



Development of a headspace-gas chromatography (HS-GC-PID-FID) method for the determination of VOCs in environmental aqueous matrices: Optimization, verification and elimination of matrix effect and VOC distribution on the Fortaleza Coast, Brazil

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ABSTRACT

An analytical protocol combining a headspace technique with gas chromatography and detection by photoionization detector and flame ionization detector (HS-GC-PID-FID) was developed. This procedure was used to measure volatile organic compounds (VOCs) in environmental aqueous matrices and was applied in determination of VOCs on the coast of Fortaleza, Brazil. At optimum operating conditions, analytical figures of merit such as linearity (R ranged from 0.9983 to 0.9993), repeatability (5.62 to 9.63% and 0.02 to 0.19% for the quantitative and qualitative analyses, respectively), detection limits (0.22 to 7.48 $\mu\text{g L}^{-1}$) and sensibility were estimated. This protocol favors a fast sampling/sample preparation (*in situ*), minimizes the use of laboratory material, eliminates the matrix effect from environmental samples, and can be applied to river, estuarine and oceanic waters. The advantage of detectors in series is that a low sensitivity in detection in one is compensated by the other. Toluene was the most abundant VOC in the studied area, with an average concentration of 1.63 $\mu\text{g L}^{-1}$. It was followed by *o*-xylene (1.15 $\mu\text{g L}^{-1}$), trichloroethene (1.08 $\mu\text{g L}^{-1}$), benzene (0.86 $\mu\text{g L}^{-1}$), ethylbenzene (0.74 $\mu\text{g L}^{-1}$), carbon tetrachloride (0.55 $\mu\text{g L}^{-1}$), *m/p*-xylene (0.48 $\mu\text{g L}^{-1}$) and tetrachloroethene (0.46 $\mu\text{g L}^{-1}$), compounds which are very commonly detected in urban runoff from most cities. The results of the VOC distribution showed that port activity was not the main source of VOCs along the Fortaleza Coast, but that the contribution from urban runoff seemed more significant.

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1. Introduction

Volatile organic compounds (VOCs) represent a class of organic substances characterized mainly by high volatility under environmental conditions. The main subgroups of these priority pollutants are halogenated volatile organic compounds (HVOCs), chlorinated short-chain hydrocarbons (CHCs) and monocyclic aromatic hydrocarbons (MAHs) [1,2]. The main reason for assessing VOCs in aquatic environments is their neurotoxic and carcinogenic effects [2].

The main anthropogenic sources of VOCs to aquatic environments are the effluents of urban and industrial activities, including wastewater, atmospheric deposition, urban and rural runoff, extraction accidents, transport and/or transformations of fossil fuels, and natural sources (petrogenic and biogenic) [1,2].

Sample preparation may largely influence the sensitivity and accuracy of measurements due to the physico-chemical properties of

VOCs. Several sample introduction modules were coupled to chromatographic systems to improve the measurement quality (e.g., headspace sampling) [3]. Headspace analysis is a technique to separate and collect volatile compounds (in the gas phase) from different sample matrices such as water, solids, and food [4,5]. Thus, headspace gas chromatography (HS-GC) is a technique of gas extraction in two modes: static or equilibrium headspace (labeled static headspace) and continuous extraction (or dynamic headspace, e.g., Purge-and-Trap (P&T)). In these two modes, the gas phase is sampled and injected directly into the GC equipment in an on-line form, avoiding loss and contamination [5]. Headspace (static or dynamic modes) and gas chromatography are the most adopted methods used by environmental agencies to determine VOCs from solid and liquid matrices [6]. However, direct aqueous injection (DAI) [7], liquid-liquid extraction (LLE) [7], membrane techniques, solid-phase extraction (SPE), solid-phase microextraction (SPME) and distillation techniques are also used as sample preparation techniques [3,8].

The static headspace technique (HS) presents a wide linear dynamic range (with a limit of detection (LOD) of up to 100 mg L^{-1}) [8], simpler instrumentation [3,9], good repeatability (coefficient of variation 4–10%)

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Table 1
Headspace gas chromatography conditions.

HS and GC conditions	HS	PID	FID
Incubation temperature (°C)	70.0		
Incubation time (min) ^a	10:0		
Syringe temperature (°C)	110.0		
Filling volume (ml)	2.0		
Filling delay (s)	5.0		
Injector temperature (°C)		230	230
Column flow (ml min ⁻¹)		3.0	3.0
Detector temperature (°C)		240 ^b	250

^a Shaking (10 s on and 20 s off, continually).

^b Lamp 10.6 eV.

and high recuperation (89–110%) [8,10,11]. Dynamic headspace technique e.g., P&T presents disadvantages such as the requirement for complex instrumentation, interference of water vapor generated at the purge stage [4], possible contamination of the trap (cross contamination) [12], narrow linear dynamic ranges and long analysis time per sample [8]. Additionally, P&T is not applicable to saline samples [13], but in some studies, this restriction is not problematic [14].

