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# Poly(etheretherketone)-turnings a novel sorbent material for lead determination by flow injection flame atomic absorption spectrometry and factorial design optimization

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ABSTRACT

A novel hydrophobic sorbent material for on-line column preconcentration and separation systems coupled with atomic spectrometry was developed. Poly(etheretherketone) (PEEK) in the form of turnings was used as packing material and evaluated for trace lead determination in environmental samples. Sample and ammonium diethyl-dithiophosphate (DDPA) reagent were mixed on-line and the Pb(II)–DDPA complex was retained effectively on PEEK-turnings. Isobutyl methyl ketone (IBMK) was adopted for efficient analyte complex elution and subsequently transportation into the nebulizer–burner system for atomization. The developed sorbent material has shown, excellent chemical and mechanical resistance, fast adsorption kinetics permitting the use of high sample flow rates without significant loss of retention efficiency. For 120 s sample preconcentration time the sampling frequency was 20 $h^{-1}$, the enhancement factor was 110, the detection limit (3 s) was $c_L = 0.32\ \mu g\ L^{-1}$, and the relative standard deviation (RSD) was $s_R = 2.2\%$, at the 50.0 $\mu g\ L^{-1}$ Pb(II) level. The accuracy of the developed method was evaluated by analyzing certified reference materials.

## 1. Introduction

Lead is one of the most toxic elements and its toxicity affects negatively almost all organs of human and animals. Its cumulative poisoning effects are serious hematological problems, anemia as well as malfunction of brain and kidney. Lead is entered into the human body through inhalation, absorption by the skin and peptic system especially by polluted drinking water as a result of corrosion or wearing of materials containing lead in the water distribution system and household plumbing [1].

Lead is commonly determined in trace levels by atomic spectrometry like electrothermal atomic absorption spectrometry (ETAAS) [2], inductively coupled plasma mass spectrometry (ICP-MS) [3] or voltammetry like differential pulse anodic stripping voltammetry (DPASV) [4], with adequate sensitivity. Nevertheless, flame atomic absorption spectrometry (FAAS) is the most widely used technique for heavy metal determination. On the other hand, frequently it cannot be used to analyze environmental samples due to insufficient detection capability and/or matrix interferences [5].

Preconcentration procedures provide the advantage of increasing the analyte concentrations to measurable levels and also the removing of the potentially interfering matrix. On-line solid phase extraction (SPE) may be used as an alternative to flow or sequential injection liquid–liquid extraction [6], because of its advantages, like high enrichment factor, high recovery, rapid phase separation, low cost, low consumption of organic solvents, and the ability to combine with different detection techniques. On-line column preconcentration is based predominantly on the incorporation of mini-columns packed with various polar or non-polar sorbent materials. The nature and the properties of the packing materials are of prime importance for effective retention of analyte [7], while some basic requirements for them should be met, like fast and quantitative adsorption, effective elution, negligible swelling and shrinking, regeneration ability, high capacity, accessibility and high chemical resistibility [8].

Several methods have been developed for FI on-line column preconcentration combined with flame atomic spectrometry for lead determination. These procedures mainly utilize various sorbent materials like: silica gel modified with niobium oxide(V) $Nb_2O_5$–$SiO_2$ [9], multiwall carbon nanotubes (MWCNTs) [10], poly(chlorotrifluoroethylene) (PCTFE) [11], merrifield chloromethylated resin (MCR) [12], functionalized amberlite XAD-2 [13], modified chitosan [14], coated alumina [15], polyurethane foam (PUF) [16–18], and poly(tetrafluoroethylene) (PTFE) in the form of turnings [19], or grafted fiber [20].

The trends in on-line solid phase extraction procedures are towards the development of new sorbent materials with exceptional properties. Poly(etheretherketone) (PEEK) is a semi-

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crystalline thermoplastic polymer (typically 35%) with outstanding characteristics, such as excellent mechanical properties, high melting point and good resistance to strong acids. It has more wide-ranging applications than most polymers. The high performance PEEK polymer was first prepared by Bonner [21]. Besides its commercial availability, the hydrophobicity of PEEK is remarkably appreciated by analytical chemists. Poly(etheretherketone) in the form of knotted tube has been adopted for on-line retention of the target analyte on the inner surface of a loop in on-line knotted reactor systems [22,23]. However, as far as we know, PEEK has not been utilized as sorbent material in column preconcentration systems either in batch or in on-line mode, probably due to the fact that it is not commercially available in the form of appropriate beads or turning.

