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ZnO-coated glass fibers for the analysis of trihalomethanes by headspace-solid phase microextraction-gas chromatography

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ABSTRACT

Li_2O–ZrO_2–BaO–SiO_2 glass fibers were produced and their surfaces were coated with zinc oxide. The fibers' surface morphology was examined by scanning electron microscopy and the zinc oxide layer was characterized by mapping the K_α and L_α lines of zinc by energy dispersive X-ray spectroscopy. The results indicated that a homogeneous and porous layer of ZnO was formed on the fibers' surface. This layer was subjected to a simultaneous determination of trihalomethanes using headspace-solid phase microextraction-gas chromatography. The study was conducted after evaluating the ideal time of incubation (15 min), extraction (15 min) and desorption (10 min), as well as the effect of the addition of salt (15%, m/v) on the analytical response. A good linear dynamic range was observed individually for trihalomethanes aqueous solutions containing 20 $\mu g\,L^{-1}$ and 500 $\mu g\,L^{-1}$ of trichloromethane, 15 $\mu g\,L^{-1}$ and 250 $\mu g\,L^{-1}$ of dichlorobromomethane and dibromochloromethane and 10 $\mu g\,L^{-1}$ and 100 $\mu g\,L^{-1}$ of tribromomethane, with all the compounds showing correlation coefficients higher than 0.9900.

1. Introduction

The use of chlorine as a disinfecting agent of water for human consumption is known to offer some advantages such as low cost and high efficiency, and that residual chlorine prevents the proliferation of potentially pathogenic microorganisms [1]. However, the use of this product may result in the formation of harmful substances such as halogenated organic compounds, including trihalomethanes (THMs) [2,3]. These compounds, which are formed by the reaction between chlorine and the fluvic or humic acids of decomposition products, are potentially carcinogenic [4]. Among all possible trihalomethanes, the ones most commonly present in water treatment plants are trichloromethane, dichlorobromomethane, chlorodibromomethane and tribromomethane [5]. The methods used to quantify trihalomethanes in water are either liquid–liquid extraction or the purge-and-trap technique, followed by quantification by gas chromatography, sometimes allied to mass spectrometry [6]. In addition to these techniques, solid-phase microextraction combined with gas chromatography has proved to be an efficient procedure to quantify these analytes [7–14]. All these procedures involve the use of fused silica fibers coated with an adsorbent in films of variable thickness. Some of these absorbents are carboxen/polydimethylsiloxane [7–13], divinylbenzene/carboxen/polydimethylsiloxane [7,9], polydimethylsiloxane [9,11–14], polyacrylate [9] and polydimethylsiloxane/divinylbenzene [7]. Such fibers have been used since pioneering efforts in implementing the SPME [15] technique achieved satisfactory performance. However, the use of these fibers is restricted to and dependent on the thermal stability of adsorbent polymers. The development of inorganic coating with higher chemical and thermal stability has been proposed as an alternative to the traditional coatings. In this context, glass fiber coating with Nb_2O_5, and later, its use in alcohol, determined by SPME/GC [16,17], as well as anodized aluminum [18] and zinc [19] wires, have been reported to produce potentially adsorbent surfaces for use in solid-phase microextraction.

Several recent papers have reported the use of ZnO-based devices for adsorbent to solid phase microextraction. ZnO nanorods [20] and nanotubes [21] were deposited onto fused silica fiber surfaces and both proved useful for BTEX analysis. Another reported application is ZnO/poly(methyl methacrylate) nanobead composite, which proved to be useful for protein analysis by mass spectrometry allied to matrix-assisted laser desorption/ionization [22]. All these applications begin with molecular adsorption on the oxide surface [23]. Based on these studies, this study seeks to explore the adsorbent properties of zinc oxide, creating a device for the determination of trihalomethanes in water by HS-SPME-GC, by deposition of zinc oxide on Li_2O–ZrO_2–BaO–SiO_2 glass fibers.

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2. Experimental

2.1. Chemicals

$Li_2O–BaO–ZrO_2–SiO_2$ glass fibers were produced as described previously [16,24]. To form ZnO on the fiber surface, $(CH_3COO)_2·2H_2O$ (from Ecibra) was dissolved in an optimal concentration of diethylene glycol [25].

