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Research Article

Evaluation of Modified Standard Procedure Performance for the Determination of Polycyclic Aromatic Hydrocarbons in Water by Gas Chromatography/Mass Spectrometry

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Abstract

Various methods were developed and validated for the analysis of Polycyclic Aromatic Hydrocarbons (PAHs), in the environmental samples. However, their analysis in relevant concentrations in environmental samples can be a challenging task. The aim of this study was to estimate the performance of a modified standard procedure for the determination of polycyclic aromatic hydrocarbons in environmental water samples using liquid-liquid extraction as a preparation step followed by gas chromatography/mass spectrometry. Implementation of long term quality control procedures after validation of the analytical procedures enables acquisition of accurate and reliable results. Three year monitoring of the quality control samples (containing 10-40 ng/L of PAHs) showed that method main characteristics, such as accuracy, precision and measurement uncertainty have constant stability and with no statistically significant changes during this period.

Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are environmental pollutants ubiquitously found in air, water, soil and food. Because of their carcinogenic and mutagenic properties, PAHs are subject to systematic monitoring in most countries worldwide. There are several US and EU guidelines proposing the analytical procedures and maximum allowable levels of PAHs in various environmental media. The list of monitored PAHs varies in different countries. In the United States, the EPA has listed 16 priority PAHs [1], whereas in Directive 2013/39/EU, naphthalene, anthracene and the sum of PAHs are marked as priority substances [2].

Increased environmental awareness and new analytical developments have increased the need for more information on the levels of organic pollutants in environmental samples. Thus, a large group of PAHs have been the focus of various studies regarding methodologies and equipment for analysis [3-5], as well as procedures and tests for determining PAHs in environmental samples (air, water, soil, bottom sediments, suspended particulate matter, organisms, etc.) [6-8].

Obtaining reliable data for the analysis of organic pollutants, especially in environmental samples, is a challenge for every analytical laboratory. Quality Assurance and Quality Control (QA/QC) results involve evaluating the reliability of both the instrument and method used, through several activities: a) utilizing (certified) reference materials, b) validating the analytical procedures applied, c) estimating uncertainties in the measurement, d) assuring the metrological coherence of the results and e) participating in different kinds of inter-laboratory comparisons [1,9].

The results obtained through various studies have shown the possibilities and limitations of various analytical techniques applied for PAHs analysis in different environmental samples [3-6]. Many studies have shown that the acquisition of accurate and reliable results of PAHs determination in environmental samples demands the application of well-planned QA/QC procedures. In this context, the aim of this study was to evaluate modified standard procedure performance for the determination of PAHs in environmental water samples utilizing liquid-liquid extraction and gas chromatography/mass spectrometry.

Materials and Methods

Samples and reagents

PAHs solution (PAH-Mix 64 in Benzene/Dichloromethane = 50/50, with a concentration of 2000 μg/mL for each compound) was purchased from Dr. Ehrenstorfer. Phenanthrene-d10 (2000

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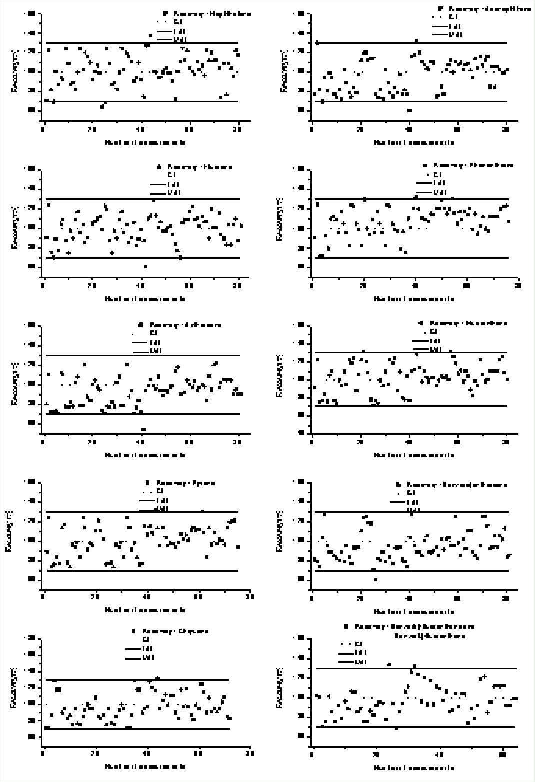

Figure 1: Recovery data (X-charts) for the water samples spiked with PAHs (CL-central line; LAL – lower action limit; UAL - upper action limit).