The optimization of analytical procedures by multivariate techniques is faster, more economical and effective than traditional "one-at-a-time" optimization, and allows the variables to be optimized simultaneously [24]. In this technique, the factorial design allows the identification of the significant variables of an experiment, and indicates conditions for better results. One of the most popular multivariate designs is the two-level full or fractional factorial, in which every factor is experimentally studied at only two levels. Due to their simplicity and relatively low cost, full factorial designs are very useful for preliminary studies or the primary steps of optimization, while fractional designs are almost mandatory when a large number of factors are involved. Doehlert designs can be used for the expanded optimization of the analytical system. They have the advantage of requiring fewer experimental runs than a full composite design, to fit a given higher order model [25,26]. Recently, several comprehensive reviews have been reported concerning the advantages and the applications of the chemometric tools for analytical methods optimization [27–29].

In the present work, PEEK-turnings were fashioned and used for the first time in on-line flow injection column preconcentration system. The feasibility and performance of the packed micro-column with PEEK-turnings, for determination of ultra-trace amounts of lead was investigated, using ammonium diethyldithiophosphate (DDPA) as complex reagent and isobutyl methyl ketone (IBMK) as eluent. DDPA was selected as chelating agent due to its good selectivity for lead, copper and cadmium in strong acidic medium [30]. All main analytical parameters including flow and chemical factors were investigated and optimized by full factorial design and Doehlert optimization method. The proposed method was evaluated by analyzing certified reference material and spiked environmental water samples.

## 2. Experimental

### 2.1. Instrumentation

A PerkinElmer, Norwalk, CT, USA (http://www.perkinelmer.com) model 5100 PC flame atomic absorption spectrometer with deuterium lamp background corrector was used as detection system. Lead electrodeless discharge lamp (EDL) operated at 10 mA was used as light source. The analytical wavelength was set at 283.3 nm resonance line and the monochromator spectral bandpass at 0.7 nm. A time-constant of 0.2 s was used for peak height evaluation. The flame composition was adjusted properly to compensate for the effect of IBMK, which serves as additional fuel during elution step. The air and acetylene flow rate was set at 10.0 and 0.9 L min$^{-1}$ respectively. In that case the nebulizer's free uptake rate was 5.3 mL min$^{-1}$. A flow spoiler was employed in the spray chamber for better nebulization conditions. The spectrometer was set to work in the FI-FAAS mode coupled with the FIAS-400 system.

**Fig. 1.** Image of the shape of PEEK-turnings from optic stereomicroscope.

A PerkinElmer Norwalk, CT, USA model FIAS-400 flow injection analysis system was coupled to the flame atomic absorption spectrometer for automatic processing of the method and operated in preconcentration mode. The whole system was controlled by a personal computer and the AA Lab. Benchtop version 7.2 application software. The FIAS-400 system consisted of two peristaltic pumps P1, P2 and a 5-port 2-position injection valve and it was connected to the spectrometer's nebulizer using a short PTFE capillary 15 cm length, 0.35 mm i.d., to minimize the dispersion of the analyte into the eluent. A flow compensation (FC) union in "T" form was used just before the nebulizer inlet, in order to compensate the nebulizer's free uptake flow rate in case of the eluent flow rate was much lower than it, as it has been reported elsewhere [11]. Peristaltic pump tubing of "Tygon" type was adopted to deliver the aqueous solutions and a displacement bottle (Tecator, Hoganas, Sweden http://www.foss.dk) was used to deliver the organic solvent IBMK. All other conduits used for various connections were of 0.5 mm i.d. PTFE tubing. A Stereomicroscope Leica MZ6 equipped with a digital CCD color video camera TK-C1381 JVC, was used for the image of PEEK-turnings.

### 2.2. Preparation of the micro-column

Due to the fact that PEEK is not presented in the market in the form of beads, granules, fiber or turnings, we manufactured 0.4 mm mean width PEEK-turnings, mechanically using a lathe. The image of the sorbent material is presented in Fig. 1. A Jour Research micro-column 30 mm length/4.6 mm i.d. was packed with 870 mg of PEEK-turnings and used for the metal adsorption. First, the turnings were washed thoroughly by ethanol followed by 1 mol L$^{-1}$ $HNO_3$ and finally with de-ionized water. No frits or glass wool were necessary at either end of the column to block the PEEK-turnings. At first, the column was flushed with de-ionized water and then with IBMK. The performance of the column was stable for at least 1000 preconcentration cycles.

