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Talanta 66 (2005) 74–79
Talanta
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Niobium(V) oxide coated on thin glass–ceramic rod as a solid phase microextraction fiber

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Received 19 July 2004; received in revised form 15 September 2004; accepted 23 September 2004
Available online 8 December 2004

Abstract

The efficiency of niobium(V) oxide as a sorbent phase for solid phase microextraction (SPME) was investigated. The thin glass–ceramic rod was coated with niobium(V) oxide using chemical vapor deposition and Nb_2O_5 as a chemical precursor. Optimum conditions for the preparation and conditioning of the fibers are presented. The fibers were used for the extraction of a mixture of alcohols and a mixture of phenols from the headspace samples. The results obtained proved the suitability of niobium(V) oxide as a new SPME fiber. The calibration graphs for alcohols and phenols in a concentration range of 50–1000 $\mu g\,l^{-1}$ were linear ($r > 0.995$) and the detection limits were below 0.8 $\mu g\,l^{-1}$ level. The repeatability for one fiber ($n = 6$) under similar conditions was between 3 and 10.4%. The fiber-to-fiber reproducibility ($n = 6$) was between 5 and 15%.

Keywords: Gas chromatography; Solid phase microextraction; Niobium(V) oxide coating; Alcohol; Phenol

1. Introduction

Solid phase microextraction (SPME) has been used for the extraction of a wide variety of volatile and semi-volatile organic compounds from environmental [1,2], biological [3,4] and food samples [5,6]. This technique has become attractive not only because of its high extraction efficiency and its not requiring solvents in the extraction step but also because of its easy coupling with gas chromatography and high performance liquid chromatography.

The result of an extraction using SPME depends on the chemical and physical characteristics of fibers such as the nature of the matrix, porosity and surface area. In the last few years, researches have been concentrated on the fiber preparation to improve the extraction performance aiming for low cost, durability, sensitivity, and a vast range of applications [7].

The sol–gel technology has been widely used to prepare SPME fibers because it can effectively create chemically bonded, porous, and highly crossed coating on the fused-silica fiber surface [8]. The sol–gel technology was used to prepare coatings of terminated PDMS [9–11], crown ether [12,13], *n*-octyltriethoxysilane [14], calyx[4]arene [15,16], fullerene [8], polyethyleneglycol [17], and low-temperature glassy carbon [18,19] for SPME fibers.

Recently, electrochemical polymerization procedures have been used to prepare SPME fibers using conductive polymers such as polypyrrole [20,21] and polyaniline [7,22]. In these cases, films of these materials were prepared on the surface of metal (Pt, Au, Ag or stainless steel) wires.

On the other hand, for inorganic coatings few studies of extraction properties have been described in the literature. The efficiency of anodized aluminum wire [23] and anodized zinc

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0039-9140/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2004.09.028

wire [24] as new fibers for SPME has been investigated. The results obtained demonstrated the suitability of these materials as new fibers for extraction and sampling of some organic compounds from gaseous and aqueous samples. The extraction behavior was attributed to the porous layer of aluminum oxide and zinc oxide formed on the aluminum and zinc surface, respectively. $CuCl_2$ microcrystal layer [25] and CuS layer [26] were obtained from the modification of copper wire and seem very effective for the extraction of volatile amines and aliphatic alcohols from aqueous and gaseous samples.

The purpose of this work is to assess the feasibility of using a new fiber consisting of a thin glass–ceramic rod coated with niobium(V) oxide as sorbent material of SPME for the determination of organic compounds in gaseous samples. This study should ensure a long life and desirable repeatability of the new fiber. The efficiency of niobium fibers in the extraction of some alcohols and phenols was studied.

2. Experimental

2.1. Reagents

Methanol, ethanol and 1-butanol were obtained from Aldrich Chemical PA. The stock solution was prepared mixing adequate volumes of methanol, ethanol and 1-butanol in a 10 ml vial, and 1.00 μl of this stock solution was introduced to a 10 ml vial to prepare a sample containing 420, 340 and 120 $\mu g\,l^{-1}$ of methanol, ethanol and 1-butanol, respectively. Phenol and 2,4-dimethylphenol were obtained from Vetec and Fluka, respectively. A stock solution of these phenols was prepared in similar way in that the alcohol mixture and the work solution were prepared dissolving appropriate volumes of the stock solution in 10 ml vials to a final concentration of 60 $\mu g\,l^{-1}$ of each compound. Others chemicals used for selectivity studies were obtained from Supelco.