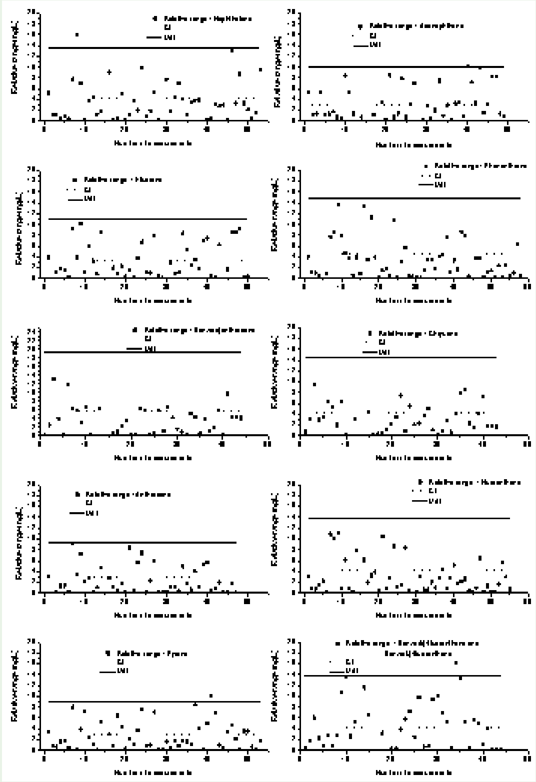

Figure 2: r-charts of the duplicate spiked real water samples (CL-central line; UAL – upper action limit).

μg/mL in methanol solution) was used as internal standard and was purchased from Supelco. Organic solvents (hexane, acetone, pentane, dichloromethane and methanol) were organic residue analysis grade and were purchased from J.T Baker and Sigma-Aldrich.

In the quality control procedure, two types of samples were used: for the X-chart, spiked distilled water, and for the r-charts, spiked real matrix samples of surface, ground and waste water.

Water preparation and analysis procedure

Water samples were prepared in accordance with a modified standard procedure [10,11] using liquid-liquid extraction of 250 mL sample with 3 mL of hexane. Extraction was performed by manual shaking for 10 minutes. 0.5 mL of hexane extract was then separated in to 2 mL vials and 2 μL of internal standard phenanthrene-d10 (100 μg/mL) added and further analyzed. The modifications in regard to the standard method are: a) instead of 180 mL of methylene-chloride which is extraction solvent proposed by the standard methods [10,11], 3 mL of hexane is used as the extraction solvent and b) after extraction, samples were not further concentrated by evaporation as proposed in standard methods, in order to avoid loss of extracted PAHs.

Instrumental analysis is performed using gas chromatography coupled with mass spectrometry on a GC System/ 5975C MSD (Agilent Technologies 7890A), in accordance with USEPA Method 8270C [12]. The injection volume is 1 μL. Chromatographic conditions are: oven starting temperature (55˚C) maintained for 1 min, thereafter the temperature rises at a rate of 25˚C/min up to 320˚C and hold for 3 min. Injection mode: pulsed split less. Injector temperature is 300 °C, ion source temperature 230˚C, quadrupole temperature 150˚C and transfer line temperature 280˚C. Acquisition mode is single ion monitoring (SIM/SCAN) with the following target and qualifier ions: naphthalene 128, 102, and 64 amu; acenaphthene 153,76 and 63 amu; phenanthrene and anthracene 178, 152 and 89 amu; pyrene and fluoranthene 202, 174 and 101 amu; fluorene 166, 139, and 82 amu; chrysene and benzo(a)anthracene 228, 114 and 200 amu; benzo (b) fluoranthene and benzo (k) fluoranthene 252, 126 and 113 amu; and phenanthrene-d10 188, 160 and 80 amu.

Method quality control

Spiked samples of concentrations of 10, 30 and 40 ng/L for the X-charts were prepared by enrichment of 250mL deionized water, after which the same sample extraction procedure as above was applied. The limits of action for the X-carts were in range from 70-130% expressed as recovery, in accordance with recommendations given in USEPA Method 8000B [13].

