), CHBrCl_2 (83, 85, 129), CHBr_2Cl (127, 129), CHBr_3 (173).

Solid-phase microextraction equipment

The SPME device for manual extraction, a holder assembly and several replaceable fibers were purchased from Supelco (Bellefonte, PA, USA). Two fiber types were compared: polydimethylsiloxane (PDMS, $100 \mu\text{m}$) and divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS, 50/30 μm). All the fibers were conditioned, prior to their use, by heating them in the injection port of the GC following the manufacturer's recommendations,

A magnetic stirrer hotplate from Selecta (IKA-Werke) was used for stirring and heating the samples during extraction. 10 mL glass vials closed with PTFE-coated silicone septa were used for SPME.

Direct immersion (DI) SPME extraction was carried out as follows: aliquots of the VOCs standard solution were added to 10 mL of Milli-Q water. The vial was then immediately closed, placed in a thermostatic water bath and the fiber immersed in the solution and kept there for 15 min at ambient temperature ($25 \text{ }^\circ\text{C}$). For headspace (HS) SPME aliquots of the VOCs standard solution were added to 5 mL of Milli-Q water with NaCl at 50% saturation, and the fiber exposed to the solution

headspace for 20 min at room temperature. During extraction in both modes, DI and HS, the solution was vigorously stirred at a constant speed with a clean PTFE-coated small magnetic stir bar. After extraction, the fiber was thermally desorbed at 250 °C for 5 min into the glass liner of the chromatograph injection port. This liner had 0.75 mm of id, special for SPME (Supelco). The injector port was operated in splitless mode. No carryover was observed. Moreover, procedural blanks were run periodically during the analysis to check for possible fiber contaminations.

Pulsed glow discharge time-of-flight system

The GD chamber used and its coupling to the mass analyser of a commercial time-of-flight instrument (Renaissance ICP-MS(TOF) from LECO, St. Joseph, MI, USA) have been previously described.^{13,24} Different MS(TOF) instrumental variables were adjusted for maximum analyte signals. A detector voltage of -2400 V was selected. All the analytical signals were measured in the analog mode.¹¹

The GD was generated by applying μs dc voltage pulses (IRCO, Model M3kS-20N, Maryland, USA) to a solid sample which acts as cathode electrode in the discharge. Iron standard material ref. MBS 50D (MBH Analytical Ltd., Herts, UK) was selected for the cathode.¹¹ The cathode surface was polished and cleaned daily to avoid potential problems related to performance deterioration and/or short-circuiting due to cathode erosion and redepositions related with long times of sputtering in the GD. A digital oscilloscope (Tektronix, TDS3012, 100 MHz, 1.25 GS s⁻¹) synchronized with the pulsed power supply allows plasma stability monitoring. 50 μs of pulse width and 500 Hz were selected for the measurements.

An appropriate synchronization^{11,25} between the GD pulse was ensured and the MS(TOF) repeller delay (RD) was selected for the quasi-simultaneous collection of different chemical information from every single pulse coming from the pulsed GD plasma. The highest elemental intensities were obtained selecting RDs of 10 μs (prepeak of the discharge pulse). The maximum signals for molecular fragments ions were obtained when selecting a RD around 50 μs (plateau time regime). Finally, the molecular ions, only detected at repeller delays greater than the GD pulse duration, were measured at RD of 90 μs (afterpeak).

In order to obtain simultaneous acquisition of elemental, structural and molecular signals, the selected microsecond-pulsed GD operating conditions were, 0.39 Torr in the first stage, and 2000V dc pulse, as optimized in previous work.¹¹ The discharge gas pressure inside the GD ion source was controlled using the nebulizer gas mass flow controller from the ICP-MS(TOF). The pressure was measured with the first stage gauge of the TOF mass spectrometer.

High purity argon (99.999% minimum purity) from Air Liquide (Oviedo, Spain) was employed as the discharge gas.

A gas chromatograph HP-5890 Series II equipped with a 30 m \times 0.25 mm id, 0.25 μm film thickness, HP-5MS fused-silica column, was used. Helium or nitrogen (Air Liquide (Oviedo, Spain), purity 99.999%) were employed, as carrier gas, with a constant pressure of 6 psi. The injector was operated in splitless mode. The temperature of the injector was maintained at 250 °C. The column temperature was held at 30 °C for 5 min, then raised

to 50 °C at a rate of 10 °C min⁻¹ and finally raised to 200 °C at 50 °C min⁻¹.

