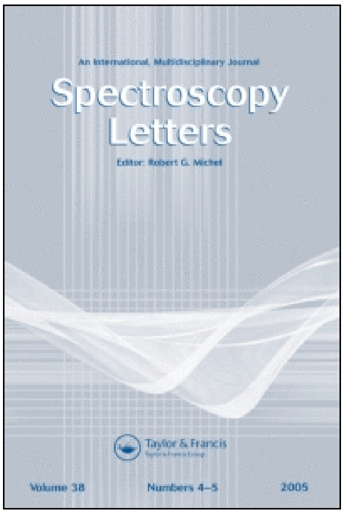

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PAN-Doped SiO_2 as a New Packing Material for the Online Preconcentration and Determination of Trace Lead (II) in Biological and Environmental Samples Using Flame Atomic Absorption

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ABSTRACT A flow injection online preconcentration and separation–FAAS method was developed for determination of trace lead in biological and environmental samples. Effects of chemicals and flow variables were studied. Under the optimal conditions, the enhancement factor can reach 101 with a sample consumption of 6.5 mL and throughput of 45 hr^{-1}. The detection limit (3σ) was 0.24 $\mu g\,L^{-1}$. At the level of 20 $\mu g\,L^{-1}$ and 40 $\mu g\,L^{-1}$ of Pb (II), the precisions (RSD, $n = 11$) were found to be 2.2% and 1.2%, respectively. The spike recoveries of real samples were in the range of 97–103%.

KEYWORDS 1-(2-pyridylazo)-2-naphthol, flame atomic absorption spectrometry, lead, online preconcentration, silica gel

INTRODUCTION

Lead is one of the most ubiquitous elements in the environment and recognized as a major health risk to humans and animals.[1,2] The determination of trace levels of lead in a variety of samples is very important in ecological and hygienic pollution and the monitoring of environmental pollution because of its high-toxicity, accumulative, and persistent character in the environment and living organism.[3] Flame atomic absorption spectrometry (FAAS) with its relative low cost and good analytical performance is nowadays the main instrument for the purpose. Though FAAS offers fast elemental analysis in the research laboratories, the direct determination of trace metals in water systems remains a challenge because of their low concentrations, interferences of the matrix, and the instruments' poor sensitivity. Therefore, preconcentration and separation procedures, including liquid–liquid extraction,[4] co-precipitation,[5] cloud point extraction,[6] electrodeposition,[7] solid-phase extraction (SPE),[8] and the like, are often necessary. Among these, SPE, especially in conjunction with a flow injection (FI) system based on the use of a microcolumn packed with solid sorbent,

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is one of the important enrichment techniques and most commonly employed for trace-metal preconcentration due to advantages such as high efficiency, simplicity, avoidance of solvent exposure, and the possibility of combination with atomic absorption spectrometry (AAS), permitting higher enrichment factors with higher sample throughput.[9]

1–(2–Pyridylazo)–2–naphthol (PAN) has two functional groups −N= and −OH for ion exchange and/or complexation of metal ions and has been applied to extraction–complexation of metal ions.[10–14] Also, it is used as a modifier loaded on solid-phase extractants, such as polyethylene powder,[15] microcrystalline naphthalene,[16] resin,[17] titanium dioxide,[18] chromosorb–106 resin,[19] and PTFE knotted reactor[20] to preconcentrate trace elements. Silica gel is a frequently used as sorbent due to its good physical and chemical properties such as porosity, high surface area, negligible capacity to resist swelling or shrinking with change in solvent conditions to withstand high linear flow rates.[21] In most of the previous studies, silica gel was loaded or functionalized with various ligands like diethyldithiocarbamate,[22] macrocycle,[23] 2–mercaptobenzothiazole,[24] 2,4,6-trimorpholino-1,3,5-triazine,[25] glycerol,[26] cadion 2B,[27] Tris(2-aminoethyl) amine,[28] aspergillus niger,[29] nitroso-R-salt,[30] 1-(2-thiasolylazo)-2-naphthol,[31] and the like, in order to develop chelating and selective sorbents for online and off-line preconcentration and separation procedures. Moreover, it has a large molecule that can be securely entrapped inside the pores of silica gel and exhibits reasonable stability.[32,33] PAN-doped silica gel has been investigated as a sorbent for the removal of metal ions from aqueous media and proved to possess several advantages including (1) high rate of attainment of equilibrium; (2) high stability towards temperature and medium; and (3) easy regeneration and complete recovery of sorbed metal ions.[33] However, the procedures in some of the reported studies are tedious and time consuming or chemical consuming, and its use as a packing material in FI online microcolumn preconcentration and separation for AAS determination of trace metals is rare. Thus, in the present work, we report the application of PAN-doped silica gel as an SPE material for the online preconcentration and fast determination of Pb ion by FAAS in environmental samples. Several analytical parameters relevant to the retention, elution, and quantitative recoveries of analyte were examined.