With the lower LOD requirement for VOC determinations to establish maximum contaminant levels (MCL) (e.g., USEPA), several methods have been developed for measurement in aqueous matrices [9,10,15,16]. A few studies on VOC determination in saline aqueous matrices from estuarine and marine environments have been reported [17]. The low VOC levels (due to dispersion, volatilization and biodegradation), salinity in the matrix and sampling difficulties (loss and/or contamination) are the main problems with VOC determinations from environmental matrices.

Offshore oil and natural gas exploration dramatically increased in Brazil during the last decade, requiring environmental assessment and annual monitoring of the production areas [18]. This paper describes a simple and efficient analytical protocol that allows fast sampling and preparation of samples, eliminates matrix effects and is highly sensitive for VOC determinations in environmental aqueous matrices with salinity and pH variations.

Only in the last two decades have studies on the distribution and impact of VOCs on the oceanic and estuarine environments been performed. No study has been reported for the Brazilian Coast, although some studies have shown pollution by semi-volatile hydrocarbons (e.g., PAHs and PCBs) in Brazil, including the city of Fortaleza [19–21]. Fortaleza is the fourth most important city in Brazil, and its main anthropogenic impacts on the coastline are the intense activity in the local port and urban runoff and industrial wastewater, as well as activities related to oil transport, discharge and refinement [20–22]. The results reported here may be useful to assess future impacts in Fortaleza, as tourism and industrial activities, including oil extraction, petrochemistry and steel production, are growing.

2. Materials

2.1. Chemicals and reagents

An internal standard mixture consisting of BTEX (benzene, toluene, ethylbenzene, and *m*-, *p*-, *o*-xylene), the main volatile organochlorines (carbon tetrachloride, trichloroethylene and tetrachloroethylene) and the internal standard ethylbenzene-d5 were obtained from Sigma-Aldrich (São Paulo, Brazil). Formaldehyde and acetone were obtained from Merck (São Paulo, Brazil). Stock solutions were produced from a primary, working standard solution, diluted with ultrapure water that was free of VOCs (Milli-Q system, Millipore). The final concentration was of 1000 µg L⁻¹. From these working standards, standard solutions of 0.5, 2.5, 25, 50, 250 and 500 µg L⁻¹ were prepared directly in screw-sealed vials (22 mL) with PTFE/silicon septa. The standard solutions were used for calibration and determination of the figures of merit. The vials and septa were purchased from Thermo (São Paulo, Brazil).

2.2. Apparatus

Experiments were carried out with a headspace autosampler Triplus HS (Thermo Electronic Corporation, Milan, Italy) and a Trace GC Ultra gas chromatograph (Thermo Electronic Corporation, Milan,

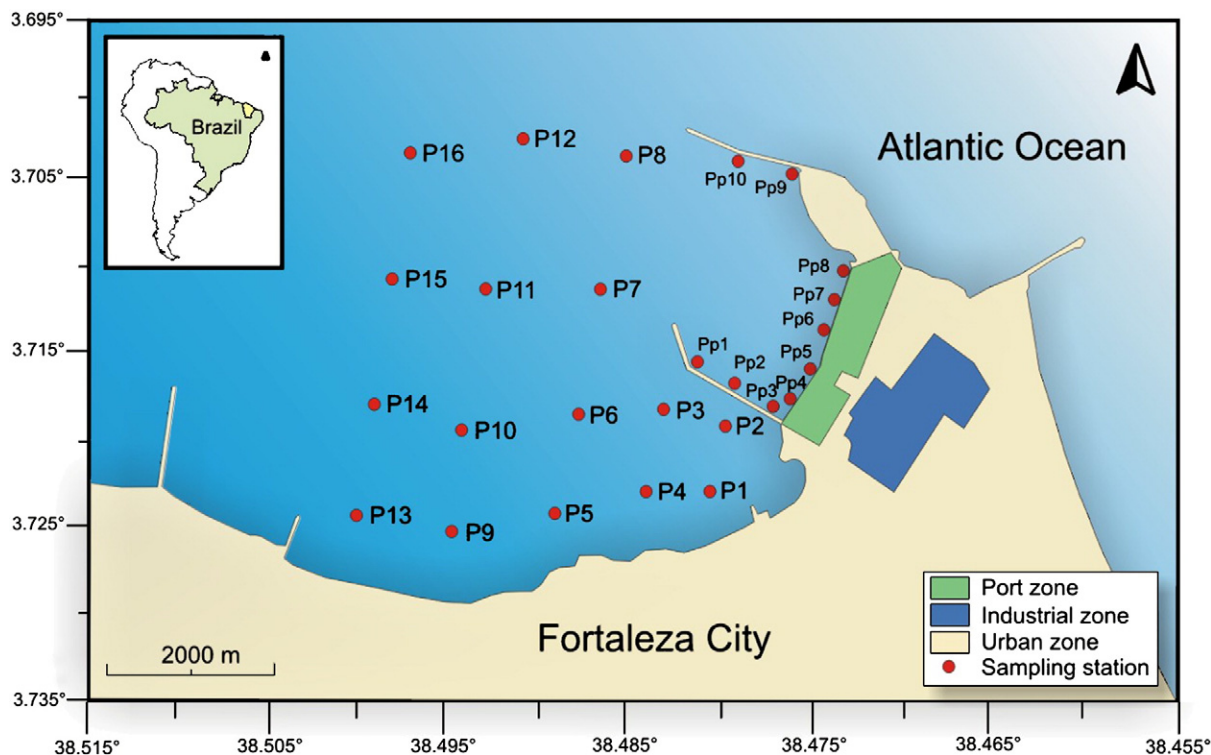


Fig. 1. Water sampling station along the Fortaleza Coast, Ceará state, Northeastern Brazil.