The coupling between the GC and the GD was carried out with a stainless steel external transfer line (1 m long) heated by using electrical heating tape (the transfer tube line must be heated to prevent condensation of the analytes within). Inside the GC oven a capillary connector (Supelco) connects the end of the capillary column to a non polar fused silica capillary (0.25 mm id, Supelco). This non polar fused silica capillary goes inside the stainless steel tube and its other end was introduced to the GD chamber through the usual gas inlet. The GD chamber and the external transfer line are connected across a stainless steel "T" piece. The longest arm of the "T" was used for the introduction of argon as plasma gas.

Results and discussion

GC carrier gas selection

The carrier gas used in the gas chromatograph (helium and nitrogen were evaluated) corresponds to about a 2% of the needed glow discharge plasma gas. Therefore, the effect of its mixture with the GD Ar plasma gas was investigated.

Helium was first employed to remain consistent with the common methodology used for gas chromatography and to compare our GC- μs GD-MS(TOF) results with those obtained by conventional GC-MS (electron impact ionization) for the same analytes. Unfortunately, to obtain the analyte's molecular parent ion requires a relatively close energy match between the metastable energy of the plasma gas and the ionization potential of the target analyte and most common halogenated compounds exhibit ionization potentials in the order of 9 to 12 eV (helium metastable energies are in the range of 20.6 to 19.8 eV). In this situation, extensive fragmentation patterns¹⁰ could occur. Therefore, nitrogen offering a lower ionization potential but maintaining rather similar chromatographic properties to those of He, was also investigated as mobile phase.

Fig. 1 shows, comparatively, different chromatograms observed using nitrogen and helium: Fig. 1a and 1b collect the signals of ³⁵Cl and ⁷⁹Br obtained in the prepeak of the GD pulse for both carrier gases, while Fig. 1c shows the observed chromatogram corresponding to the fragment ion at *m/z* 47, obtained in the GD plateau time regime. As can be seen, in Fig. 1a and 1b, highest signals (elemental information) especially for chlorine, were obtained using helium as carrier gas. However, nitrogen provided the best intensity for fragments (Fig. 1c) and the molecular peaks (Fig. 1d). So, in order to fully exploit the molecular information capabilities of our prototype, nitrogen was the carrier gas selected for further experiments.

Qualitative analysis

As already stated, elemental information is mostly obtained in the prototype¹¹ during the prepeak time regime, in the plateau spectra preferably fragment ion information is collected and molecular weight information of the analyte parent ion is obtained in the afterpeak. The type of information can be selected in our approach just by changing the repeller delay of the MS(TOF). Thus, prepeak, plateau and afterpeak mass spectra were obtained for each chromatogram peak (analyte).

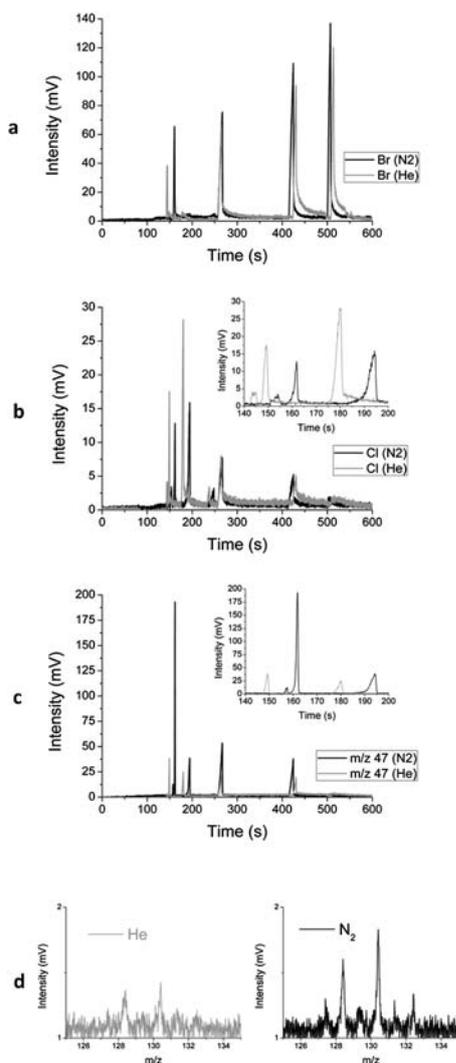


Fig. 1 Carrier gas selection. a) Chromatograms obtained in nitrogen and in helium for $^{79}\text{Br}^+$ in prepeak time regime. b) Chromatograms obtained in nitrogen and in helium for $^{35}\text{Br}^+$ in prepeak time regime. c) Chromatograms obtained in nitrogen and in helium for m/z 47 in plateau time regime. d) Bromochloromethane molecular peak in both carrier gases, obtained in the afterpeak. Black line corresponds to the use of nitrogen as carrier gas and grey line to helium as carrier gas.