The chromatographic assays were performed using the following certified standards: trichloromethane (TCM) 99.9% HPLC grade, purchased from Tedia ($1.47\,g\,mL^{-1}$), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and tribromomethane (TBM), all 95% $5000\,\mu g\,mL^{-1}$, from Ultra Scientific, and dichloromethane (used as I.S.) 99.95%, purchased from Carlo Erba. Working standards were prepared by serial dilution with final concentrations in the range of $10–500\,\mu g\,L^{-1}$, included with the $500\,\mu g\,L^{-1}$ of internal standard. Dilutions were prepared with methanol, HPLC grade (Aldrich), and ultra-pure water.

2.2. Instrumentation

The chromatographic analysis was performed with a Varian 3900 gas chromatograph equipped with a flame ionization detector and a CombiPAL headspace system. The analytical column was RTX-624, 6% cyanopropylphenyl–94% dimethylpolysiloxane (30 m × 0.53 mm, 0.30 μF film thickness), from RESTEK. The carrier gas was ultra-pure helium applied at 2 mL/min constant flow. The injector temperature was 280 °C, operating in splitless mode, and the detector temperature was 280 °C. The initial oven temperature was set at 40 °C, ramped up at 10 °C/min to 130 °C and held there for 7 min, then ramped up at 10 °C/min to 200 °C and held for 10 min.

2.3. HS-SPME procedure

The actual length of the SPME fiber in the extraction and in the injection procedures was controlled at 0.5 cm. The samples were conditioned in a sealed vial at 60 °C for 60 min and the ZnO-coated glass fiber was left in contact with the headspace of the samples for 15 min. The fiber was immediately retracted back into the needle and transferred to the injection port of the gas chromatograph. Desorption time was 10 min.

Quantification of the THMs in aqueous media, from 10 to $500\,\mu g\,L^{-1}$ ($n = 5$), was based on the peak area ratios (analyte/internal standard) plotted as a function of THM concentration. Each standard was analyzed in triplicate.

2.4. SEM images

The morphology of the fiber surface was examined by scanning electron microscopy, before metallization with gold in a SCD 050 Bal-Tec coater, using an EVO 050 Zeiss microscope equipped with an EDX IXRF 500 Digital Processing system.

3. Results and discussion

The glass fibers used in this work are well known since they have been used in previous studies [16,17,24]. The advantage of these glass fibers is their relatively low melting temperature (about 1000 °C). The initial glassy surface (see Fig. 1A) was covered with ZnO by repeatedly immersing the fiber in a zinc acetate solution using diethylene glycol as solvent, followed by heating. The ZnO layer was prepared by MOD applying the dip-coating method combined with the Pechini polymeric precursor method. The presence of ZnO on the fiber is confirmed by the SEM micrograph in Fig. 1B, showing the initial smooth glassy surface coated with a porous layer. This was also confirmed by the EDS spectrum of the modified fiber, Fig. 2, in which the peaks at 1.05 keV and 8.89 keV are assigned to the zinc L_α and K_α lines, respectively.

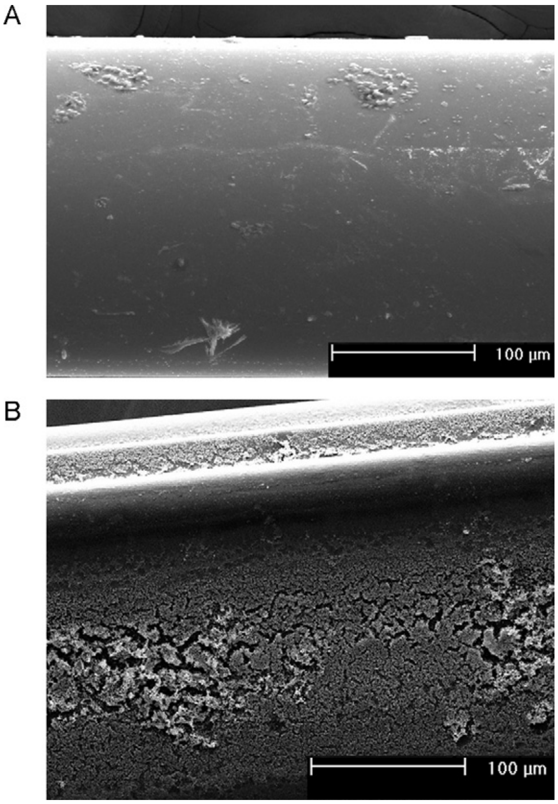

Fig. 1. Secondary electron micrographs of: (A) glass fiber surface, and (B) surface coated with a ZnO layer.

