

# A new solid phase microextraction fiber for aromatic hydrocarbons

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A novel solid phase microextraction fiber for the extraction and consequent gas chromatographic determination of benzene, toluene, ethylbenzene, o-xylene and p-xylene is suggested. The fiber was prepared by coating a stainless steel wire with a thin film of a high temperature Silicone Temperature adhesive. The parameters affecting the extraction and gas chromatographic determination of analytes, such as extraction temperature and time, salt addition, desorption temperature and time were investigated. An optimised headspace extraction was carried out at room temperature for 20 min in the presence of 0.4 g mL<sup>-1</sup> of NaCl in the sample solution. Desorption of the analytes was carried out for 60 s at 260 °C. The accuracy, linearity, detection limits were determined.

**Key words:** headspace solid phase microextraction, silicone coating, gas chromatography, BTEX

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## INTRODUCTION

Solid phase microextraction (SPME) proposed by Pawliszyn and coworkers [1] is a simple and rather inexpensive method which involves no organic solvents. SPME can integrate sampling, extraction, preconcentration and sample introduction into a single step, so it has received increasing attention and has become an attractive alternative to common sampling techniques, in particular for volatile and semivolatle compounds [2]. Up to now, only seven kinds of SPME coatings have been commercially available: polydimethylsiloxane (PDMS), PDMS – divinyl benzene (DVB), polyacrylate, carboxen – PDMS, carbowax (CW) – DVB, CW – templated resin, and stable flex DVB-carboxen – PDMS [3]. Commercial SPME fibers utilize a thin polymer film coated on a silica fiber as an extraction phase. However, the preparation of the film for commercial devices is carried out simultaneously while drawing the silica rods. This process requires very expensive equipment, which accounts for the high price of commercially available SPME fibers. Furthermore, silica fibers are fragile and must be handled with great care. So, more robust SPME fibers with a long life and relative low cost are highly desired. This is the reason why in recent years investigations have

been directed to the development of fibers based on coated metal wires.

Lee et al. [2, 4] proposed a new approach for SPME using porous layer coated metal fibers with porous bonded silica particles immobilised on stainless steel fibers using a high temperature epoxy. Faraizadeh et al. constructed SPME using alumina powder and polyvinyl chloride or activated charcoal and polyvinyl chloride with a piece of silver wire as fiber support [5–7]. SPME coatings can also be prepared electrochemically. One of the elaborations of this kind is anodized aluminium wire as SPME fiber proposed by Djozan et al. [8]. Another promising alternative is the use of conductive polymers such as polypyrrole, polyaniline and their derivatives as the extraction phases [9–13]. The polymer films can be prepared easily by chemical or electrochemical methods. In [10] it was shown that incorporation of metallomacrocyclics into a conducting polymer drastically changed the properties of the polymer and so enabled to modify its selectivity.

In the present study, a simple and rapid method for the preparation of a new fiber consisting of stainless steel wire coated with high temperature resistant silicone adhesive “Silicone Temperature” is investigated.

## EXPERIMENTAL

### Reagents

Benzene (99.9%), toluene (99%), ethylbenzene (99%), *o*-xylene (98%), *p*-xylene (99%), 2-butanone (99.5%), *n*-pentanol (98%) and *n*-butyl acetate (99%) were purchased from Aldrich, ethanol (GC grade) and NaCl (analytical grade) were purchased from Reachim (Ukraine). All the reagents were used without further purification. A standard stock solution of benzene, toluene, ethylbenzene, *o*-xylene and *p*-xylene was prepared in ethanol by weighing and contained 1.72–1.76 mg ml<sup>-1</sup> of each analyte. The stock solution was stored refrigerated at +4 °C. Working standard solutions were prepared daily by diluting the stock standard solution with distilled water to the required concentrations.

A standard solution of 2-butanone, *n*-pentanol, *n*-butyl acetate and *o*-xylene was prepared in distilled water by weighing and contained 40 mg l<sup>-1</sup> of each compound.