As an example, the MS fragmentation patterns of eluted dibromochloromethane observed with our prototype at the different discharge time-regimes are collected in Fig. 2 (the signals observed at m/z 54 and m/z 56 correspond to sputtered iron from the cathode). First, for comparison, the mass spectra of the standard NIST, obtained *via* electron impact ionization with electron energy of 70 eV, is collected in Fig. 2a. Fig. 2b shows the collected prepeak mass spectra of dibromochloromethane (that is, halogen elemental ions). ^{35}Cl could be only observed in this part of the pulse time regime. It was checked that the measured bromine isotopic ratios (right inset of Fig. 2b) are very close to the theoretical ratios.

Fig. 2c shows the observed spectrum in the plateau region. As can be seen, the mass spectra detected in the instrument are rich in structural information and also provides a similar pattern to standard NIST EI mass spectra. As an example, the mass

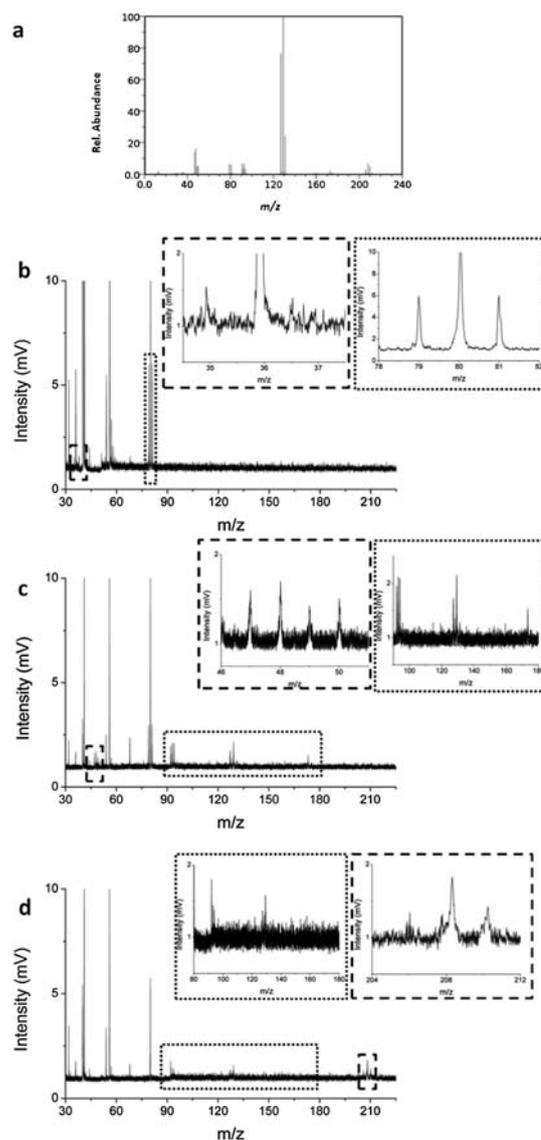


Fig. 2 Mass spectra of dibromochloromethane obtained with GC-micro-pulsed dc-GD-MS(TOF) after injection of a mixture of VOCs and comparison with the corresponding NIST spectra. a) Reference NIST spectra obtained by electron impact (70 eV). b) Prepeak region. c) Plateau time regime. d) Afterpeak region.

spectrum of ClC fragment ions (m/z 47, 48, 49, 50) is shown inside an insert.

Fig. 2d illustrates that the molecular weight peaks (m/z 206, 208, 210) of analyte parent ions could only be detected during the afterpeak. Moreover, it can be observed in the left insert that signals from fragments decrease as compared to those shown in Fig. 2c for the plateau (right inset).

GC- μ sGD-MS(TOF) analytical performance characteristics

The analytical performance characteristics of the developed prototype were evaluated at the optimised operating conditions, using nitrogen as carrier gas, for each analyte.