For the preparation of the fibers, Li_2CO_3 (Vetec PA), $ZrOCl_2{\cdot}8H_2O$ (Vetec 98% PA), $Ba(CH_3CO_2)_2$, Nb_2Cl_5 and SiO_2 (Aldrich Chemical PA) were employed.

2.2. Apparatus

The gas chromatographic investigations were carried out using a Shimadzu 14 B gas chromatograph equipped with a flame ionization detector (FID) and a split–splitless injector. A CBP-20 fused silica capillary column of 25 m × 0.25 mm i.d. and a phase thickness of 0.22 μm obtained from Shimadzu, was used for GC separations of the alcohol mixture and phenol mixture, respectively. The temperature program used for the analyses was as follows: the initial temperature of 40 °C was held for 6 min and then increased to 150 °C at 10 °C min^{-1}. This temperature was held for 3 min. Then the temperature was increased to 250 °C at 20 °C min^{-1} and held for 2 min. The injector and detector temperatures were 280 and 300 °C, respectively. The samples were injected in the splitless mode.

Surface characteristic studies of the prepared niobium(V) oxide fibers were performed by scanning electron microscopy using a Philips XL model equipped with an energy dispersive microprobe. The identification of niobium on the glass–ceramic rod was made by a superficial mapping program, Color Map.

An electric furnace EDG-1800 model was used to prepare the thin glass–ceramic rod. The Nb_2O_5 fibers were adapted to the commercial SPME fiber holder obtained from Supelco (Bellefonte, PA, USA).

2.3. Preparation of the fibers

Fiber base. The niobium oxide sorbent coating was deposed over thin glass–ceramic rods (∼100 μm o.d.) prepared by melting appropriate amounts of Li_2CO_3, $ZrOCl_2{\cdot}8H_2O$, $Ba(CH_3CO_2)_2$ and SiO_2 for 3 h at 1100 °C. The final material has the following approximated composition: 29% Li_2O, 1% ZrO_2, 5% BaO, and 65% SiO_2. The molten mass was drawn to form the uncoated base ceramic fibers using a homemade device (Fig. 1). A total mass of 20 g was enough to produce ∼60 cm of raw glass–ceramic fibers (good for ca. 12 coated fibers)

Coating process. The glass–ceramic fibers were coated using chemical vapor deposition. The fibers (4 cm length) were exposed for 3 h to Nb_2Cl_5 vapors coming from this reagent heated at 140 °C (sublimation temperature) in a proper device under sub-atmosphere pressure. Fibers using different preliminary surface preparation and post-coating conditioning were produced. As for the surface preparation, prior to chemical vapor deposition, both raw glass–ceramic fibers and fibers previously conditioned at 300 °C for 3 h were used. Also, two different approaches were adopted for the post-coating conditioning. The first approach involved immersion of the coated fibers in water for 24 h for hydrolysis of the Nb-based coating, followed by heating in a GC injector at 300 °C for 2 h. In the other procedure, only thermal conditioning in the GC injector was used. Before thermal conditioning, the fibers were fitted in discarded commercial SPME fiber assemblies, where the

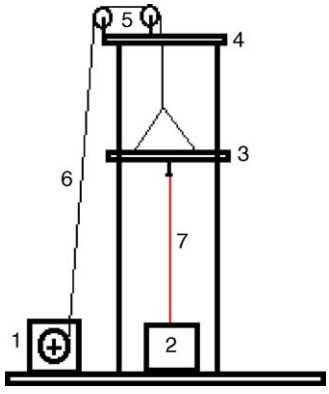


Fig. 1. Design of the fiber maker: (1) peristaltic pump, (2) furnace, (3) platform that allows movement, (4) fixed platform, (5) pulley system, (6) steel cable and (7) point of the steel that makes contact with the melted glass mass.

original (worn) fiber was removed by dipping in 3% HF in an ultrasonic bath for 30 s. The performance of the different Nb_2O_5 fibers was tested for extraction of alcohol or phenol solutions.

2.4. Analytical procedure

A 1.0 μl aliquot of the stock solution of the alcohol mixture was introduced to a 10 ml sealed glass vial. After homogenizing the vial atmosphere (keeping in room temperature for 30 min), the needle of the SPME device was passed through the septum of the vial, containing the analytes. The fiber was exposed to the headspace mixture for 35 min at room temperature. The fiber was retracted into the needle that was removed from the vial and immediately inserted into the GC injection port. The analytes were then analyzed by gas chromatography. In this work was not studied the effect of the temperature and salting-out on the extraction process.