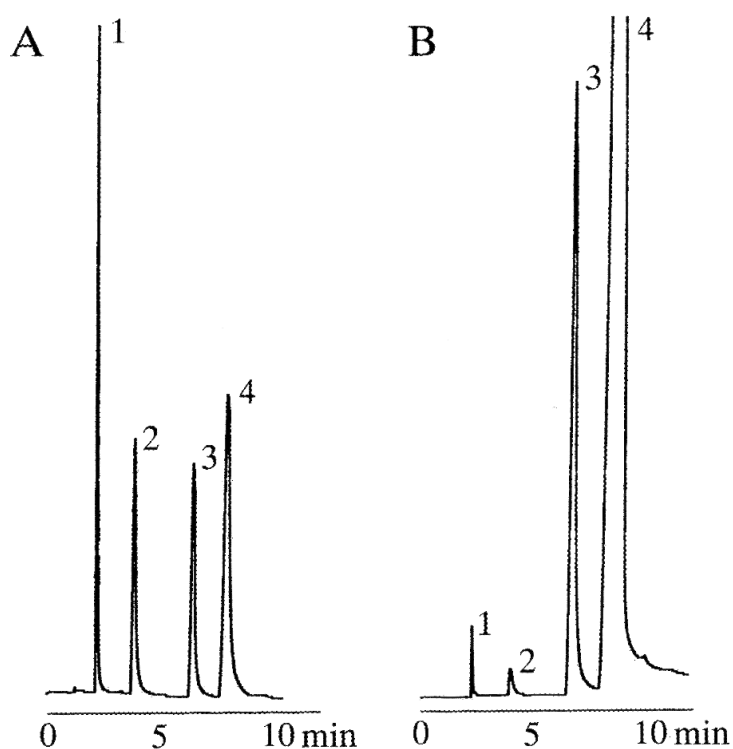
The Silicone Temperature adhesive was purchased from Technicoll (Poland).

### Instrumentation

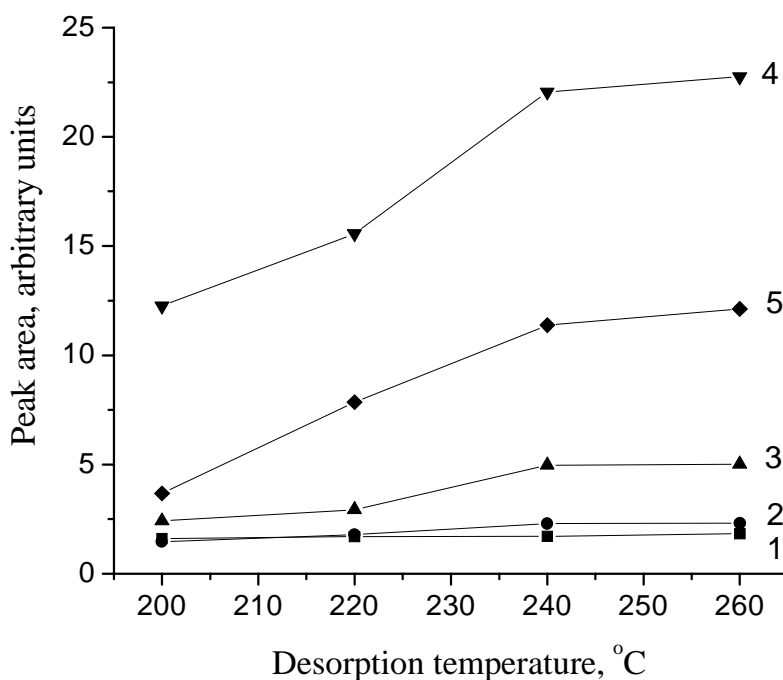
SPME was carried out from the headspace. 5 ml of standard solution was placed in a 13 ml vial closed with a silicone rubber septum containing cap. The vial was positioned in a water-jacketed vessel on a magnetic stirrer (RH3, MLV, Germany) and kept at a selected temperature with a circulating water-bath (UH, MLW, Germany).

Homemade SPME fiber was housed in its manual holder (Supelco Bellefonte, PA, USA).