Calibration graphs were constructed at each time regime of the glow discharge by measuring the intensities observed for elemental, fragments and molecular ions of each analyte. In

order to calculate the figures of merit in the prepeak time regime we selected the signal from ^{79}Br for those analytes containing bromine, while the ^{35}Cl ion signal was measured for Cl_3CH and Cl_4C . In the plateau time regime the signals from a ClC fragment (m/z 47) and a BrC (m/z 91) were selected for the quantification. In all cases a good linearity was achieved (with regression coefficients higher than 0.99). Relative standard deviations obtained at ten times detection limits (DLs) levels and observed for five replicate injections, were in the average range of 5–15%. Such precision figures are rather satisfactory and the linearity particularly noteworthy, considering that samples were manually injected in the gas chromatograph and no internal standardization was used for any of those GC- μGD -MS(TOF) measurements.

The criterion followed for DLs calculation was the minimum concentration of each analyte producing a net signal equal to three times the standard deviation of the background intensity (ten replicates) in each case. Table 1 collects the calculated DLs using either He or N_2 as mobile phase. As expected, the use of helium as carrier gas provided better DLs than nitrogen for elemental ions, but attainable detection limits for fragments are better using nitrogen (as we have already observed in the chromatograms above). Our results show that DLs achieved for the element and the fragments were improved above one order of magnitude as compared with previous results^{9,26} measuring their analytes (it is important to note that the studied analytes in previous reports are not the same as those selected in our work) in the same pulse regimes.

SPME for sample preparation and preconcentration

In order to develop a SPME procedure for the preconcentration of the VOCs from the water samples the parameters influencing the SPME process such as the extraction time, extraction temperature, extraction mode, desorption time, desorption temperature and salt effect, were optimised using the Agilent GC-MS.

First, two fiber coatings were compared, a 100 μm PDMS and a 50/30 μm DVB/CAR/PDMS. For the optimization, a 50 mg L^{-1} solution containing each one of the analytes was used as working solution. This solution was stirred magnetically during 15 min at 25 $^\circ\text{C}$ for the extraction step and then the analytes in the fibers were desorbed into the injector. In these experiments the extraction mode (either headspace or direct immersion) and different extraction temperatures were assayed for both fibers.

Table 2 Final optimized SPME parameters used in this work

Fiber coating	50–30 μm CAR/DVB/PDMS
Extraction Mode	Headspace
Extraction Time	20 min
Extraction Temperature	25 $^\circ\text{C}$
Desorption Time	5 min
Desorption Temperature	250 $^\circ\text{C}$
Salt Effect	50% saturation

Using optimum conditions for each fiber coating the best sensitivity was obtained with DVB/CAR/PDMS in headspace mode.

Then, the effect of the extraction time was studied between 5 and 30 min (to extract the maximum amount of analyte, equilibrium should be reached). In our case, the maximum signal was obtained for 20 min extraction time. Finally, the influence of desorption parameters was investigated, including desorption temperature and heating time of the fiber into the GC injector. As we work in HS, salts can be added to the working solution at high levels without damaging the fiber coating (the analyte amount extracted by the fiber can be increased if its solubility in water is decreased by changing the ionic strength). The effect of ionic strength on extraction efficiency was evaluated by analyzing the amount of VOCs extracted from sample solutions containing 0, 50 and 100% of saturation with sodium chloride. The best results were obtained with 50% NaCl saturation of the sample solutions. Table 2 collects the final optimized SPME parameters.

HS SPME-GC-MS and HS SPME-GC- μGD -MS(TOF) analytical performance characteristics

The analytical performance characteristics of the HS SPME sample preparation and GC- μGD -MS(TOF) system for final determinations were compared with those typical of HS SPME-GC-MS with EI for ionization, a reference methodology for the analysis of THMs in water samples.

The GC-MS sensitivity of this latter commercial instrument was enhanced using the SIM mode, that is, only ions of a particular m/z value were monitored (two or three per analyte). Therefore, the fact that our pulsed GD prototype provides simultaneously the complete mass spectra of each analyte (in the three time regimes of the GD pulse) should be stressed here.

