



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

Rivelino M. Cavalcante*, Márcia V.F. de Andrade, Rozane V. Marins, Lincoln D.M. Oliveira

Laboratório de Biogeoquímica Costeira-LBC-Sector de Análise Orgânica, Instituto de Ciências do Mar-LABOMAR-Universidade Federal do Ceará-UFC, Av. Abolição, 3207-Meireles, CEP: 60165-081-Fortaleza-CE, Brazil

ARTICLE INFO

Article history:

Received 24 March 2010

Received in revised form 27 May 2010

Accepted 27 May 2010

Available online 2 June 2010

Keyword:

Headspace

Matrix effect

Analytical protocol

Marine pollution

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.

© 2010 Elsevier B.V. All rights reserved.

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%)

* Corresponding author. Instituto de Ciências do Mar (LABOMAR), Universidade Federal do Ceará, Av. Abolição 3207-CEP 60165-081, Fortaleza, CE, Brazil. Tel.: +55 85 3366 7035; fax: +55 85 3366 7001.

E-mail address: rivelino@labomar.ufc.br (R.M. Cavalcante).

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,

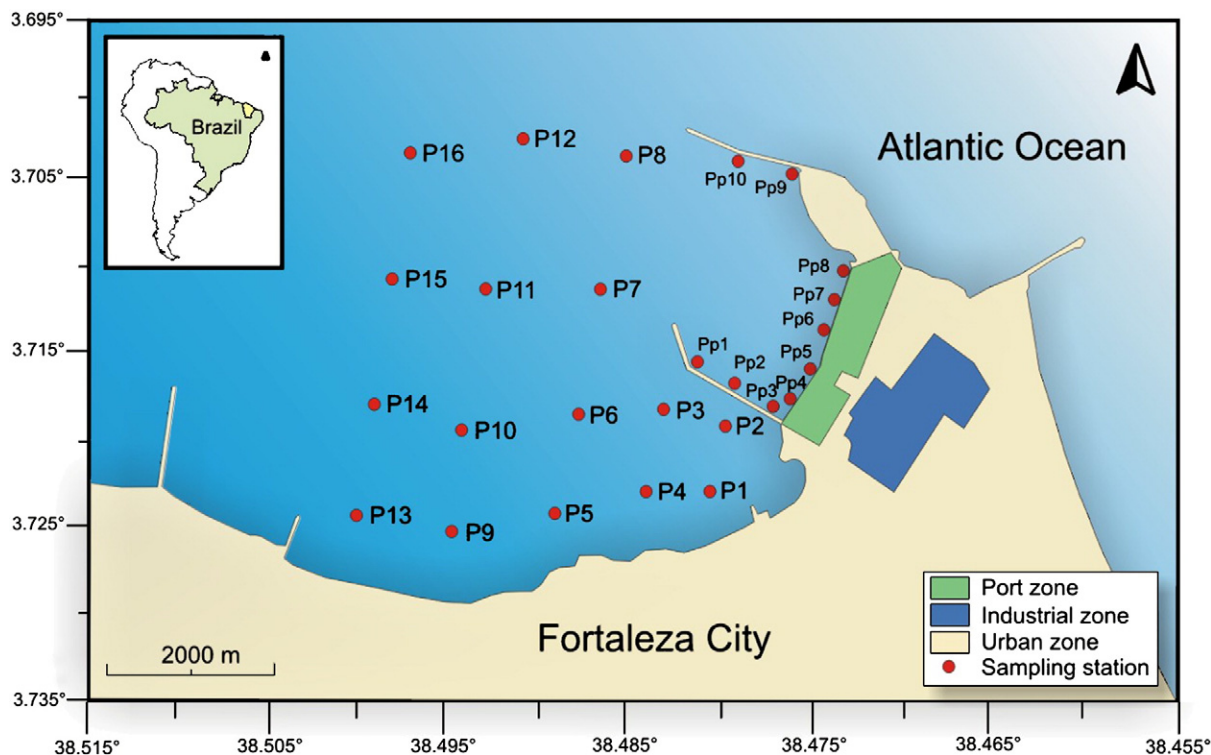


Fig. 1. Water sampling station along the Fortaleza Coast, Ceará state, Northeastern Brazil.

Download English Version:

<https://daneshyari.com/en/article/1227933>

Download Persian Version:

<https://daneshyari.com/article/1227933>

[Daneshyari.com](https://daneshyari.com)