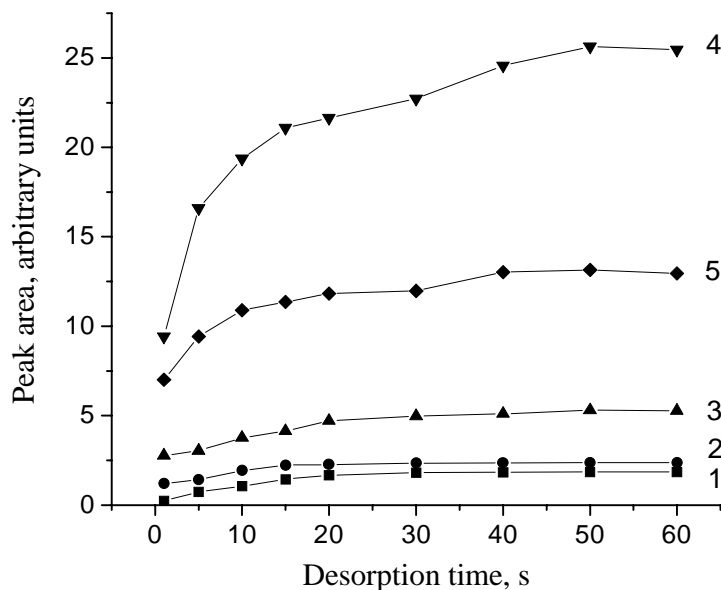
Gas chromatography was carried out in a Varian 3400 gas chromatograph equipped with a flame ionisation detector coupled a SP4290 with integrator (Spectra-Physics) and a RTX-CL Pesticides fused silica capillary column (30 m × 0.53 mm i.d.) (Restec, Bellefonte, PA, USA). The injector temperature was 250 °C, the detector temperature being 100 °C and the column temperature 40 °C. The following gas flow rates



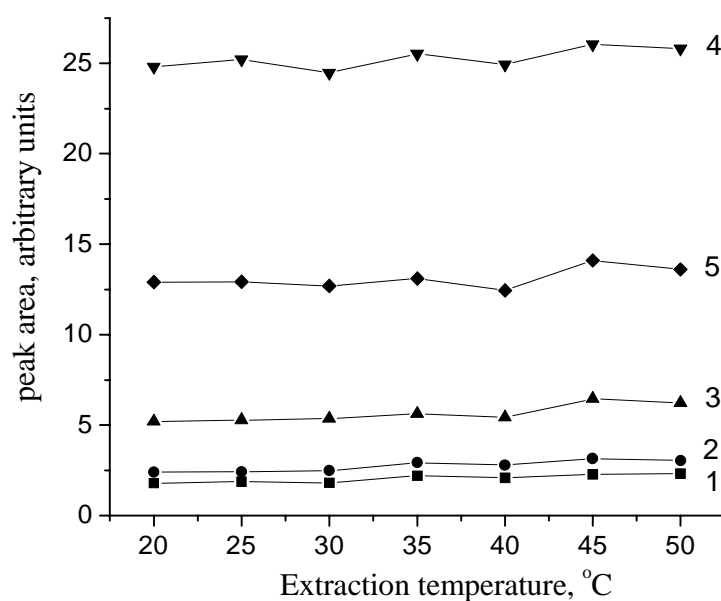
**Fig. 1.** Chromatogram of a standard solution of 2-butanone (1), *n*-pentanol (2), *n*-butyl acetate (3) and *o*-xylene (4). A – syringe injection, B – headspace SPME. Gas chromatographic conditions were: the injector temperature 260 °C, the detector temperature 100 °C, the column temperature 40 °C, gas flow rates were: nitrogen 10, make-up gas 20, hydrogen 30 and air 300 ml min<sup>-1</sup>



**Fig. 2.** The effect of desorption temperature on the peak area of 1 – benzene (4.4 mg l<sup>-1</sup>), 2 – toluene (4.3 mg l<sup>-1</sup>), 3 – ethylbenzene (4.3 mg l<sup>-1</sup>), 4 – *p*-xylene (4.3 mg l<sup>-1</sup>) and 5 – *o*-xylene (4.4 mg l<sup>-1</sup>). The SPME fiber was exposed for 15 min to headspace at room temperature and desorbed for 2 min



**Fig. 3.** Effect of desorption time on the peak area of 1 - benzene ( $4.4 \text{ mg l}^{-1}$ ), 2 - toluene ( $4.3 \text{ mg l}^{-1}$ ), 3 - ethylbenzene ( $4.3 \text{ mg l}^{-1}$ ), 4 - p-xylene ( $4.3 \text{ mg l}^{-1}$ ) and 5 - o-xylene ( $4.4 \text{ mg l}^{-1}$ ). The SPME fiber was exposed for 15 min to headspace at room temperature and desorbed at  $260 \text{ }^{\circ}\text{C}$



**Fig. 4.** Effect of extraction temperature on the peak area of 1 - benzene ( $4.4 \text{ mg l}^{-1}$ ), 2 - toluene ( $4.3 \text{ mg l}^{-1}$ ), 3 - ethylbenzene ( $4.3 \text{ mg l}^{-1}$ ), 4 - p-xylene ( $4.3 \text{ mg l}^{-1}$ ) and 5 - o-xylene ( $4.4 \text{ mg l}^{-1}$ ). The fiber was exposed to headspace for 15 min and desorbed at  $260 \text{ }^{\circ}\text{C}$  for 60 s

were used: carrier (nitrogen) 10, make-up gas 20, hydrogen 30 and air  $300 \text{ ml min}^{-1}$ .

