INTRODUCTION

Sample preparation procedures for environmental applications of gas chromatography/mass spectrometry (GC/MS) analysis are often criticized for being rather time-consuming and laborious. Therefore many efforts of different scientific groups are focused on elimination of these drawbacks. Recently various approaches to simplify and/or improve sample preparation before mass spectrometry analysis were developed. Several reviews deal with these modern approaches [1, 2].

Certainly the most radical innovation involves ambient ionization methods. The main merits of ambient ionization are simplicity and almost complete absence of sample preparation. Since the reporting of desorption electrospray ionization (DESI) in 2004 [3] several dozens of similar methods were developed. Some of them have great perspectives in studying organic pollutants in the environment [4–6].

Membrane inlet mass spectrometry (MIMS) is also quite perspective, but not so widely used. It has been applied for the real-time analysis for almost 35 years. Since MIMS allows avoiding sampling and sample cleaning, it is a good alternative to the classic variants of GC/MS. The main trends in the development of this technique, especially created for the portable mass-spectrometers, are reviewed in [7].

Determination of Polycyclic Aromatic Hydrocarbons in Water by Gas Chromatography/Mass Spectrometry with Accelerated Sample Preparation1

O. V. Polyakova, D. M. Mazur, V. B. Artaev, and A. T. Lebedev

Chemical Department, Lomonosov Moscow State University, Moscow, 119991 Russia

LECO Corporation, 3000 Lakeview Avenue, St. Joseph, MI, USA

Abstract—A novel simplified sample preparation method for quantitative analysis of polycyclic aromatic hydrocarbons (PAH) in water samples by gas chromatography/mass spectrometry (GC/MS) was proposed. The method requires just 1 mL of water and 1 mL of dichloromethane. The detection limits of PAH with the use of high resolution GC/MS are about 1 μg/L, while the limits of quantification—10 μg/L. These limits correspond to those for the standard 8270 method of the United States Environmental Protection Agency.

Keywords: PAH, GC/MS, high resolution mass spectrometry, quantitative analysis, express-analysis

DOI: 10.1134/S106193481313008X
romethane per 1 liter of water) and brings to unavoidable losses of analytes, especially while filtrating and concentrating the extracts. In this case the limits of quantification of all analytes are quite high (10 µg/L of water and higher). Considering that since the development of this method many years have passed and sensitivity of mass spectrometers have raised significantly, we have attempted to improve the method, making it cheaper, faster, more sensitive and reliable. As the first step 17 priority polycyclic aromatic hydrocarbons (PAH), which we quantified earlier in the samples of Moscow snow in 2011–2012 [21, 23], were chosen.

EXPERIMENT

All experiments were performed with time-of-flight (TOF) high resolution mass-spectrometer GC-HRT (LECO Corporation, Saint-Joseph, USA) with resolving power up to 50000 with multiple reflecting geometry of mass analyzer (ion source with electron ionization, temperature 300°C, electron energy 70 eV, mass range m/z from 40 to 300). The registration involved 400 s delay after introducing the sample into the column, the registration speed—4 full scans per second. During our experiments we used resolving power 25000.

Chromatography was performed with Agilent 7890 (USA) with autosampler 7693 (chromatographic capillary column DIOXIN2 (Restek, USA) 40 m length, internal diameter 180 µm and phase thickness 0.18 µm; gas-carrier—helium at speed of 1 mL/min; the column temperature was programmed as follows: 40°C (5 min)—10°C/min up to 250°C—6°C/min up to 330°C (5 min); interface temperature—330°C. 2 µL of sample were introduced into the injector heated at 270°C in splitless mode; after 75 s the injector was blown with a flow of helium at 20 mL/min speed. All results were processed with ChromaTOF-HRT 1.8 software of LECO Corporation (USA), that includes instrument control, spectra registration and data processing.