The same procedure was adopted to extract phenols by the Nb_2O_5 fiber. The extraction time was 15 min.

3. Results and discussion

3.1. Optimum fiber preparation

In these studies the six types of Nb_2O_5 fibers, as described in Section 2, were prepared and used for extraction of some alcohols. The efficiency of these fibers for the alcohol extraction from the headspace is shown in Fig. 2. It should be mentioned that preliminary experiments determined that uncoated glass–ceramic fibers have discarded affinity towards the tested analytes; therefore, the following results can only be attributed to sorption by the Nb_2O_5 coating. Fig. 2 compares the extraction efficiency of coated fibers according to the different procedures above described for the extraction of aliphatic alcohols from the gaseous sample. The extraction efficiency of all studied alcohols on the fiber type 2B (thermal treatment, hydrolyze and thermal conditioning) was higher than the other types of fibers, especially for ethanol and 1-butanol. These results indicated the procedure used to obtain fiber 2B produced a thickness and porosity of the oxide layer higher than the other procedures. The surface physical characteristics of fiber type 2B were studied by SEM. Fig. 3 shows that a considerable amount of Nb_2O_5 was formed on the surface of the modified glass. In this figure the presence of Nb_2O_5 on the glass–ceramic rod surface can also be observed through Color Map study. The white sites on the glass–ceramic surface correspond for niobium.

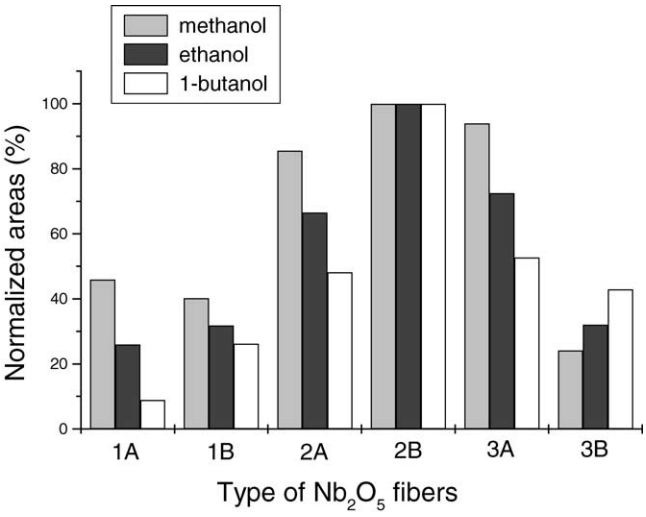
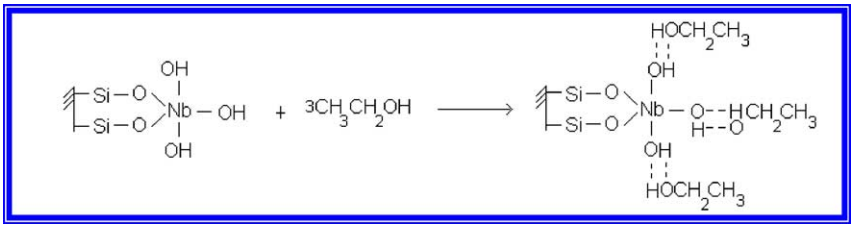


Fig. 2. Comparison of fiber selectivity for various alcohols. Experimental conditions: sample volume 10 ml; concentration 420, 340 and 120 $\mu g\,l^{-1}$ of methanol, ethanol and 1-butanol, respectively; extraction time 35 min, extraction at room temperature, desorption time 5 min, desorption temperature 250 °C.

3.2. Fiber selectivity

Because of the high capacity of the ionic exchange presented by the Nb_2O_5 fiber a great selectivity of this type of fiber was expected in the presence of polar compounds. Eq. (1) illustrates probable interaction between Nb_2O_5 fiber and polar compounds.



Alcohols and phenols were chosen, such as, polar compounds in this study. Toluene was used to test the adsorbent characteristic of the Nb_2O_5 coating. The results indicated that Nb_2O_5 fiber presents a universal adsorbent characteristic and, therefore, it presents the capacity to adsorb a wide range of the compounds.