### 2.3. Reagents and sample treatment

All chemicals were of analytical reagent grade and were provided by Merck (Darmstadt, Germany, http://www.merck.de). Ultra-pure quality water was used throughout which was produced by a Milli-Q system (Millipore, Bedford USA, http://www.millipore.com). Working standard solutions of lead were prepared by appropriate stepwise dilution of a 1000 mg L$^{-1}$ stock standard solution (Titrisol, Merck) to the required μg L$^{-1}$ levels in 0.1 mol L$^{-1}$ $HNO_3$. The chelating reagent solution 0.5% (m/v) DDPA was prepared daily by dissolving the appropriate amount of DDPA (Aldrich) in water. IBMK was used after saturation with water. The following standard reference materials were utilized for accuracy purposes: National Institute of Standard and Technology NIST CRM 1643e (trace elements in water); International Atomic Energy Agency (IAEA) IAEA-433 (marine sediment)

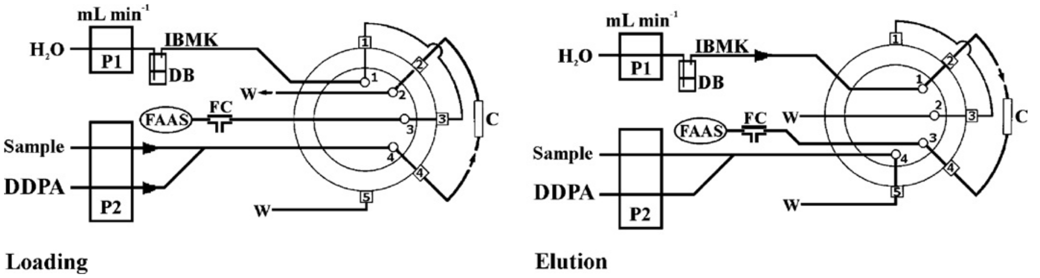

**Fig. 2.** Schematic diagram and operation sequences (loading and elution) of the on-line FI column preconcentration method for lead determination with FAAS. DDPA, complexing reagent 0.5% (m/v) DDPA; FC, flow compensation unit; P1, P2, peristaltic pumps; DB, displacement bottle for IBMK propulsion; C, micro-column packed with PEEK-turnings; W, waste.

**Table 1**
Operation sequences of the on-line FI column preconcentration method for lead determination under the optimum values.

| Step | Valve position | Pumps | | Delivered medium | Flow rate (mL min$^{-1}$) | Time (s) | Operation |
|---|---|---|---|---|---|---|---|
| | | P1 | P2 | | | | |
| 1 | Load | OFF | ON | Sample<br>0.5% (m/v) DDPA | 11.0<br>0.5 | 120 | Loading/preconcentration |
| 2 | Elute | ON | OFF | IBMK | 2.7 | 40 | Elution/measurement |

and Community Bureau of Reference Brussels, Belgium BCR 278-R (trace elements in mussel tissue).

An amount of ca. 0.2 g of certified reference materials (tissue or sediment) or 0.8 g of wet tissue samples, were precisely weighed into sealed Teflon crucibles and were wetted by nitric acid, followed by perchloric and hydrofluoric acids (only for sediments). The $HNO_3$–$HClO_4$–HF acid mixture was in a volume ratio of 3:2:1. The digestion procedure was carried out at 130–140 °C, in a stainless-steel pressurized bomb. The digestion parameters were selected according to the recommendations of the manufacture. After cooling the system the digests were properly diluted with ultra-pure water and used for the analysis. Natural water samples ground, river, costal seawater, marine sediments and mussel tissues were collected from the area of northern Greece. They were filtered through 0.45 μm membrane filters, acidified to 0.1 mol L$^{-1}$ $HNO_3$ and stored at 4 °C in acid-cleaned polyethylene bottles, in order to determine the "dissolved metal" fraction.

### 2.4. Procedure

The schematic diagram of the on-line FI manifold with the main operation parameters is presented in Fig. 2. The manifold was operated in the time-based mode. The two operation sequences and details of the FIAS-400 program are given in Table 1.

In the primary step (Fig. 1, loading), the injection valve was in the "LOAD" position. By actuating pump P2, sample solution was mixed with complexing reagent and the mixing solution passed through the column for a suitable preconcentration time (120 s). The formed metal complex was adsorbed on the surface of the PEEK-turnings. In the mean time, pump P1 was remained inactive and the nebulizer of the FAAS was aspirating air through the flow compensation (FC) adapter. For the duration of the second step, the injection valve was twisted to the "ELUTE" position, pump P1 was activated propelling the eluent IBMK through the column, while pump P2 was remaining inactive. The eluted analyte was delivered directly to the nebulizer for atomization and measurement of the absorption. In order to keep the dispersion of the analyte as low as possible, IBMK flows through the column in reverse direction than that of the sample. The recorded transient signal of the absorbance was sharp and the peak height was proportional to metal concentration in the sample. Five replicate measurements per sample were made in all instances.