The other peaks are due to gold (used as conducting material): lines M_α at 2.15 keV and L_α at 9.74 keV; silicon (from the glass composition): line K_α at 1.75 keV; barium (from the glass composition): lines L_α at 4.48 keV and L_β at 4.86 keV, and oxygen with K_α at 0.45 keV. The peak at 6.41 keV is due to iron in the specimen stub.

3.1. Chromatographic analysis

A typical chromatogram recorded in our studies is displayed in Fig. 3. The first eluted compound is the solvent methanol, followed by dichloromethane, the internal standard. The THMs were eluted in the following sequence: trichloromethane (reten-

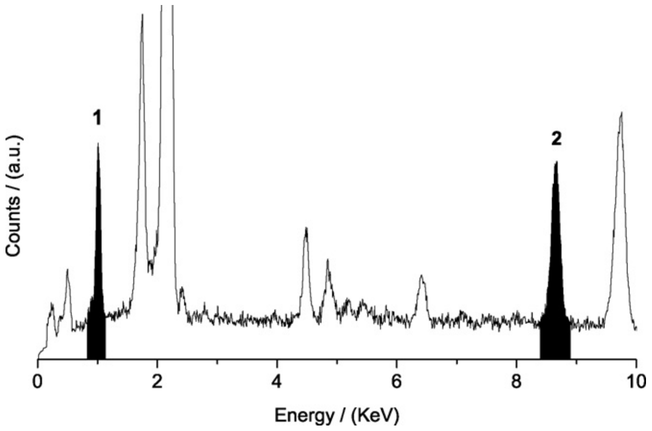

Fig. 2. EDS spectrum of the zinc oxide-coated glass fiber.

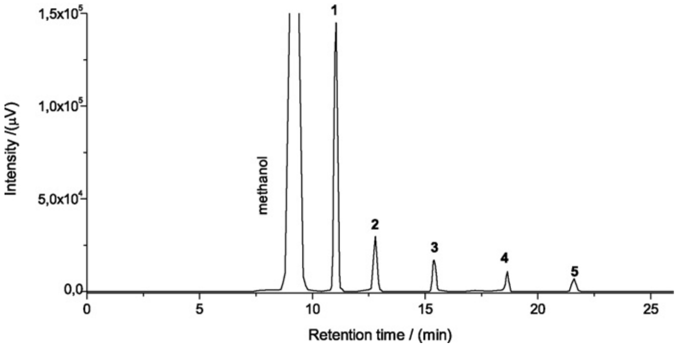

Fig. 3. HS-SPME-GC chromatogram of a THM solution in methanol using ZnO-coated glass fiber with as SPME support. Order of elution: 1 – dichloromethane (I.S.), 2 – trichloromethane, 3 – dichlorobromomethane, 4 – dibromochloromethane, and 5 – tribromomethane.

tion time (r.t.) of 12.8 min), dichlorobromomethane (r.t. 15.4 min), dibromochloromethane (r.t. 18.6 min) and tribromomethane (r.t. 21.6 min). This is in accordance with the molar masses of the compounds, as expected when using this chromatographic column.

The following factors were studied to optimize the procedure: incubation, extraction and desorption times, and the effect of added salt. In all these studies, a mixture of THMs with an individual concentration of 200 μg L^{-1} dissolved in methanol was used and the temperature of extraction in the headspace was 60 °C, with magnetic stirring at 300 rpm.