3.3. Optimization of extraction time

The equilibrium time among the Nb_2O_5 fiber and the analytes was studied and it was defined as the time after which the amount of extracted analyte remains constant. The extraction time was obtained after making extractions of alcohols and phenols from headspace samples in the time range from 5 to 60 min. The exposure time profiles are illustrated in Fig. 4, and the time extraction chosen was 35 min for alcohols and 15 min for phenols.

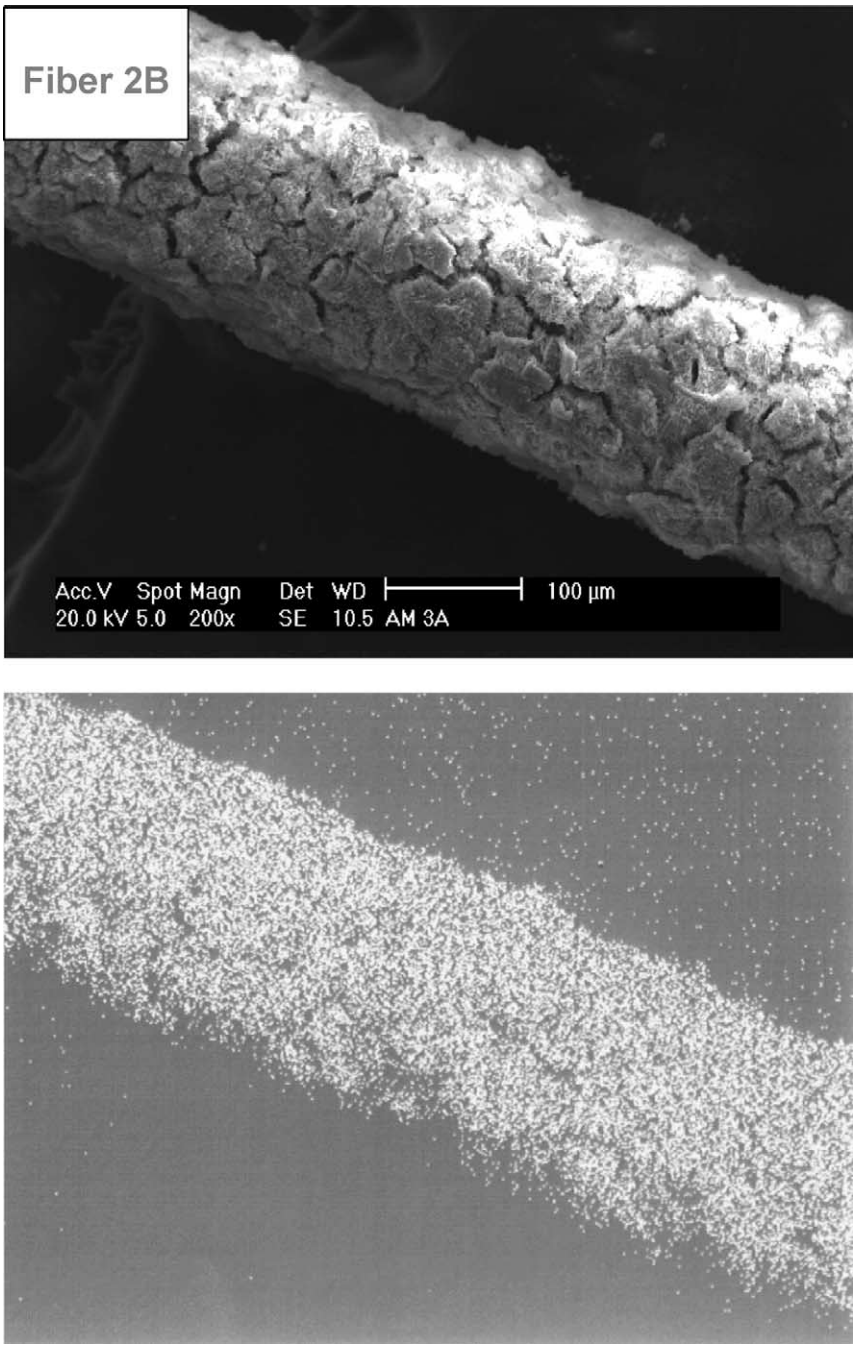


Fig. 3. Scanning electron micrograph and Color Map of the Nb_2O_5 on the glass–ceramic surface.