### 2.5. Multivariate optimization strategy

Several factors influence the sample preconcentration by on-line SPE and an attempt to evaluate their influence on the extraction efficiency is necessary. Hence, the optimization of the system performance was studied by applying a two-level full factorial design in order to study the preliminary effects of the variable on the analytical signal as well as their interactions with each other. All major parameters in the on-line method such as loading flow rate (LFR), elution flow rate (EFR) and loading (preconcentration) time (LT) as well as chemical parameters such as sample acidity (Ac) and reagent concentration (R) were investigated in the following study. The total number of required runs is given by equation $2^n$ where $n$ is number of variables. The significant variables are found by analysis of variance (ANOVA) and using $p$-value at 95% significant level. Then the significant factors are further optimized with Doehlert design [28] as final optimization. All experiments were carried out in duplicate, using 200 μg L$^{-1}$ Pb solution. Then the Lagrange's criterion equation [25,26,31] was used for the determination of the critical point of the second order equation and is based on the calculation of the Hessian determination of response. The experimental data were processed by using Statistica 6.0 software [32].

## 3. Result and discussion

### 3.1. Optimization study of the experimental parameters

At the beginning, a $2^5$-level full experimental design was set up. High (+) and low (−) levels of the five studied factors were: acidity (Ac), 0.02 and 0.0001 mol L$^{-1}$; DDPA (R), 0.2% (m/v) and 0.01% (m/v); loading flow rate (LFR), 12.0 and 6.0 mL min$^{-1}$; elution flow rate (EFR), 3.6 and 1.8 mL min$^{-1}$ and loading time (LT) 120 and 30 s. The total number of experiments was 32 for the five factors and each experiment was carried out in duplicate. The experimental matrix of the $2^5$ factorial design together with the recorded mean absorbance are given in Table 2. Table 3 reports the analysis of variance (ANOVA) in order to evaluate the significance of the main effects as well as the interaction effects. As it is shown, all the parameters were proved significant except the elution flow rate (EFR), which was proved to be insignificant factor in the studied range. This may be attributed to the fact that the investigated elution flow range is limited only to the range that is capable to manage

**Table 2**
The experimental matrix of $2^5$ full factorial design and the obtained analytical responses.

| Experiment | Ac | R | LFR | EFR | LT | Mean absorbance |
|---|---|---|---|---|---|---|
| 1 | – | – | – | – | – | 0.018 |
| 2 | – | – | – | – | + | 0.015 |
| 3 | – | – | – | + | – | 0.033 |
| 4 | – | – | – | + | + | 0.019 |
| 5 | – | – | + | – | – | 0.018 |
| 6 | – | – | + | – | + | 0.035 |
| 7 | – | – | + | + | – | 0.026 |
| 8 | – | – | + | + | + | 0.033 |
| 9 | – | + | – | – | – | 0.026 |
| 10 | – | + | – | – | + | 0.064 |
| 11 | – | + | – | + | – | 0.021 |
| 12 | – | + | – | + | + | 0.056 |
| 13 | – | + | + | – | – | 0.048 |
| 14 | – | + | + | – | + | 0.116 |
| 15 | – | + | + | + | – | 0.050 |
| 16 | – | + | + | + | + | 0.105 |
| 17 | + | – | – | – | – | 0.030 |
| 18 | + | – | – | – | + | 0.018 |
| 19 | + | – | – | + | – | 0.038 |
| 20 | + | – | – | + | + | 0.018 |
| 21 | + | – | + | – | – | 0.030 |
| 22 | + | – | + | – | + | 0.027 |
| 23 | + | – | + | + | – | 0.029 |
| 24 | + | – | + | + | + | 0.029 |
| 25 | + | + | – | – | – | 0.031 |
| 26 | + | + | – | – | + | 0.080 |
| 27 | + | + | – | + | – | 0.032 |
| 28 | + | + | – | + | + | 0.068 |
| 29 | + | + | + | – | – | 0.053 |
| 30 | + | + | + | – | + | 0.134 |
| 31 | + | + | + | + | – | 0.058 |
| 32 | + | + | + | + | + | 0.129 |

with nebulizer uptake. Among the second order interactions, that of reagent concentration and sample loading time (R *by* LT) was the most significant at this probability level. This is attributed to the fact that an increase of the loading time and decrease of the reagent concentration may lead to increased analyte losses due to lack of complexing reagent and reduction of column retention efficiency.