In the evaluation of the incubation time based on the chromatographic response, no significant variations were observed between 15 and 60 min. This evaluation was performed after holding the THMs solution in sealed vials at 60 °C for 15, 30, 45 and 60 min, followed by placing fiber in contact with the headspace for 15 min. Thereafter, an incubation time of 15 min was adopted for the other determinations.

Equilibrium in the partition between the active sites on the fiber surface and the analytes was reached after 15 min of contact, as illustrated in Fig. 4. The compounds were extracted according to their respective individual vapor pressures [26]. The most extracted compound was TCM, followed by DCBM, DBCM and TBM. The apparent decrease in the extraction rate of DBCM and DCBM after 20 min was probably due to competition between the solvent and other analytes for the adsorption sites.

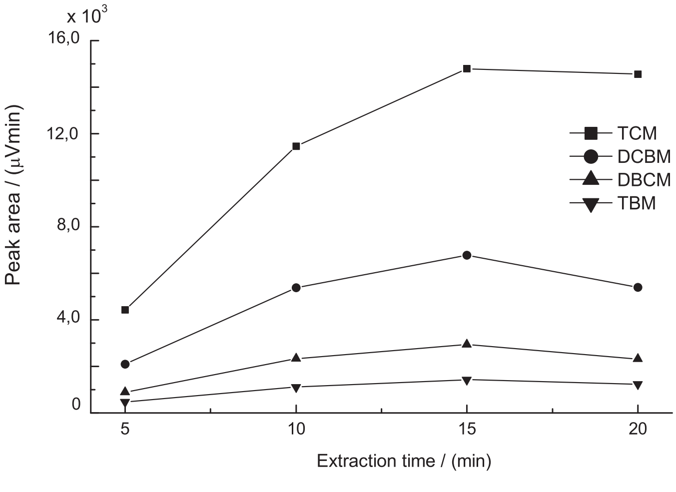

Fig. 4. Extraction time profile at 60 °C of the THMs (200 μg L^{-1}) using zinc oxide-coated glass fiber. Desorption time of 10 min at 280 °C.

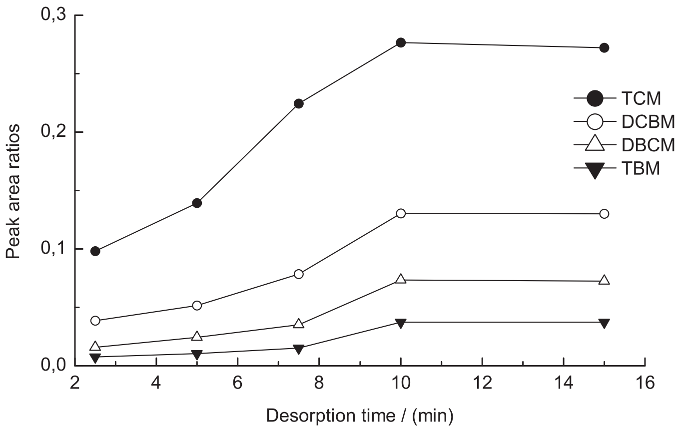

Fig. 5. Effect of time from 2.5 to 15 min at 280 °C on the desorption rate. Extraction time of 15 min at 60 °C. THMs 200 μg L^{-1}.

The peak area of trichloromethane was broader than that of the other THMs. The peak areas of DCBM, DBCM and TBM decreased the extent to which chlorine was replaced by bromine. This was not due solely to the different molar concentrations (the individual concentration was 200 μg L^{-1}) and the composition of the gas mixture in the headspace, but can also be attributed to the particularities of the photoionization detector (PID). It is known that the presence of a heteroatom bonded to aliphatic compounds causes suppression of the PID signal [27]. This suppression is greater the larger the atomic mass of the heteroatom [28]. Therefore, the peak area of $CHCl_3$ is expected to be broader than that of $CHBrCl_2$, and so on. Therefore, the higher peak area of chloroform does not imply greater affinity to ZnO-coated fiber.

Fig. 5 shows the results of the determination of ideal desorption time at 280 °C after 15 min in THMs headspace contact. The analytes were desorbed completely between 7.5 and 10 min. An analysis of the analyte extraction at each tested time interval reveals that tribromomethane requires more time to be desorbed, indicating greater affinity with the fiber surface. This behavior was the opposite of that observed in the study of the ideal extraction time. Therefore, the greater extraction of trichloromethane was probably due mostly to the composition of the headspace.