A SPME holder was purchased from Supelco (Bellefonte, PA, USA).

#### SPME fiber preparation

A 1.0 g amount of high-temperature resistant adhesive was added to 1.0 ml of toluene and well mixed. Stainless steel wire ( $300 \text{ }\mu\text{m}$  o.d.) mounted in a

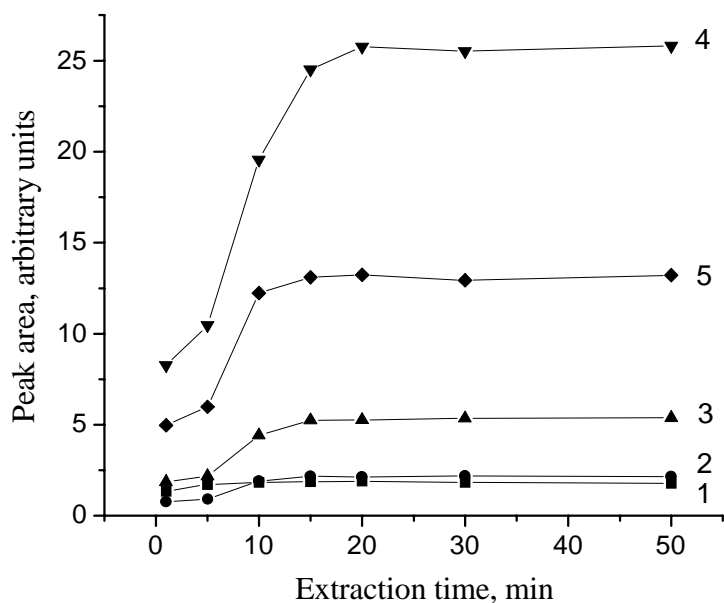
SPME device was first cleaned with ethanol in an ultrasonicator for 10 min, dried at room temperature and then a 2-cm tip was carefully dipped into the coating composite. The coated metal wire was dried at room temperature for 10 h and then conditioned under nitrogen in an injection port of a gas chromatograph at  $300 \text{ }^{\circ}\text{C}$  for 1 h.

#### RESULTS AND DISCUSSION

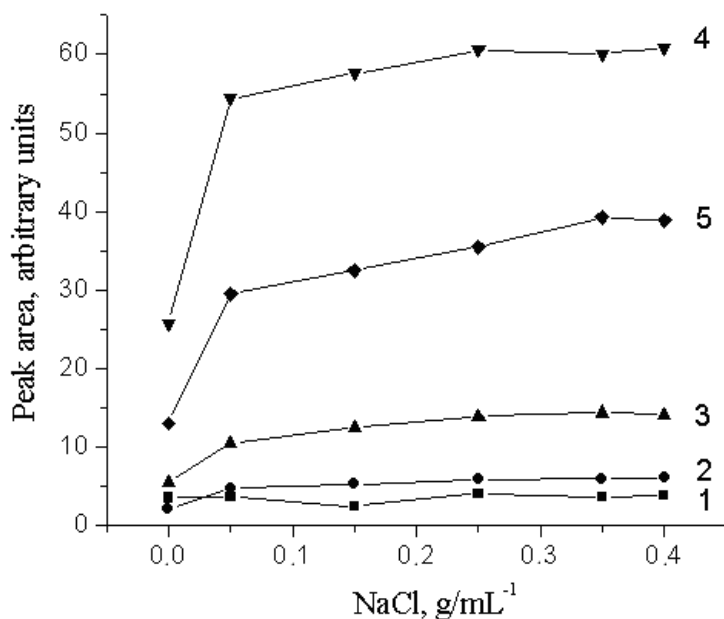
To examine the selectivity of the fiber prepared, it was tested for four different classes of compounds. To this end, the fiber was held for 15 min in the headspace of the aqueous solution containing  $40 \text{ mg l}^{-1}$  of 2-butanone, n-pentanol, n-butyl acetate and o-xylene. A GC comparison of the SPME and syringe injection is shown in Fig. 1. A large increase in o-xylene peak is evident in the SPME case indicating the suitability of the fiber for the analysis of aromatic hydrocarbons. On the other hand, fiber extraction resulted in a decrease of n-pentanol and 2-butanone peaks. This indicates that selectivity of the fiber can be observed for aromatic hydrocarbons in the presence of alcohols and ketones. On the basis of these results, the further work consisted in optimisation of SPME of aromatic hydrocarbons.