Thus, using the SPME optimized parameters (Table 2) key analytical performance characteristics (detection limits, precision and accuracy) were evaluated for the analytes mixture and by the

Table 1 VOCs detection limits using the developed GC- μGD -MS(TOF). Two different carrier gases (helium and nitrogen) are compared

Analyte	PREPEAK		PLATEAU			
	DL/ a ng N_2	DL/ a ng He	DL/ng m/z 47 N_2	DL/ng m/z 47 He	DL/ng m/z 91 N_2	DL/ng m/z 91 He
BrClCH	3	1.8	4.3	6.9	3.6	4.3
Cl_3CH^*	6.7	2.2	1.1	2.5	—	—
Cl_4C^*	3.1	1	0.7	1.6	—	—
Br Cl_2CH	3.8	1.4	1.1	2.7	2	3.4
Br $_2\text{ClCH}$	1.7	0.7	1	2.1	0.8	2.9
Br $_3\text{CH}$	1.8	1	—	—	1.1	3.4

^a DLs were calculated using the elemental ion intensity of ^{79}Br (except for Cl_3CH and Cl_4C , which is calculated using ^{35}Cl) obtained in the prepeak.

two techniques. Also, the linearity was studied in the 1–100 $\mu\text{g L}^{-1}$ range. Results showed that the six analytes have linear responses in the assayed range and their observed regression coefficients (R^2) were at least of 0.99 for all VOCs by both techniques.

The precision and accuracy (expressed as repeatability and as the percent relative recovery, respectively) were determined by a 10 replicate analysis of Milli-Q water spiked with the standard mixture of the six VOCs at final concentration levels equivalent to those permitted by the corresponding EU regulation (25 $\mu\text{g L}^{-1}$ for each of the analytes). The observed RSD were between 1% (CCl_4) and 18% (CHBrCl_2) and the recoveries ranged from 88% (CHBrCl_2) to 109% (CHCl_3) by more conventional HS SPME-GC-MS (EI ionization) methodology. As Table 3 shows, RSD and recoveries obtained with the pulsed GD system, were very similar to those observed by the conventional GC-MS method.

The limits of detection using HS SPME-GC-MS, with EI ionization, were calculated as three times the standard deviation of the background intensity (10 replicates) divided by the calibration slope. The DLs varied between 0.4 (CHBr_2Cl) and 0.6 (CHCl_3) μg of analyte/L for the THMs. Such DLs are of the same order of those previously reported.²⁷ With our $\mu\text{SGD-MS(TOF)}$ detection system, the corresponding detection limits were calculated using the elemental ion intensity signals of ^{79}Br (except for CHCl_3 and CCl_4 which is calculated using ^{35}Cl) obtained in the prepeak, and the intensity of fragment ions at m/z 47 and m/z 91 in the plateau time regime. Such calculated DLs are collected in Table 3 as well. As can be seen, DLs values meet the requirements of the current EU legislation for total trihalo-methanes in drinking waters.¹⁷

The comparison of both detection modes showed that slightly better DLs can be obtained with the commercial GC-MS (see Table 3), but the GC- $\mu\text{SGD-MS(TOF)}$ prototype offers the possibility to obtain elemental, structural and molecular information, and so allowing in the same instrument an unambiguous identification and quantification of the organics.

Validation of HS SPME-GC- $\mu\text{SGD-MS(TOF)}$ method and real sample analysis

The actual recoveries of THMs analysed in water samples by the proposed new analytical method were calculated by using a standard reference material (SRM 1639) containing four organic compounds at different certified concentration levels. For this purpose an adequate amount of standard reference

Table 4 Recovery of the HS SPME-GC- $\mu\text{SGD-MS(TOF)}$ method for THMs in water by using a standard reference material (SRM 1639)

Analyte	% Recovery	Measurement peak (m/z)
Cl_3CH	101 \pm 11	35
BrCl_2CH	88 \pm 8	79
Br_2ClCH	98 \pm 6	79
Br_3CH	89 \pm 11	79

material was added to Milli-Q water and then analyzed with the HS SPME-GC- $\mu\text{SGD-MS(TOF)}$ methodology. The average recoveries obtained for the THMs were between 88% and 101% as shown in the recovery results collected in Table 4.

Once the proposed method has been validated, it was applied to the determination of VOCs in real samples of drinking waters and river waters from the north of Spain. Fig. 3 shows the concentrations of the found compounds calculated in the pre-peak (since as seen before, this part of the pulsed GD time regimes is the most sensitive). It should be printed out, however, that also the structural (plateau) and molecular (afterpeak) spectra were obtained simultaneously providing an additional unambiguous identification of the different organic analytes.