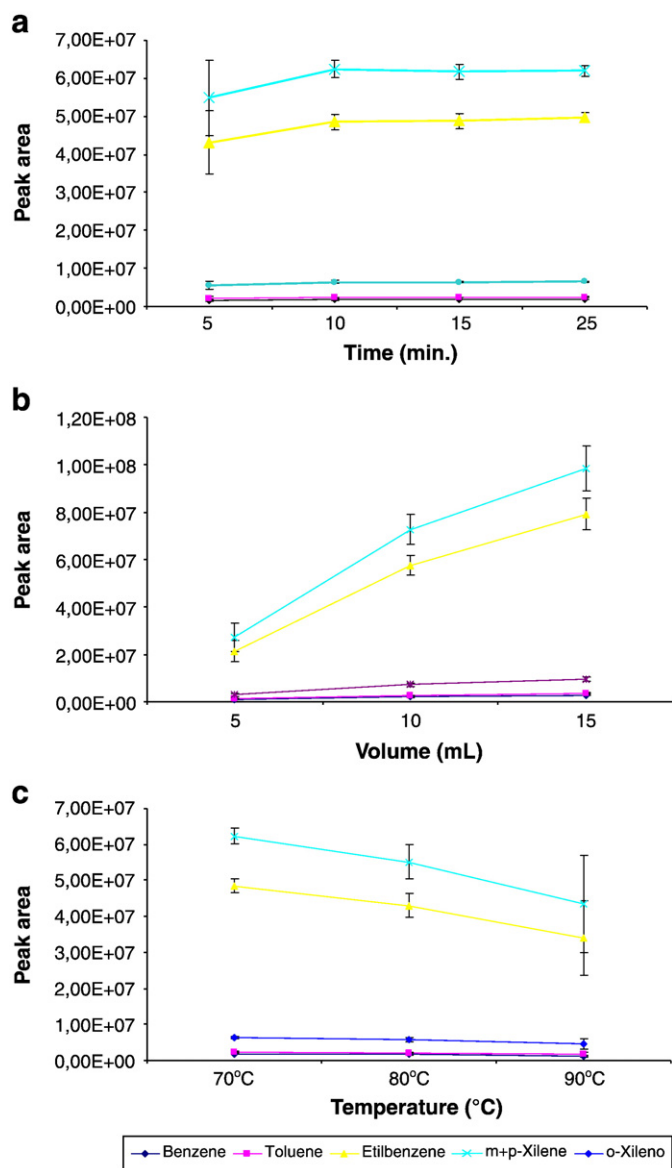


Fig. 2. (a) Sample incubation time; (b) optimum sample volume and (c) optimum incubation oven temperature.

Italy) equipped with two detectors, a photoionization detector (PID) and a flame ionization detector (FID), connected in series. The 54-space autosampler included a robotic arm and a headspace generation unit, which combined an oven to heat and shake the samples, and a 3-mL syringe to transfer the gas into the GC equipment. The optimized operating conditions for the HS autosampler and GC equipment are shown in Table 1.

Samples were injected in the splitless mode for 0.8 min, and chromatographic separation was performed on an OV-624 Ohio Valley (Ohio, USA) capillary column (60 m, 0.32 mm i.d., film thickness 1.8 μm). The initial oven temperature was 40 °C for 2 min and then increased to 140 °C at 40 °C min^{-1} and 140 to 200 °C at 7 °C min^{-1} . Synthetic air and H_2 gas were used for the FID, and N_2 was used as carrier gas and makeup.

3. Experimental

The work was developed in two stages. Firstly, the optimum conditions of the HS technique combined with gas chromatography were determined (HS-GC-FID-PID), and the matrix effect and its elimination, as well as the analytical figures of merit to VOC determinations, were verified. Secondly, the developed protocol was applied to VOC

determinations in water samples from the coastline of Fortaleza for the first time.

3.1. HS-GC-PID-FID validation

A series of experiments was carried out to optimize the partitioning of the VOCs into the headspace of the vials, thus maximizing the sensitivity of the HS-GC-PID-FID technique. For the HS-GC validation, the following conditions were verified: sample incubation time (e.g., 5, 10, 15 and 25 min), sample volume (e.g., 5, 10 and 15 mL) and oven temperature (e.g., 70, 80 and 90 °C).