3.4. Effect of humidity

The interference of water vapor in the fiber's ability to adsorb the studied organic compounds was investigated. Standard samples with relative humidities ranging from 15 to 75% were prepared and the efficiency of extraction was monitored by GC. This study indicated that the presence of more than 30% water vapor in the headspace samples decreased the amount of analytes extracted. Therefore, the water molecules can deactivate the fiber surface by blocking the active sites.

3.5. Repeatability and reproducibility

In order to investigate the repeatability, one fiber was used for six extraction tests under similar conditions and the relative standard deviations (R.S.D.s) were 3–10.4%. The extraction efficiency remained the same for the whole time of this study. To investigate fiber-to-fiber reproducibility six similarly prepared fibers were tested. The R.S.D. were 5–15%. These results (Table 1) indicated that the proposed fiber is very stable and can be used for several extractions without a considerable change in coating property. Besides, the

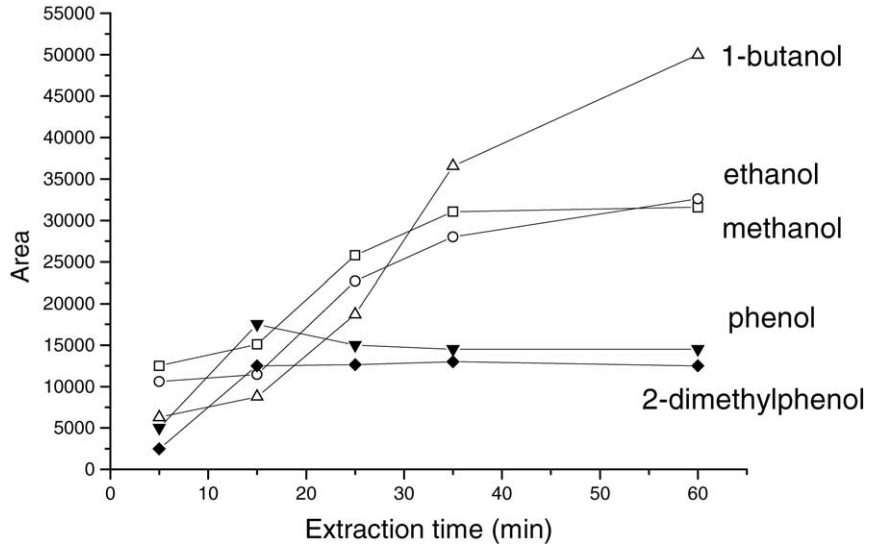


Fig. 4. Adsorption time profile for alcohols and phenols from a gaseous sample. Extraction conditions as described in the text.

Table 1
Characteristic parameters of calibration graphs, analytical features and investigation repeatability and reproducibility of the determination of alcohols and phenols in the headspace sample using Nb_2O_5 fiber

Compounds	LD ($\mu g\,l^{-1}$)	Correlation coefficient	Repeatability for one fiber R.S.D.[a] (%)	Reproducibility for fiber-to-fiber R.S.D.[a] (%)
Methanol	0.5	0.9999	3.0	5.0
Ethanol	0.4	0.9999	6.1	6.3
1-Butanol	0.05	0.9953	10.4	7.0
Phenol	0.5	0.9950	9.4	15.0
2,3-Dimethylphenol	0.8	0.9996	8.9	12.5

The concentration of each compound was $\sim$500 $\mu g\,l^{-1}$.
[a] $n = 6$.