Following the results of the previous design ($2^5$-level full experimental design), the elution flow rate (EFR) was kept constant at 2.7 mL $\text{min}^{-1}$, and subsequently a $2^4$-level full factorial design was applied for the remaining four significant factors at different optimization range. In this case the studied two levels of the factors were: Ac, 0.1 and 0.05 mol $\text{L}^{-1}$; R, 0.4% (m/v) and 0.2% (m/v); LFR, 13.0 and 11.0 mL $\text{min}^{-1}$ and loading time (LT) 150 and 120 s. The experimental matrix of factorial design with the recorded analytical responses is given in Table 4. ANOVA analysis was also carried out and the results are given in Table 5. In this case, the effect of sample acidity (Ac) and the loading flow rate (LFR) was not significant in the range 0.05–0.10 mol $\text{L}^{-1}$ $HNO_3$ and 13.0–11.0 mL $\text{min}^{-1}$ respectively. In contrast, the influence of the reagent concentration (R) and sample loading time (LT) were significant at the 95% probability level.

**Table 3**
Analysis of variance (ANOVA) results for effect of the variables.

| Factors and interactions | SS | df | MS | $F_{exp}$ | *p* |
|---|---|---|---|---|---|
| Ac | 504.03 | 1 | 504.03 | 17.2872 | 0.000741 |
| R | 13489.03 | 1 | 13489.03 | 462.6463 | 0.000000 |
| LFR | 3982.78 | 1 | 3982.78 | 136.6013 | 0.000000 |
| EFR | 0.78 | 1 | 0.78 | 0.0268 | 0.872023 |
| LT | 5330.28 | 1 | 5330.28 | 182.8178 | 0.000000 |
| Ac *by* R | 205.03 | 1 | 205.03 | 7.0322 | 0.017404 |
| Ac *by* LFR | 0.28 | 1 | 0.28 | 0.0096 | 0.922981 |
| Ac *by* EFR | 0.28 | 1 | 0.28 | 0.0096 | 0.922981 |
| Ac *by* LT | 3.78 | 1 | 3.78 | 0.1297 | 0.723464 |
| R *by* LFR | 2574.03 | 1 | 2574.03 | 88.2840 | 0.000000 |
| R *by* EFR | 140.28 | 1 | 140.28 | 4.8114 | 0.043391 |
| R *by* LT | 6583.78 | 1 | 6583.78 | 225.8103 | 0.000000 |
| LFR *by* EFR | 0.28 | 1 | 0.28 | 0.0096 | 0.922981 |
| LFR *by* LT | 1092.78 | 1 | 1092.78 | 37.4802 | 0.000015 |
| EFR *by* LT | 94.53 | 1 | 94.53 | 3.2422 | 0.090642 |
| Error | 466.50 | 16 | 29.16 | | |
| Total SS | 34468.47 | 31 | | | |

SS, sum of square; df, degrees of freedom; MS, mean squares.

**Table 4**
The experimental matrix of $2^4$ full factorial design and the obtained mean analytical responses.

| Experiment | Ac | R | LFR | LT | Mean absorbance |
|---|---|---|---|---|---|
| 1 | – | – | – | – | 0.118 |
| 2 | – | – | – | + | 0.119 |
| 3 | – | – | + | – | 0.117 |
| 4 | – | – | + | + | 0.122 |
| 5 | – | + | – | – | 0.163 |
| 6 | – | + | – | + | 0.172 |
| 7 | – | + | + | – | 0.167 |
| 8 | – | + | + | + | 0.166 |
| 9 | + | – | – | – | 0.122 |
| 10 | + | – | – | + | 0.126 |
| 11 | + | – | + | – | 0.124 |
| 12 | + | – | + | + | 0.127 |
| 13 | + | + | – | – | 0.163 |
| 14 | + | + | – | + | 0.166 |
| 15 | + | + | + | – | 0.160 |
| 16 | + | + | + | + | 0.168 |

**Table 5**
Analysis of variance (ANOVA) results for effect of the four factors and their second order interactions.

| Factors and interactions | SS | df | MS | $F_{exp}$ | *p* |
|---|---|---|---|---|---|
| Ac | 2.250 | 1 | 2.250 | 0.2228 | 0.656816 |
| R | 7744.000 | 1 | 7744.000 | 766.7327 | 0.000001 |
| LFR | 2.250 | 1 | 2.250 | 0.2228 | 0.656816 |
| LT | 100.000 | 1 | 100.000 | 9.9010 | 0.025477 |
| Ac *by* R | 56.250 | 1 | 56.250 | 5.5693 | 0.064756 |
| Ac *by* LFR | 1.000 | 1 | 1.000 | 0.0990 | 0.765728 |
| Ac *by* LT | 12.250 | 1 | 12.250 | 1.2129 | 0.320934 |
| R *by* LFR | 12.250 | 1 | 12.250 | 1.2129 | 0.320934 |
| R *by* LT | 1.000 | 1 | 1.000 | 0.0990 | 0.765728 |
| LFR *by* LT | 0.250 | 1 | 0.250 | 0.0248 | 0.881141 |
| Error | 50.500 | 5 | 10.100 | | |
| Total SS | 7982.000 | 15 | | | |