As we can see, the measured concentration of the VOCs in all water samples analyzed turned out to be lower than the

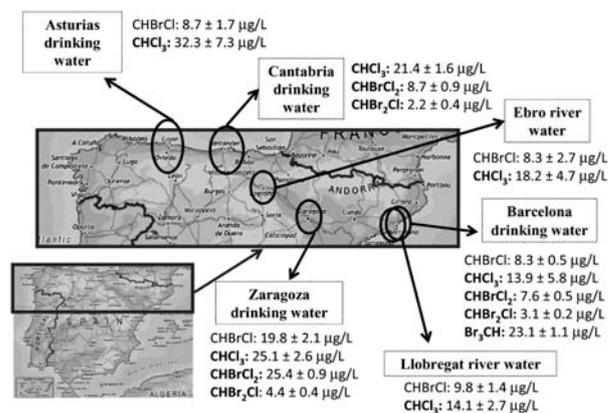


Fig. 3 Determination of VOCs in drinking water and river water samples taken in northern Spain.

Table 3 Analytical performance characteristics observed for the determination of VOCs using the developed HS SPME-GC- $\mu\text{SGD-MS(TOF)}$ strategy (nitrogen was used as carrier gas)

Analyte	PREPEAK			PLATEAU					
	DL ^a / $\mu\text{g L}^{-1}$	% RSD	% Recovery	m/z 47			m/z 91		
				DL/ $\mu\text{g L}^{-1}$	% RSD	% Recovery	DL/ $\mu\text{g L}^{-1}$	% RSD	% Recovery
BrClCH	5.7	4	108	21	20	106	14	5	115
Cl_3CH^*	9.8	12	116	17	20	109	—	—	—
Cl_4C^*	13	7	112	13	14	95	—	—	—
BrCl_2CH	6	11	118	14	7	95	14	2	113
Br_2ClCH	2	6	93	6	11	80	5	10	115
Br_3CH	3	7	103	—	—	—	7	3	108

^a DLs were calculated using the elemental ion intensity of ^{79}Br (except Cl_3CH and Cl_4C , which is calculated using ^{35}Cl) obtained in the prepeak.

maximum level permitted by the Spanish and European legislations ($100 \mu\text{g L}^{-1}$). Moreover, the results obtained for drinking waters in central Asturias²³ were in good agreement with previous analysis reported using other analytical techniques (total THMs in the range 0.4 to $52.5 \mu\text{g L}^{-1}$).²³

Conclusions

A novel hybrid analytical technique GC- $\mu\text{GD-MS(TOF)}$ has been successfully developed and optimized to separate with good chromatographic resolution and determine with good accuracy and precision six volatile organic compounds in water samples. Moreover, the capabilities of the developed microsecond pulsed GD-MS(TOF) system for the simultaneous acquisition of molecular, fragments and elemental MS information has been demonstrated. In other words, in a single GD pulse, elemental, structural and molecular information (see Fig. 2) can be obtained for each eluted analyte, thus allowing their unequivocal MS fingerprint identification.

Two chromatographic carrier gases have been evaluated and helium showed the best elemental sensitivity. However, nitrogen provided higher signal intensities for analyte fragments and molecular peaks. In order to have an unambiguous characterization of the analytes along with the determinations, nitrogen was selected as carrier gas, despite its comparatively lower elemental sensitivity. The analytical figures of merit obtained compare very favourably with those reported so far in previous similar tuneable GD ion sources approaches.^{9,26}

Additionally, to improve the sensitivity of the proposed GC- $\mu\text{GD-MS(TOF)}$ to be useful for real samples analysis, HS SPME was selected as sample preparation/preconcentration technique. The developed HS SPME-GC- $\mu\text{GD-MS(TOF)}$ methodology proved to provide in the prepeak rather similar DLs to those observed by HS SPME-GC-MS using EI ionization (the reference methodology for these compounds), meeting the current EU legislation requirements for total trihalomethanes.¹⁷

Real sample analysis of drinking water and river water were carried out successfully with the MS prototype and the methodology here presented. To our knowledge this is the first application of GC- $\mu\text{GD-MS(TOF)}$ for the analysis of real samples.

To conclude, it has to be stressed that the achieved instrumental sensitivity could be even further improved by operating the MS(TOF) in digital instead of in the used here analog mode.¹¹

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