#### Desorption conditions

The injection port temperature is an important factor in fiber desorption as well as gas / coating distribution constants of the adsorbed analytes rapidly decrease with temperature increase. Desorption temperatures in the range  $200\text{--}280 \text{ }^{\circ}\text{C}$  were investigated. No higher temperatures were considered, because they might cause a shorter fiber lifetime ( $300 \text{ }^{\circ}\text{C}$  is the recommended temperature limit for the silicone adhesive used for fiber coating). The fiber was immersed into the headspace above 5 ml of standard solution of aromatic hydrocarbons for 15 min at room temperature and then thermally desorbed for 2 min. The profiles presented in Fig. 2 show that the peak areas increased with increasing the temperature up to  $240\text{--}260 \text{ }^{\circ}\text{C}$  and then flattened. So, for the further experiments the desorption temperature of  $260 \text{ }^{\circ}\text{C}$  was selected.



**Fig. 5.** Effect of extraction time on the peak area of 1 – benzene ( $4.4 \text{ mg l}^{-1}$ ), 2 – toluene ( $4.3 \text{ mg l}^{-1}$ ), 3 – ethylbenzene ( $4.3 \text{ mg l}^{-1}$ ), 4 – p-xylene ( $4.3 \text{ mg l}^{-1}$ ) and 5 – o-xylene ( $4.4 \text{ mg l}^{-1}$ ). Desorption was carried out at  $260 \text{ }^{\circ}\text{C}$  for 60 s.



**Fig. 6.** Effect of NaCl content on the peak area of 1 – benzene ( $4.4 \text{ mg l}^{-1}$ ), 2 – toluene ( $4.3 \text{ mg l}^{-1}$ ), 3 – ethylbenzene ( $4.3 \text{ mg l}^{-1}$ ), 4 – p-xylene ( $4.3 \text{ mg l}^{-1}$ ) and 5 – o-xylene ( $4.4 \text{ mg l}^{-1}$ ). The fiber was exposed to headspace for 20 min and desorbed at  $260 \text{ }^{\circ}\text{C}$  for 60 s.

At  $260 \text{ }^{\circ}\text{C}$ , the effect of desorption time on desorption efficiency was studied. Desorption times from 1 s to 60 s were investigated. For more volatile benzene, toluene and ethylbenzene the desorption profiles seemed to increase with time up to about 20–30 s (Fig. 3). For xylenes desorption period is a bit longer, however, 50–60 s are sufficient for their complete desorption. In

the further work desorption time 60 s was therefore used.

#### Extraction conditions

In the case of SPME of volatile compounds, agitation is required to facilitate equilibration between the bulk of the aqueous sample and the fiber. We used a vigorous agitation of the solution (600 rpm), which on the other hand, did not result in the spattering that could change the properties of the fiber surface.

Optimisation of the extraction temperature was studied by exposing SPME fiber in the headspace for 15 min. Dependence of the peak area on the temperature of the sample vial was studied. The sample temperature ranged within  $20\text{--}50 \text{ }^{\circ}\text{C}$ , but no significant changes in the extraction efficiency were observed (Fig. 4). Therefore further investigations were carried out at room temperature.