Data for r-charts were obtained by measuring duplicate samples of real water matrices and spiked real water matrices with different concentrations of PAHs and following the relative difference between the two measurements. The limits for the r-charts were set based on 20 measurements obtained during the initial validation experiment.

Results and Discussion

For quality control, the method was monitored with two types of control charts over three years of measurement: X - chart, showing

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the accuracy/precision of the measurements of spiked water samples and the r – chart, showing precision between two measurements of the same sample. The results obtained during the method monitoring are shown in Figures 1 and 2. Table 1 presents the minimum and maximum recovery values, as well as the precision data obtained from the X and r- charts.

The obtained results for accuracy (Figure 1) show that most of the measurements for the investigated PAHs lie in the defined range, from 70-130% [13] expressed as recovery. Similar recovery values were obtained by other researchers [14]. The results are randomly distributed around the recovery value of 100%. The results presented in the X- charts show that all PAHs analyses were under statistical control during the period 2013-2015. For most of the analyzed PAHs, in 1-3 control sample results were outside the upper or lower action limits. However, given that the number of measured control samples was around 80 over the three years, the number of samples exceeding the limits was less than 4%, which can be considered as statistically satisfactory. During the monitoring period, no statistically important trends were observed, and at no point did seven or more control values gradually increase or decrease consecutively. The measured minimum and maximum values (Table 1) are similar for all analyzed PAHs. The precision data obtained from the X-charts shows similar trends and are in the range 14-16.4%. This all suggests the method is stable with no statistically significant changes, according to the literature [15].

The results presented in Figure 2 show that most of the measurements for the investigated PAHs were in the defined range, calculated according to the NORD test protocol [15]. Only in three cases (one value for naphthalene, pyrene and benzo (k) fluoranthene was this limit exceeded. This represents less than 2% of the measurements made, and the results presented in the r-charts can therefore be considered to be under statistical control during the period 2013-2015. The measured precision data obtained from the r-charts (Table 1) show similar trends and are in range of 2.48-4.33%. This confirms that method performance during the three year period was not significantly different from the limits obtained during the validation procedure, which is satisfactory, according to the literature [15].

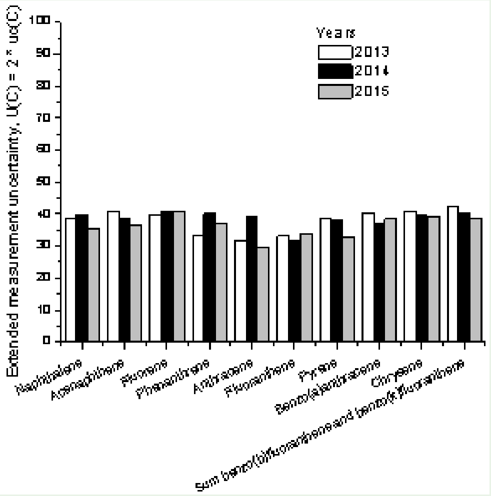

Figure 3: Extended measurement uncertainty over the 3 year period.

Table 1: Minimum and maximum recovery values and precision data obtained from the X and r-charts.

Compound	Min (%)	Max (%)	Precision X-chart	Precision r-chart
Naphthalene	65	138	15.9	3.53
Acenaphthene	61	133	16.4	3.05
Fluorene	61	129	14.0	3.20
Phenanthrene	72	132	14.3	3.31
Anthracene	54	122	14.2	2.48
Fluoranthene	52	131	16.5	3.12
Pyrene	73	131	15.0	2.60
Benzo(a)anthracene	60	127	14.6	3.24
Chrysene	72	132	15.8	2.58
Benzo(b)fluoranthene and Benzo(k)fluoranthene	68	133	15.2	4.33

In Figure 3, the extended measurement uncertainties for the PAHs analyses over the 2013-2015 periods are presented. All measured uncertainties were around 30-40% for all investigated PAHs.

The measured uncertainties were very similar for all three years indicating that the method properties are constant and stable [16].

Conclusion

The results of a three year quality control program for a method, analyzing PAHs in water samples are presented in this paper. During this period, the method is shown to display no statistically significant changes in comparison with the parameters set during the validation experiments. The results obtained for the accuracy control samples were between the lower and upper limits of actions, and low variations between duplicate water samples show good measurement precision. It can be concluded that modified liquid-liquid extraction combined with GC/MS analysis can be used as a reliable method for the determination of PAHs in environmental water samples.

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