ZnO deposition on quartz surfaces by the Pechini method, as we did with glass fibers, has shown that zinc oxide crystallizes like wurtzite in response to annealing above 500 °C [29]. In our studies, the heat treatment of the ZnO layer and the chromatographic analysis were performed at lower temperatures (up to 380 °C), which prevented crystallization of the oxide, indicating that the zinc oxide on the glass fiber surface was amorphous.

The presence of salts may interfere in the response of HS-SPME-GC, since the properties of the solution may change [30]. To ascertain the extent of this interference, we added NaCl to the THMs solution to obtain concentrations (m/v) of 5%, 10%, 15% and 20%. The results are shown in Fig. 6. First, we noted a reduction of the response at 5% of NaCl, followed by an intensification of the peaks at other salt concentrations. The best results were achieved after the addition of 15% of NaCl.

3.2. *Chromatographic determination of THMs in aqueous solution*

To verify the applicability of ZnO-coated glass fiber for the determination of THMs in aqueous media by HS-SPME-GC, the optimized parameters obtained for alcoholic solutions were used to determine the concentration of these analytes individually in standard aqueous solutions. The calibration curves obtained for all the THMs showed good linearity, with a correlation coefficient (r^2) exceeding 0.99. Table 1 lists the correlation coefficients obtained for each compound, as well as the detection and quantification limits and the reproducibility using a single fiber. The percent relative stan-

Table 1
Linear dynamic ranges and coefficients to the standard aqueous solutions of THMs using glass fiber coated with zinc oxide in HS-SPME-CG.

THM	Concentration range (μg L^{-1})	Correlation coefficient (r^2)	Detection limit (μg L^{-1})	Quantification limit (μg L^{-1})	%RSD ($n = 3$)
TCM	20–500	0.9987	5	10	4.1
DCBM	15–250	0.9994	2	5	2.3
DBCM	15–250	0.9994	2	5	3.0
TBM	10–200	0.9983	1	2	2.7

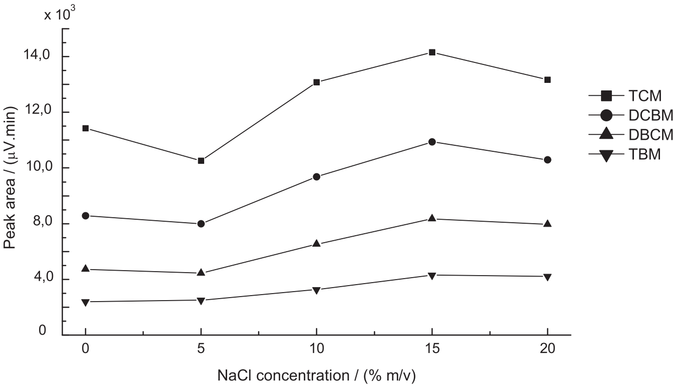

Fig. 6. Effect of the addition of salt (NaCl) at 60 °C. Incubation and extraction time of 15 min. Desorption time of 10 min.

dard deviation (%RSD) was calculated batch to batch. The limits of detection and of quantification obtained for the fiber used here are similar to those found in the analysis of trihalomethanes using conventional fibers [7,11,14].

Only one fiber was used in all these studies. Although we did not check its reusability, these studies and the linearity of the results indicate that ZnO-coated glass fibers are potentially applicable for the development of an analytical method for the determination of trihalomethanes.

4. Conclusion

A device for HS-SPME-GC analyses was constructed with Li_2O–ZrO_2–BaO–SiO_2 glass fiber coated with ZnO. Chromatographic studies using this device with trihalomethane solutions indicated that the optimal extraction time was 15 min and desorption time was 10 min. The addition of 15% NaCl (w/v) contributed to improve the chromatographic response. The quantitative determination of trichloromethane, dichlorobromomethane, dibromochloromethane and tribromomethane showed good linearity ranging from 10 μg L^{-1} to 500 μg L^{-1} in the THMs aqueous solutions.

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