3.2. Matrix effect verification

To evaluate the influence of the components of the aqueous matrix on the gas chromatographic determination (signal abundance, separation and resolution), a synthetic sample, free of VOCs was prepared. The ultrapure water at different salinities (10, 25 and 36‰) and pHs (6.8, 7.6 and 8.3), was sonicated and heated [17]. Afterwards, the ultrapure water was spiked with VOCs (synthetic sample) and evaluated its response.

To evaluate the growth of microorganisms related to organic substance biodegradation, the growth of colonies was examined [22,23]. Samples from the Coco River and estuary (salinities 8 and 23‰, respectively) and from oceanic water (salinity 32‰) were analyzed. Formaldehyde and acetone (3, 6 and 8%) were added in these aqueous samples as a matrix modifier to evaluate the decrease in microbiological activity.

3.3. Sampling sites and sampling procedure

The sampling sites on the Fortaleza Coast were established in the areas of intense port activity, and sink of urban runoff and refinery wastes. Surface seawater samples were collected during a two-day period in February 2009 at twenty six stations (Fig. 1).

A superficial seawater sample (14.5 mL) for VOC determination was collected from each sampling point directly in the 22 mL glass vials with 0.3 mL formaldehyde (3%) as a matrix modifier and 0.2 mL ethylbenzene-d5 (20 $\mu\text{g L}^{-1}$) as a internal standard (IS), then sealed immediately. Samples from the same site were collected in duplicates. All 15-mL samples were stored at 4 °C in the dark. VOC determinations were accomplished in the laboratory less than 12 h after the sampling.

3.4. Quality control/analytical quality assurance

The following standard operation procedure (SOP) was used to minimize background contamination. All glass devices were cleaned by rinsing with ultrapure water and kept overnight in a muffle furnace at 450 °C to remove organic contaminants. The septa were cleaned for 20 min in an ultrasonic bath filled with deionized water, were rinsed with deionized ultrapure water and dried in an oven at 105 °C. The septa and vials were not reused. To improve accuracy, one blank field sample was analyzed after every five seawater samples. System blanks, free of VOCs,

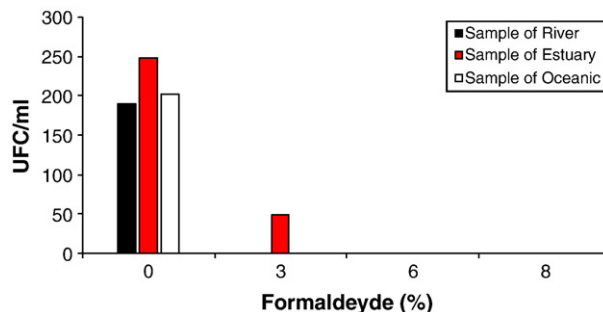


Fig. 3. Reduced microbiologic growth using formaldehyde (3, 6 and 8%).

Table 2

Analytical figures of merit and chromatographic dates of the studied VOCs.

Analytes	Linearity					Repeatability ^a	
	Regression equation	Calibration range ($\mu\text{g L}^{-1}$)	Correlation coefficient (<i>R</i>)	LOD ($\mu\text{g L}^{-1}$)	<i>t_R</i> (min)	Peak area	<i>t_R</i>
Carbon tetrachloride ^b	$y = 0.0013x - 0.002$	0.50–500	0.9991	3.28	5.66	9.83	0.19
Benzene	$y = 0.0388x - 0.0679$	0.50–250	0.9986	0.22	5.77	7.93	0.02
Trichloroethene	$y = 0.0391x - 0.0495$	0.50–250	0.9990	0.27	6.05	7.21	0.02
Toluene	$y = 0.0614x - 0.1272$	0.50–250	0.9987	7.48	6.70	5.62	0.03
Tetrachloroethene	$y = 0.0554x - 0.1242$	0.50–250	0.9983	0.24	7.05	8.20	0.02
Ethylbenzene	$y = 0.0613x - 0.1117$	0.50–250	0.9989	0.33	7.65	8.15	0.08
<i>m/p</i> -Xylene	$y = 0.1418x - 0.2106$	0.50–250	0.9990	0.31	7.73	8.19	0.03
<i>o</i> -Xylene	$y = 0.0536x - 0.0904$	0.50–250	0.9989	0.47	8.07	7.95	0.04

^a RSD of retention time and peak areas ($n = 10$).^b By FID.

were analyzed before every standard of the calibration curve. Blank analytical samples of the gas chromatographic methods were also used to minimize background contamination and to avoid carryover between samples.

4. Results and discussion

4.1. Optimum analytical parameters

4.1.1. Sample incubation time, sample volume and oven temperature in the headspace generation unit

Fig. 2a shows the incubation time for the VOCs studied in the headspace module. The equilibrium between the liquid and gas phases was established in 10 min. The other shorter equilibrium times tested led to lower PID and FID signals. Therefore, a 10-minute incubation time was selected for subsequent experiments.

Sample volume is also a critical parameter in headspace methods. In the literature, several sample volumes (5 to 15 mL) have been reported using headspace techniques [9,15]. Our experiments (Fig. 2b) indicate that 15 mL provides a higher signal; thus, the sample volume of 15 mL was applied during this study.