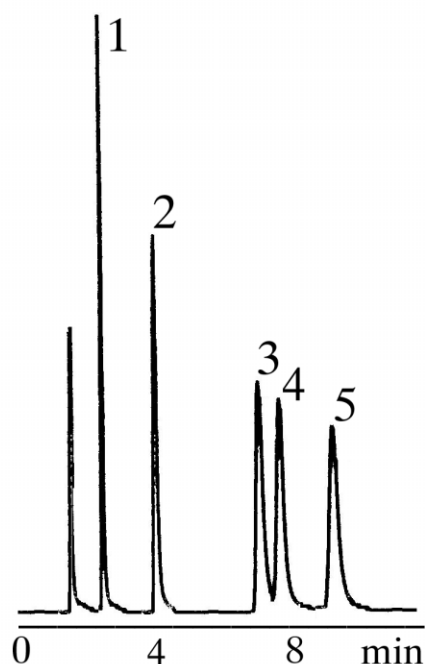
A proper sampling time was adjusted exposing the fiber to the headspace for 1–50 min. As is shown in Fig. 5, after 20 min the extraction equilibrium was established for all analytes.

Addition of the salt to could improve the sensitivity for analytes of the SPME method because of the increased ionic strength in the aqueous phase and salting the analytes out of solution into the headspace phase and the fiber. To increase the ionic strength, we added NaCl which is commonly used for this purpose. To the standard solution of aromatic hydrocarbons different portions up to saturation of NaCl were added. From the curves presented in Fig. 6 it is evident that the addition of NaCl enhances extraction efficiency. In further experiments,  $0.4 \text{ g ml}^{-1}$  of NaCl was added. A chromatogram of aromatic hydrocarbons at optimised SPME conditions is presented in Fig. 7.

#### Accuracy, linearity and detection limits

The quality parameters of the SPME methods such as linearity, repeatability and limits of detection (LOD) were calculated under the optimised conditions described above. The repeatability of the method was determined by a five-repetitions analysis of two different concentrations of the analytes under optimum conditions. Relative standard deviations (RSDs) are listed in Table 1.

For all the tested aromatic hydrocarbons, the limits of detection (all LODs based on  $S/N = 3$ ) are presented in Table 2 and are lower than those



**Fig. 7.** The chromatogram of standard solution of 1 – benzene (4.4 mg l<sup>-1</sup>), 2 – toluene (4.3 mg l<sup>-1</sup>), 3 – ethylbenzene (4.3 mg l<sup>-1</sup>), 4 – p-xylene (4.3 mg l<sup>-1</sup>) and 5 – o-xylene (4.4 mg l<sup>-1</sup>). The fiber was exposed to headspace for 20 min and desorbed at 260 °C for 60 s. For gas chromatographic conditions see Fig. 1

**Table 1. Repeatabilities of SPME of aromatic hydrocarbons (n = 5)**

Compound	Concentration, mg l <sup>-1</sup>	RSD, %
Benzene	2.20	17.2
	0.55	13.5
Toluene	2.17	13.1
	0.54	7.8
Ethylbenzene	2.17	15.1
	0.54	4.0
p-Xylene	2.15	11.5
	0.54	7.4
o-Xylene	2.20	9.1
	0.55	9.2

**Table 2. BTEX detection limits**

Compound	Detection limit, μg l <sup>-1</sup>
Benzene	0.17
Toluene	0.07
Ethylbenzene	0.11
p-Xylene	0.10
o-Xylene	0.08

of the commercial PDMS fiber [14] up to two orders of magnitude. The linearity ranges were within 9 mg l<sup>-1</sup>. For all the analytes good linearities

were observed, with correlation coefficients > 0.996 (n = 9).

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## NAUJAS KIETAFAZĖS MIKROEKSTRAKCIJOS STRYPELIS AROMATINIAMS ANGLIAVANDENILIAMS NUSTATYTI

### Santrauka

Pasiūlytas naujas kietafazės mikroekstrakcijos strypelis benzenui, toluenui, etilbenzenui, o-kisilenui bei p-kisilenui ekstrahuoti ir nustatyti dujų chromatografijos metodu. Strypelis pagamintas nerūdijanėia viela plonai padengus aukštatemperatūriais silikoniniais klijais „Silicone temperature“. Ištirti ekstrakciją bei dujų chromatografiną nustatymą sąlygojantys parametrai (ekstrakcijos temperatūra ir trukmė, druskos kiekis tirpale, desorbcijos temperatūra ir trukmė). Optimizuota ekstrakcija iš viršerdvės buvo atliekama 20 min kambario temperatūroje esant tirpale 0,4 g ml<sup>-1</sup> NaCl. Desorbcija buvo atliekama 60 s 260°C. Nustatytos analiėø aptikimumo ribos, ėvertintas rezultatø pasikartojamumas.