MATERIALS AND METHODS

Apparatus

TAS 990 atomic absorption spectrometer (Beijing Purkinje General Instrument Co., Ltd., Beijing, China) equipped with hollow cathode Lead lamp (Beijing ShuGuangMing Electronic Lighting Instrument Co., Ltd., Beijing, China) was used for the element determination under the following conditions: wavelength was 283.3 nm, both slit widths were 0.4 nm. The flame conditions (2.2-L-min^{-1} acetylene and 9.4-L-min^{-1} air) were employed according to the standard recommendations. The peak height absorbance was used for quantitative analysis.

A model FIA-3100 flow injection system (Vital Instruments Co., Ltd., Beijing, China) consists of two peristaltic pumps and a standard rotary injection valve (eight ports on the rotor and eight ports on the stator). It was employed for the FI online SPE. The microcolumn that we used to capture the analyte in aqueous solution was made of a PTFE tube with an effective length of 1 cm and an inner diameter of 2 mm. Tygon pump tubings (Vital Instruments Co., Ltd., Beijing, China) were used to deliver samples and reagents. The rotation speed of the two peristaltic pumps, their stop and go intervals, and the actuation of the injection valve were all programmed (Table 1). Polytetrafluoroethylene tubings (0.5-mm i.d.) were used for all connections. These connections were kept as short as possible to minimize the dead volumes.

TABLE 1 Operational Sequence and the Preferences of the Fi Online Preconcentration System Coupled With FAAS

			Pumped medium		Flow rate (mL · min^{-1})		
Step	Function	Time (s)	Pump 1	Pump 2	Pump 1	Pump 2	Valve position
1 (Fig. 1a)	Sampling	60	—	Sample	Off	6.5	Fill
2 (Fig. 1b)	Elution	20	0.8-mol-L^{-1} HCl	—	4.3	Off	Injection

A Model Qwave-2000 microwave digestion system (Questron Co., Mississauga, Canada) was used to digest the samples. All instrumental parameters for the sample digestion were chosen according to the recommendations of EPA.

For pH measurements, a Delta320 METTLER (Mettler Toledo, United States) pH meter was used.

Reagents and Materials

All reagents (Sinopharm Chemical Reagent Co., Ltd., China) that we used had the highest available purity and were at least of analytical grade. Doubly deionized water (DDW, $18.2\,\mathrm{M\Omega\,cm^{-1}}$) obtained from a WaterPro water system (Labconco Corporation, Kansas City, MO, United States) was used throughout the experiments. Standard Pb (II) solutions were prepared daily by appropriate dilution of a stock solution ($1000\,\mathrm{mg\,L^{-1}}$; NRCSM, Beijing, China) with DDW. The working solutions were prepared by series dilution of the stock solution immediately prior to their use.

The certified reference materials (CRM; NRCSM, Beijing, China)—GBW07605 (bush branches and leaves) and GBW 07602 (tea leaves)—were analyzed to check the accuracy of the developed method.