Oven temperature is an important parameter to sensitivity [9,15]. The increase in temperature reduces solubility of VOCs, favoring the formation of the gaseous phase [24]. The highest signal was obtained at 70 °C (Fig. 2c). A viable and likely explanation is that due to the higher temperatures (80 and 90 °C), the formation of more water vapor occurs into the headspace of the vials (gas phase), decreasing the amount of the analytes of interest. In addition, there is a possibility of accidents with the syringe, once the pressure is increased under higher temperatures [10,15]. Therefore, the temperature of 70 °C was selected.

4.2. Matrix effect verification

According to IUPAC [25], the combined effects of all sample components, other than the analytes of interest, included in measurement quality is denoted the “matrix effect” in analytical chemistry. The matrix effect, which is promoted by salinity changes (effect of ionic strength), pH alteration and by the elimination of microbiological activity (due to the use of matrix modifier), was investigated based on the change in the analytical signal in VOC determinations in aqueous matrix.

The effect of ionic strength is increased by the presence of salt, reducing VOC solubility in water and thereby increasing VOC volatility [25]. In methodologies that use extraction by contact with the sample matrix (e.g., hollow-fiber liquid phase microextraction, HF-LPME), the salt favors the decrease in signal abundance (negative matrix effect) [26]. However, headspace formation methodologies contribute to signal intensity [15,24]. Thus, the addition of salt in one aqueous system that is not saline favors the volatilization and, consequently, the increase in the signal intensity [9]. Menéndez et al. [10], observed

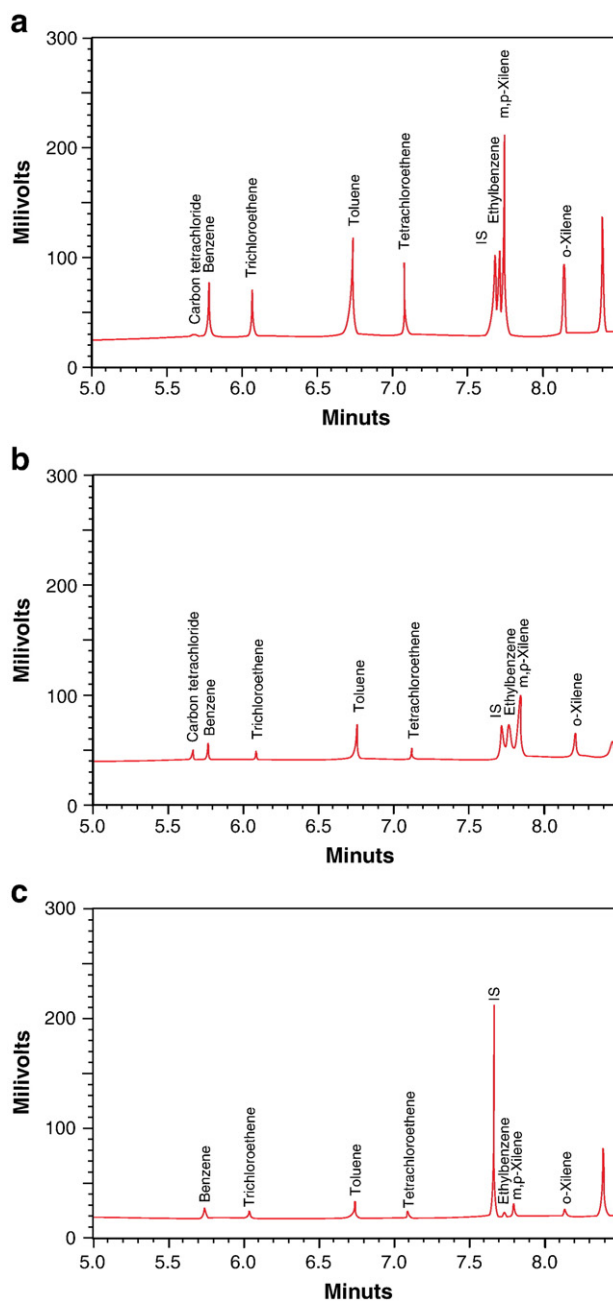


Fig. 4. (a) HS-GC-PID and (b) HS-GC-FID, chromatogram of VOC standard solution containing $5 \mu\text{g L}^{-1}$, (c) HS-GC-PID chromatogram of VOC determination.

Table 3

Analytical figures of merit from others methods.