Finally, according to the results of the previous 4-factor factorial, a Doehlert design for the remaining two significant factors was employed. In this design the acidity of Pb(II) solution was kept constant at 0.10 mol $\text{L}^{-1}$ $HNO_3$ while the loading flow rate was adjusted at 11.0 mL $\text{min}^{-1}$. The final optimization of reagent (DDPA) concentration and loading time (LT) should be carried out with a second-order design, such as Doehlert matrix for obtaining the response surface. Table 6, presents the seven experiments

**Table 6**
Doehlert matrix design for optimization of the DDPA reagent concentration (R) and loading time (LT) in the proposed method for lead determination.

| Experiment | R | LT | Absorbance |
|---|---|---|---|
| 1 | 0.2 | 150 | 0.118 |
| 2 | 0.3 | 130 | 0.134 |
| 3 | 0.3 | 170 | 0.157 |
| 4 | 0.4 | 150 | 0.17 |
| 5 | 0.5 | 130 | 0.166 |
| 6 | 0.5 | 170 | 0.188 |
| 7 | 0.6 | 150 | 0.178 |

**Table 7**
Analytical results for lead determination in certified reference materials with the proposed method.

| Certified reference material | Unit | Certified (range) | Found[a] | Recovery (%) |
|---|---|---|---|---|
| CRM 1643e (trace element water) | $\mu g\,L^{-1}$ | 19.63 ± 0.21 | 19.1 ± 0.7 | 97.3 |
| IAEA-433 (marine sediment) | $mg\,kg^{-1}$ | 26.0 (25.4–26.6) | 25.1 ± 1 | 96.5 |
| BCR 278-R (mussel tissue) | $mg\,kg^{-1}$ | 2.00 ± 0.04 | 1.9 ± 0.2 | 95.0 |

[a] Mean value ± standard deviation based on three replicates ($n = 3$).

which were carried out based on Doehlert matrix structure (Fig. 3). In this experiment four levels used for the reagent concentration variable and three for the loading time. The following quadratic Eq. (1), predicts the relation between the studied variables and the response surface:

$$\mathrm{Abs} = -0.2537 + 0.61125\,[\mathrm{DDPA}] + 0.00305\,\mathrm{LT} - 0.55\,[\mathrm{DDPA}]^2 - 0.000008\,\mathrm{LT}^2 - 0.000125\,[\mathrm{DDPA}]\,\mathrm{LT} \quad (1)$$

The surface response was obtained based on the above given quadratic model (Eq. (1)) obtained from analysis data of Doehlert matrix. Then it is possible to apply Lagrange's criterion for this equation to show that:

$$\mathrm{H}([\mathrm{DDPA}]_0,\ \mathrm{LT}_0) = 0.0000176 > 0$$

$$\frac{\partial^2(\mathrm{Abs})}{\partial[\mathrm{DDPA}]^2} = -1.10 < 0$$

$$\frac{\partial^2(\mathrm{Abs})}{\partial \mathrm{LT}^2} = -0.000016 < 0$$

Thus, there is a maximum point and in order to calculate it the following system of equations has to be resolved:

$$\frac{\partial(\mathrm{Abs})}{\partial(\mathrm{DDPA})} = 0.61125 - 1.1\,[\mathrm{DDPA}] - 0.000125\,\mathrm{LT} = 0 \quad (2)$$

$$\frac{\partial(\mathrm{Abs})}{\partial \mathrm{LT}} = 0.00305 - 0.000016\,\mathrm{LT} - 0.000125\,[\mathrm{DDPA}] = 0 \quad (3)$$

The solution of Eqs. (2) and (3) gives the maximum points of [DDPA] and LT which were 0.53% (m/v) and 186.4 s respectively. As a result the optimum concentration of the DDPA was 0.5% (m/v) and the optimum loading time 186 s (~3 min). However, as a compromise to have a reasonable total cycle time for the analysis, the adopted loading time was 120 s. Nevertheless, when a very low concentration sample is to be analyzed, the loading time can be extended up to 8 min, using in this case a separate calibration curve.