Calibration solutions of PAHs for all the experiments and solutions of internal standards (perdeuterated naphthalene,acenaphthene, phenanthrene, chrysene and perylene) were prepared from standard Restek (USA) mixtures. Distilled water used in experiments was HPLC grade, dichloromethane and sodium sulphate produced by Sigma-Aldrich (USA). All experiments were performed with time-of-flight mass spectrometer GC-HRT (LECO). In the present study 1 mL of water solution, containing calculated amounts of PAHs (1–100 ng), and 1 mL of dichloromethane as an extraction solvent were used. Using anhydrous sodium sulphate as a reagent to bind water, we also took into account that simultaneously we improve the extraction due to “salting-out” effect. This procedure is widely used in classic LLE for decreasing the solubility of organic compounds in water and increasing their extractability. After addition of all anhydrous sodium sulphate (~1.5 g) aquatic phase was totally bounded and organic compounds were quantitatively transferred into organic phase. Actually water phase was replaced by organic (in this experiment by dichloromethane). All sampling procedure takes 5–10 min, and there is no need to concentrate the sample. Therefore there are no losses of volatile components. Furthermore, the sample preparation could be totally implemented outside the laboratory, in field conditions at sampling place.

To establish recoveries and detection limits response factors (RF) for all analyzed PAHs were established by using 5 internal standards (perdeuterated naphthalene,acenaphthene,phenanthrene,chrysene and perylene). These deuterated compounds are used in classic version of 8270 EPA method [22], since they cover all retention time range and PAHs’ molecular masses. Therefore, solutions of PAHs and internal standards at concentration 10, 40 and 100 ng/mL were prepared. RFs for individual PAHs were calculated to the nearest by retention time deuterated standard. Table 1 demonstrates average RFs (at 3 concentrations and 3 repetitions). Individual PAHs were divided into several groups according to the internal standard used for calculations. Reproducibility of the results was quite high and RFs were near 1, what is very important for minimizing the analysis error [8]. In case of methylnaphthalenes RF is lower, because ions with m/z 141 and 142 have approximately equal intensities, i.e. overall intensity of ion current decreases by about 2 times in comparison to non-substituted hydrocarbons.

RESULTS AND DISCUSSION

Declared sensitivity of Pegasus GC-HRT (LECO, USA) mass spectrometer exceeds 1 pg. Therefore it allows decreasing significantly the volumes of water sample and organic solvent required for analysis while using 8270 US EPA method. Calculations show, that the volume of the water sample and extracting solvent could be decreased down to 1 mL and all the extraction procedure could be performed in a 5 mL vial. In case of quantitative extraction, 1 µL of extract is introduced into the injector in splitless mode. While working at detection limit of 8270 EPA method (10 µg/L), 10 pg of each hydrocarbon should enter the ion source. Such amount of analyte should be easily determined by a modern instrument, particularly by Pegasus GC-HRT (LECO).

In the present study 1 mL of water solution, containing calculated amounts of PAHs (1–100 ng), and 1 mL of dichloromethane as an extraction solvent were used. Using anhydrous sodium sulphate as a reagent to bind water, we also took into account that simultaneously we improve the extraction due to “salting-out” effect. This procedure is widely used in classic LLE for decreasing the solubility of organic compounds in water and increasing their extractability. After addition of all anhydrous sodium sulphate (~1.5 g) aquatic phase was totally bounded and organic compounds were quantitatively transferred into organic phase. Actually water phase was replaced by organic (in this experiment by dichloromethane). All sampling procedure takes 5–10 min, and there is no need to concentrate the sample. Therefore there are no losses of volatile components. Furthermore, the sample preparation could be totally implemented outside the laboratory, in field conditions at sampling place.

To establish recoveries and detection limits response factors (RF) for all analyzed PAHs were established by using 5 internal standards (perdeuterated naphthalene,acenaphthene,phenanthrene,chrysene and perylene). These deuterated compounds are used in classic version of 8270 EPA method [22], since they cover all retention time range and PAHs’ molecular masses. Therefore, solutions of PAHs and internal standards at concentration 10, 40 and 100 ng/mL were prepared. RFs for individual PAHs were calculated to the nearest by retention time deuterated standard. Table 1 demonstrates average RFs (at 3 concentrations and 3 repetitions). Individual PAHs were divided into several groups according to the internal standard used for calculations. Reproducibility of the results was quite high and RFs were near 1, what is very important for minimizing the analysis error [8]. In case of methylnaphthalenes RF is lower, because ions with m/z 141 and 142 have approximately equal intensities, i.e. overall intensity of ion current decreases by about 2 times in comparison to non-substituted hydrocarbons.