Techniques and detections	BTEX		VHOC		Sample volume (mL)	REF.
	Linearity	LOD ($\mu\text{g L}^{-1}$)	Linearity	LOD ($\mu\text{g L}^{-1}$)		
P&T-GC-MS		0.00192–0.02205		0.00041–0.00657	60	14
P&T-GC-MS		0.100			5.0	7
P&T-GC-ECD				0.020–0.025	5.0	7
HS-GC-MS		0.050–0.200			8.0	7
HS-GC-MS		0.170–0.260			15	16
HS-GC-MS	0.600–750	0.140–0.200			15	15
HS-GC-FID	10–80	1.0–2.0			11	10
HS-SPME-GC-FID	0.800–2000	80–600			11	10
DAI-GC-ECD				1.0–4.0	0.001	7
HS-SPDE-MS	0.01–500	0.0001–0.0006			10	11
P&T-GC-PID	0.4–1.2	0.0073–0.0132			25	23
HS-GC-PID-FID	0.50–250	0.22–7.48	0.50–500	0.24–3.28	15	This study

Techniques: HS-SPDE (headspace solid-phase dynamic extraction); DAI (direct aqueous injection); P&T (Purge & Trap); SPME (solid-phase micro-extraction).

that the saturation of aqueous samples (leaching of tar residues) with NaCl led to only slightly better benzene determination results, whereas for the other BTEX, no favorable, and sometimes even unfavorable effects, were observed. In this study, the analytical signal of VOC determinations did result in significant changes when salinity and pH varied (*t*-test at a level of 0.005%; Statistical 5 software). Thus, the established analytical protocol can be used for the measurement of samples from riverine, estuarine and oceanic waters, as the VOCs determination is not dependent on salinity and pH changes.

The matrix modifier mainly decreases or eliminates any effect from the studied matrix without altering the natural levels of the analyte of interest. The matrix modifier also aims at improving the recovery rates or signal abundance [20]. According to Dongqiang et al. [23], 75.86 to 85.86% of BTEX are lost by means of biodegradation in seawater, even though many environmental studies do not take this into consideration. Several elements and chemical substances, called matrix modifiers, are thus used to prevent (decrease or eliminate) this effect. Microbial degradation, in wastewater and tap water, is generally prevented by adding HCl (6 N or 50% in water) or HNO_3 to obtain a final pH lower than 2 [16,27]. So, for chlorinated matrix it is recommended the use of a reducing agents (ascorbic acid, sodium thiosulfate and sodium sulfite) [27]. However, some considerations should be taken into account with regards to the use of substances as matrix modifiers of a saline matrix. The addition of sulfur compounds leads to the formation of SO_2 that can interfere with the chromatographic technique [27]. The acid addition to create seawater with a pH of 2 will change the buffering capacity of seawater, consequently altering the sample matrix.

Alternatively, formaldehyde was used as a matrix modifier to decrease microbiological activity. This study showed that 3% formaldehyde was sufficient to eliminate or decrease the microbiological growth in samples of river (salinity 8‰), estuary (salinity 23‰) and seawater (salinity 32‰) (Fig. 3) without interfering with the gas chromatographic method. Acetone was also tested but presented co-elution problems.

4.3. HS-GC-PID-FID validation

The validation of the gas chromatographic method involves a procedure that suggests that the method yields the expected results with adequate consistency, precision and accuracy [3–5,7,14]. Therefore, the measurements of repeatability, sensibility, linearity and detection limits were appraised.

Repeatability applied in the same operational conditions during a short time interval, was expressed as the relative standard deviation (RSD). It is important to assess the repeatability of at least two parameters in the gas chromatographic method: the retention time (confirming the identity of the analyte of interest) and the peak area or height (quantifying the analyte of interest). The repeatability of the

method ranged from 5.62 to 9.63% of the peak area (quantitative analysis) and from 0.02 to 0.19% of the retention time (qualitative analysis), showing satisfactory precision (Table 2). Intra-day repeatability, expressed as RSD, was also evaluated during two consecutive weeks and no significant alteration was observed.

Analytical curves containing carbon tetrachloride, benzene, trichloroethene, toluene, tetrachloroethene, ethylbenzene, *m*-, *p*- and *o*-xylene, at different concentrations (between 0.5 and 500 $\mu\text{g L}^{-1}$), were obtained by plotting the peak area against the analyte concentration for each compound. The compounds *m*-Xylene and *p*-xylene were identified and quantified together as they co-eluted (Fig. 4). The figures of merit of the calibration curves (correlation coefficient ranged from 0.9983 to 0.9993) are summarized in Table 2 and a good linearity of the calibration curves was obtained.

Due to the diversity in the chemical nature of the studied VOCs, PID (sensitive for aromatic molecules) and FID (sensitive for non aromatic hydrocarbons) detectors were used in a series. The choice of detectors was determined by the highest sensitivity by considering the highest slope of the calibration curve of each VOC. Except for carbon tetrachloride, the studied VOCs showed higher sensitivity when detected by PID rather than by FID.

The values for the limit of detection (LOD) were calculated using the formula: $\text{LOD} = 3s_{\text{blank}}/\text{slope}$ of calibration graphs, where s_{blank} is the standard deviation of the ten blank values of the eight linear fits for the individual analyte of interest (Table 2).

The analytical protocol presented satisfactory figures of merit for all of the analytes of interest. The LODs satisfied even the maximum contaminant level (MCL) established for benzene and toluene (1–5 $\mu\text{g L}^{-1}$) in addition to other studied VOCs included in the Drinking Water Standards. The LODs were better than the ones established by environmental legislations from Brazilian, American and European agencies [28,29].

Considerable background contamination was observed for toluene, which increased the LOD in blank samples (Table 2). The presence of this

Table 4

Summary of VOC concentrations observed in the studied area.