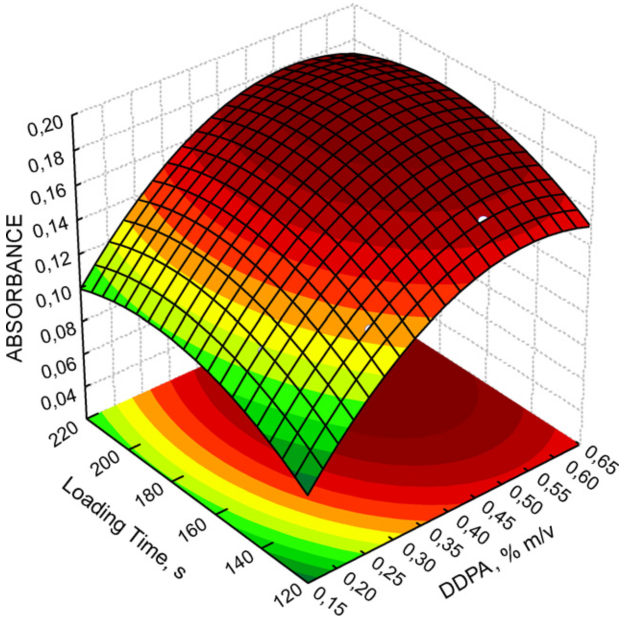

**Fig. 3.** Response surface obtained using Doehlert matrix to optimize reagent concentration and sample loading time.

### 3.2. *Interference studies*

In order to evaluate the selectivity of the proposed on-line preconcentration system the interference effect of various elements was investigated using the proposed method on the determination of 30.0 $\mu g\,L^{-1}$ Pb(II), taking as a criterion for an interference the deviation of the percentage recovery more than ±5%. High concentrations of alkali and alkaline earth metals, which are abundant usually found in high concentrations in natural waters and other samples, were tested. $Na^+$, $K^+$ $Ca^{2+}$, $Mg^{2+}$ and $Ba^{2+}$ up to 1000 $mg\,L^{-1}$ did not caused any interference. Also NaCl did not interfere at concentrations up to 35 $g\,L^{-1}$. The recovery of the analytes was tested in presence of the most common of transition metals.

The tolerable concentrations of Al(III), Cr(III), Fe(III) and Mn(II) was 10 $mg\,L^{-1}$. Also for Zn(II) and Ni(II) was 3.0 $mg\,L^{-1}$, for Co(II), Cu(II), was 1.0 $mg\,L^{-1}$ and for Cd(II) and Hg(II) was 0.5 $mg\,L^{-1}$.

### 3.3. *Figures of merit and validation of the on-line method*

The analytical performance of the developed on-line method, under the optimized conditions, show good correlation coefficient ($r > 0.999$) within a linear range from 3.6 up to 300 $\mu g\,L^{-1}$. For a preconcentration time of 2 min, the detection limit, calculated by 3 s criterion, was found to be $c_L = 0.32\ \mu g\,L^{-1}$, while the quantification limit was $c_Q = 3.6\ \mu g\,L^{-1}$ and calculated as the concentration that gives a response equivalent to 10 times the standard deviation of the blank ($n = 12$) and defines the lower limit of the linear range. The regression equation of the calibration curve was calculated as $A = 0.0014 + 0.0010[\mathrm{Pb(II)}]$ ($\mu g\,L^{-1}$, $n = 5$). By using direct aspiration of aqueous standard solutions into FAAS without preconcentration the calibration curve was calculated as $A = 0.0012 + 0.00909[\mathrm{Pb(II)}]$ ($mg\,L^{-1}$, $n = 5$). The enhancement factor, calculated as the ratio of the slopes of calibration curves with and without preconcentration, was 110 and the sampling frequency was 20 $h^{-1}$. The precision of the method evaluated as relative standard deviation (RSD), was $s_r = 2.2\%$, calculated from 11 replicate measurements at the 50.0 $\mu g\,L^{-1}$ concentration level of Pb(II).

The accuracy of the proposed method was evaluated, by determining the lead concentration of the certified reference material NIST CRM 1643e (trace elements in water); IAEA-433 (marine sediment) and BCR 278-R (mussel tissue). The certified values and the analytical results are listed in Table 7. The obtained recovery was ranged from 95.0 to 97.3% showing that the proposed method is suitable for water, sediment and biological tissues analysis.