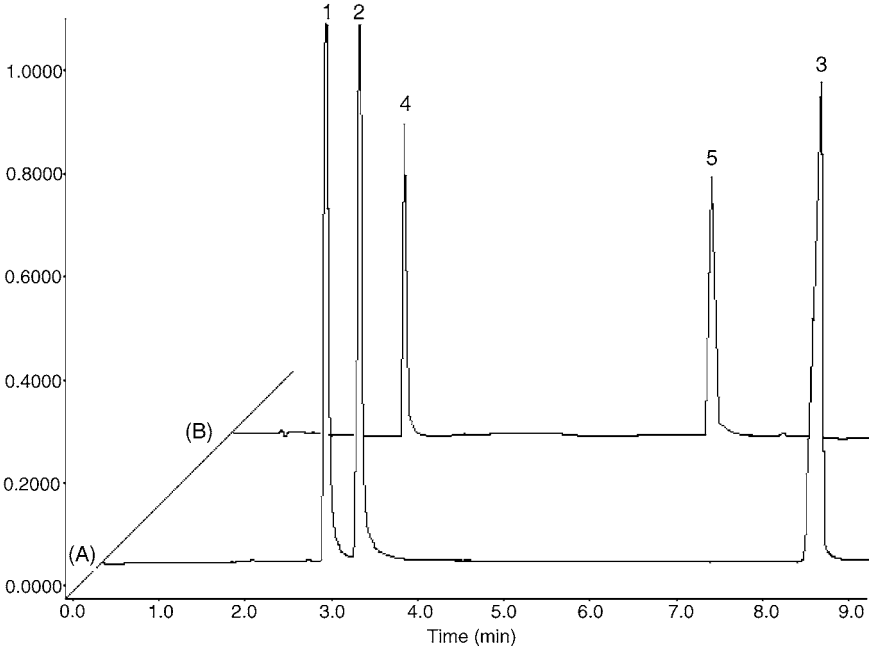


Fig. 5. Gas chromatograms obtained from the extraction of (A) alcohols and (B) phenols using the Nb_2O_5 fiber. The concentration of each compound was $\sim$500 $\mu g\,l^{-1}$. The experimental parameters were the same as described in the text. Compounds: (1) methanol, (2) ethanol, (3) 1-butanol, (4) phenol and (5) 2-dimethylphenol.

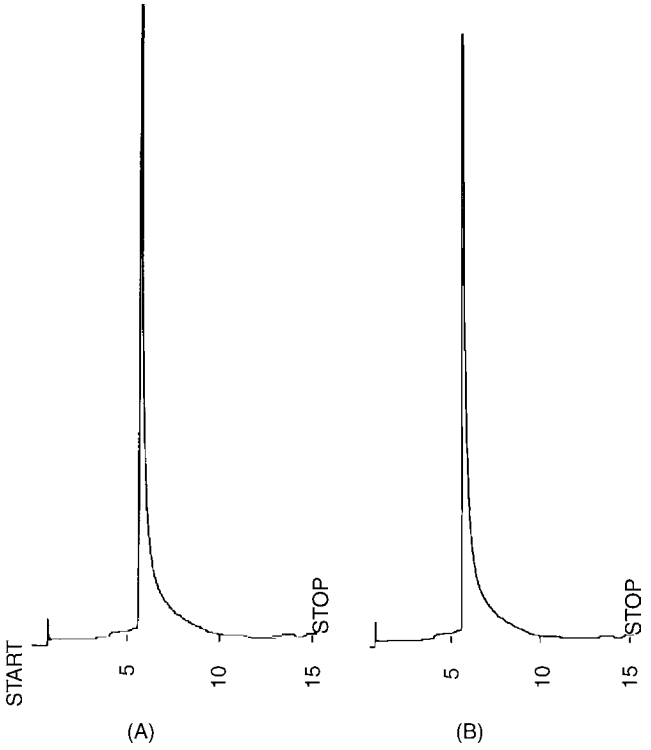


Fig. 6. A comparison study between the Nb_2O_5 fiber (A) and commercially available PDMS/Carboxen fiber (B) for the extraction of 2-nitrophenol in a concentration of ~500 $\mu g\,l^{-1}$.

preparation process of the Nb_2O_5 fiber has good reproducibility.

3.6. Quantitative characteristics

Table 1 shows some analytical performances of the extractions using Nb_2O_5 fiber. As can be seen, the linearity of the calibration graphs for all the analytes is good ($r > 0.995$) in a dynamic range of 50–1000 $\mu g\,l^{-1}$. The detection limit (S/N = 3) for the studied compounds is below 0.8 $\mu g\,l^{-1}$ by using GC–FID analysis. Fig. 5 shows the gas chromatograms obtained for extraction of alcohols and phenols using the Nb_2O_5 fiber. Fig. 6 presents a comparison between the efficiency of the fiber prepared in our laboratory and the commercially available PDMS/Carboxen fiber for extraction of 2-nitrophenol. This figure indicates an excellent efficiency of the Nb_2O_5 fiber.

4. Conclusion

The Nb_2O_5 fiber proved good adsorptive properties for polar compounds from aqueous and gaseous samples. This characteristic can be attributed because of its stronger exchange capacity. Advantages as high-temperature resistance and long durability also can be attributed because of the proposed new SPME fiber.

Acknowledgement

A.F. de Oliveira and C.B. da Silveira thank Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for fellowships.

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