	VOCs ($\mu\text{g L}^{-1}$)	
	Range	$\bar{x} \pm s$
C. tetrachloride	Nd–3.95	0.55 \pm 0.88
Benzene	Nd–2.81	0.86 \pm 0.87
Trichloroethene	Nd–4.05	1.08 \pm 1.38
Toluene	Nd–4.07	1.63 \pm 1.49
Tetrachloroethene	Nd–2.13	0.45 \pm 0.50
Ethylbenzene	Nd–6.37	0.74 \pm 1.45
<i>m/p</i> -Xylene	Nd–1.91	0.48 \pm 0.52
<i>o</i> -Xylene	0.18–6.80	1.15 \pm 1.80

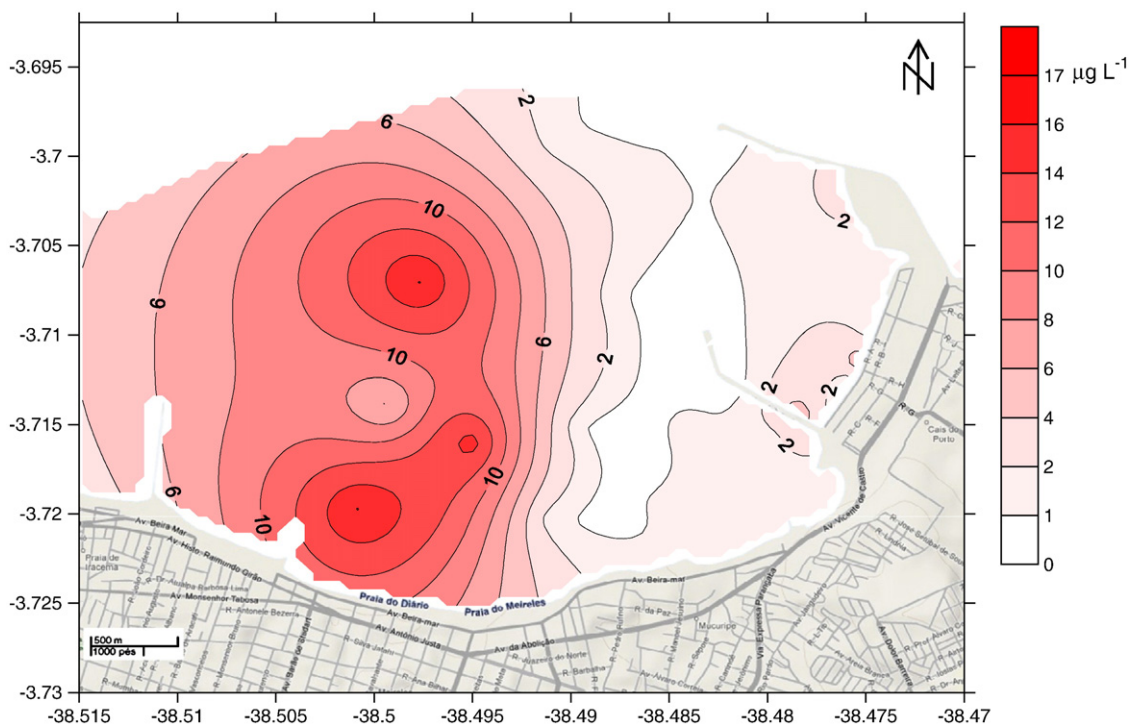


Fig. 5. Spatial VOC distributions concentrations in Fortaleza coastline.

compound and other VOCs in method blanks can be attributed to several effects, namely, carryover, artifact formation or contamination from laboratory air, among others [14,30]. The presence of the benzene in the blanks was attributed to artifact formation from the sorbent material Tenax TA (using P&T) [14]. A sample of the laboratory air revealed the presence of chloroform and dichloromethane. In the case of dichloromethane, the laboratory environment acted as a source of contamination [14]. Trace levels of the halocarbon can be removed only by prolonged purging with purified hot gas [30], although cleaning accessories contaminated with 1,1,1-trichloroethane by drying with a stream of nitrogen and baking at 100 °C overnight was insufficient to eliminate the trace contaminant [13]. The purity of “blank” water (free of the VOCs) used in standard preparations and background verification is also important [30]. The distillation of water with flowing helium produced blank water of sufficient purity to permit the VOC measurement at the ng L^{-1} level [13]. Because of the difficult elimination of the background contamination some cares should be taken during the analytical process and an efficient standard operation procedure (SOP) should be employed to decrease the effect of the background contamination on the global analysis. Only after adoption of an SOP were we able to reduce dichloromethane, chloroform and benzene contamination to background levels. This reflected on the quality of the analysis. Toluene, however, could only be decreased but not totally eliminated; fortunately, it did not significantly influence the quality of the analysis.