The proposed method was applied also to the analysis of local natural water samples, marine sediments and mussel tissues. The recovery (R) was evaluated by adding known volume of standard solutions of analytes in the examined samples. The recovery was calculated from the "added" samples after subtraction of the con-

**Table 8**
Analytical results for determination of lead in environmental and biological samples.

| Sample | Unit | Added | Found[a] | Recovery (%)[b] |
|---|---|---|---|---|
| Ground water | $\mu g\,L^{-1}$ | 0 | $<c_L$ | |
| | | 30.0 | 29.3 ± 0.1 | 97.7 |
| River water | $\mu g\,L^{-1}$ | 0 | 3.5 ± 0.2 | |
| | | 30.0 | 32.5 ± 2 | 96.7 |
| Coastal seawater | $\mu g\,L^{-1}$ | 0 | 4.8 ± 0.3 | |
| | | 30.0 | 34.0 ± 3 | 97.3 |
| Coastal marine sediment DW[c] | $mg\,kg^{-1}$ | 0 | 95 ± 7 | |
| | | 50.0 | 143 ± 12 | 96 |
| Mussel tissue FW[d] | $mg\,kg^{-1}$ | 0 | 0.57 ± 0.06 | |
| | | 2.0 | 2.5 ± 0.2 | 96.5 |

[a] Mean value ± standard deviation based on three replicates ($n = 5$).
[b] Recovery obtained from spiked samples.
[c] Dry weight.
[d] Fresh weight.

**Table 9**
Features of selected on-line solid phase extraction methods for lead determination by FAAS and comparison with the proposed method using PEEK-turning as sorbent material.

| Sorbent material | Reagent | Eluent | EF | $f$ ($h^{-1}$) | PT (s) | $c_L$ ($\mu g\,L^{-1}$) | Linear range ($\mu g\,L^{-1}$) | $s_r$ (%) | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| MW carbon nanotubes | – | $HNO_3$ | 44.2 | 14 | 240 | 2.6 | 8.6–775 | 7.7 | [10] |
| PCTFE-beads | APDC | IBMK | 220 | 30 | 90 | 1.2 | 3.0–150 | 2.1 | [11] |
| MCR-resin DDTC functionalized | – | Methanol (acidified) | 48 | 20 | 120 | 1.3 | –400 | 1.4 | [12] |
| MCR-resin DDTC sorbed | – | Methanol (acidified) | 27 | 20 | 120 | 3.0 | –400 | 4.4 | [12] |
| PTFE-fiber | Acrylic acid | $HNO_3$ | 49 | 55 | 60 | 0.26 | 2.5–250 | 1.9 | [20] |
| PUF-loaded | TAM | HCl | 45 | 27 | 120 | 2.2 | 1.0–150 | 6.8 | [16] |
| PUF | APDC | IBMK | 131 | 36 | 60 | 1.8 | 3.0–250 | 3.4 | [17] |
| PTFE-turnings | APDC | IBMK | 330 | 15 | 180 | 0.8 | 1.6–100 | 2.6 | [19] |
| $C_{18}$ | DDTP | Ethanol | 166 | – | 750 | 1.8 | 5.0–50 | 4.6 | [33] |
| Chromosorb 102 | DDTC | Ethanol | 25.4 | – | 120 | 2.5 | 50–600 | < 4 | [34] |
| PEEK-turnings | DDPA | IBMK | 110 | 20 | 110 | 0.32 | 3.6–300 | 2.2 | This work |

EF, enhancement factor; $f$, sampling frequency; PT, preconcentration time; $c_L$, detection limit; $s_r$, relative standard deviation; MW, multiwall; PCTFE, poly(chlorotrifluroethylene), ADPC, ammonium pyrrolidine dithiocabamate; DDTC, diethyl-dithiocarbamate; MCR, merrifield chloromethylated resin; TAM, 2-(thiazolylazo)-5-dimethylaminophenol.

centration found in "not spiked" samples. The obtained results are presented in Table 8, and the recoveries were satisfactory (95.5–97.7%).

For comparative purposes, the performance characteristics of the proposed method and other selected on-line solid phase extraction (SPE) preconcentration methods coupled with FAAS, reported in the literature are given briefly in Table 9. The proposed method shows good sensitivity and precision with reasonable preconcentration time.

## 4. Conclusions

In the present work, the applicability of PEEK-turnings as sorbent material was presented for the first time. A FI on-line solid phase extraction method using a micro-column filled with PEEK-turnings was developed for flame atomic absorption spectrometric determination of lead in environmental and biological samples. The highlight of the proposed method is related to the excellent resistivity on chemicals, hydrophobic nature as well as simplicity of the manifold. The proposed column is free from regeneration necessity. PEEK-turnings is a very promising sorbent material in the field of on-line preconcentration and analytical separations due to their chaotic geometry and the large surface area which is offered. It has been also indicated that samples with difficult matrices, like seawaters and tissues digests could be analyzed successfully by the proposed method.

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