The linearity and LOD reported in the VOC measurement in recent papers are summarized in the Table 3. Currently, the interface between sample introduction modules and detection techniques, such as PID, FID, MS and ECD, are contributing to the improvement of the analytical quality of organic compounds. The lowest LOD found in the literature using P&T was achieved by combining GC-MS, GC-ECD and GC-PID (Table 3). However, recently applied automated in-tube sorptive extraction devices, known as headspace solid-phase dynamic extraction (HS-SPDE-MS) [11] and P&T-GC-PID [23], led to the lowest ratio in the LOD and lower sample volume for BTEX determinations found in the literature (Table 3). The LOD found for HS-GC-MS, HS-GC-FID, and HS-

SPME-GC-FID are lower than that of P&T-GC using the same detection technique (Table 3).

Unfortunately, most of the literature focused on the determination of VOCs in drinking water, which is not a very complex matrix. However, the only P&T-GC-MS method, using a volume of 60 mL, allowed the simultaneous determination of halocarbons, monocyclic aromatic hydrocarbons, and chlorinated monocyclic aromatic hydrocarbons (27 VOCs) in seawater at the ng L^{-1} concentration level [14]. As a result, P&T-GC-MS surpassed P&T-GC-ECD, the method considered the main approach to evaluate halogenated volatile organic compounds [3,14] (Table 3).

For the first time, an analytical protocol using HS-GC, interfaced with PID and FID in series, was applied for VOC determinations in seawater. The advantage of two detectors in series is that low sensitivity in one of the detectors is compensated by the other detector. The proposed protocol can also be used to simultaneously determine the main subgroup of VOCs with LOD and the suitable environmental levels. The main advantage of this protocol is the combination of sampling and sample preparation in a single step *in situ*, thus bypassing laboratory work, the use of other materials, as well as the preventing possibility of contamination and sample loss during several steps.

4.4. VOC distributions in the studied area on the Fortaleza Coast

VOCs were measured for the first time on the Fortaleza Coast; their average concentrations are summarized in Table 4. Toluene was the most abundant VOC and ranged from not detected (Nd) to $4.07 \mu\text{g L}^{-1}$ (average $1.63 \mu\text{g L}^{-1}$). Toluene was followed by *o*-xylene (average $1.15 \mu\text{g L}^{-1}$) then trichloroethene (average $1.08 \mu\text{g L}^{-1}$). Carbon tetrachloride, benzene, tetrachloroethene, ethylbenzene, and *m/p*-xylene all had an averaged concentration of 0.46 to $0.86 \mu\text{g L}^{-1}$.

The salinity and water temperature varied from 27.5 to 33.3‰ and from 23.2 to 25.7 °C, respectively; no significant correlations were observed with the VOC distributions.

The VOC levels found in Fortaleza were lower than those reported at industrial zone, e.g., Southampton Water (2.48 – $232.55 \mu\text{g L}^{-1}$) [31,32]; however, the values matched those reported for some European estuaries

(Nd-7.10 $\mu\text{g L}^{-1}$) [32,33] located on the coastline of central southern England. At urbanized coastal environments, such as on this study, the observed levels were comparable to those found in the Irish Sea (1.7–4.3 $\mu\text{g L}^{-1}$) [34] and on the waters of the southern of North Sea (Nd-4.20 $\mu\text{g L}^{-1}$) [2].

The spatial distribution of VOC concentrations based on the kriging model was plotted using Surfer 8 (Golden Software, Inc.) (Fig. 5). Based on the surface distribution of VOC concentrations, port activities were not a main source of VOCs in the studied area. The zone with the largest concentrations (levels > 10.0 $\mu\text{g L}^{-1}$) was in front (onshore), where the release of the urban pluvial water system (urban runoff) occurred. Non-point activities, such as urban runoff, are considered the main sources of organic pollutants in urban zones [35–37] and in Fortaleza [36]. According to Schwarzenbach et al. [37], the washout of the streets in urban centers promoted by rains (urban runoff) efficiently carries residues of the main energy source (e.g., petroleum) used to the aquatic environment, and is responsible for 4–10% of the load of organic pollutant to the oceans [38]. Data from partitioning VOCs between air and water suggest that urban land surfaces are the primary non-point source, while urban air is the secondary source for most VOCs in the USA. VOCs commonly detected in urban waters across the USA include gasoline-related compounds (e.g., toluene and xylenes) and chlorinated compounds (e.g., chloroform, tetrachloroethane and trichloroethene) [35], which are the more abundant VOCs focused on in this study.

5. Conclusions

An analytical protocol developed using HS-GC interfaced with PID and FID detectors was applied for the first time with success in VOC determination in seawater. The main advantage of the protocol is the two-step determination that greatly decreased the risk of contamination or sample loss that often occurs in well-known processes such as biodegradation and volatilization. This protocol is also applicable to the main environmental aqueous matrix. The sampling is fast and does not require expensive materials or extensive laboratory work. The analytical protocol presented better figures of merit than other reported methods. The LOD was suitable for environmental analysis and complied with the Drinking Water Standards legislations established by Brazilian, American and European agencies.

The results of the VOC distribution showed that port activity was not the main source along the Fortaleza Coast. The contribution from urban runoff seemed more significant. Our results should stimulate further research that could possibly include other factors such as marine currents dynamics, atmospheric deposition, seasonal variation and font characterization.

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