Sample Preparation

Certain amounts of the sample (0.2000 g for bush leaves and branches and 0.2006 g for tea leaves) were mixed with 5 mL of concentrated HNO_3 and 2 mL $HClO_4$, digested with Qwave-2000 microwave digestion system, and gently heated on a hot-plate until white fumes appeared. After cooling, the clear digest was adjusted to the optimal pH range with buffer solution and then diluted to an appropriate volume for the determination of Pb (II).

Preparation of PAN/SiO$_2$

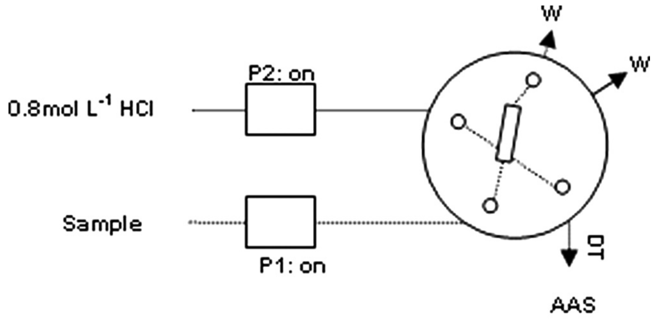
The preparation of PAN-doped sol–gel was conducted according to the previous studies.[31] In a 200-ml beaker, 10.0 ml of tetraethoxysilane, 10.0 ml of double distilled water, and 25-ml ethanol solution of PAN in the presence of 10^{-2}-mol · L^{-1} ammonium fluoride as a catalyst were mixed, allowed to gel, and dried in oven to constant weight. After drying, the glasses were crushed and sieved with 80 and 100 meshes. The sieved glasses were thoroughly washed with 0.8-mol · L^{-1} HCl and subsequently with distilled water to remove the undoped reagent. The entrapped PAN on the sorbent was $20\,\mathrm{mg\,g^{-1}}$ by spectrophotometric determination. The obtained material was denominated as PAN/SiO_2.

Microcolumn Preparation

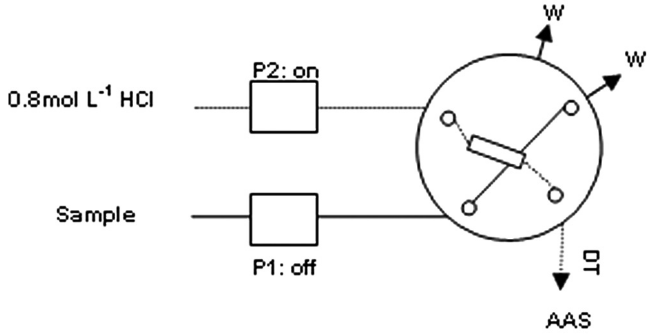
45 Mg of PAN/SiO_2 were packed into the microcolumn. The microcolumn was end-capped with glass wool (to prevent the sorbent from being swept out by a liquid flow) and connected to the injector valve. The packed column was sequentially washed with DDW, 0.8-mol-L^{-1} HCl, and DDW until no lead signal was detected with AAS.

Procedures

The FI manifold and its operation sequence for the online SPE are shown in Fig. 1 and Table 1, respectively. In Step 1 (Fig. 1a), Pump 1 was activated so that the sample solution was loaded onto the microcolumn; the effluent from the column was flowing to waste. At the same time, Pump 2 started to introduce diluted HCl solution to FAAS for baseline. In Step 2



(a) Sample Loading



(b) Elution

FIGURE 1 Manifold for the FI online SPE coupled with FAAS system for lead determination. AAS, atomic absorption spectrometry; P1 and P2, peristaltic pumps; DT, delivery tubing; W, waste. Valve position, (a) Sample loading, (b) Elution.

(Fig. 1b), Pump 2 started to work while Pump 1 was stopped and the injection valve turned to the inject position to introduce diluted HCl solution for eluting the analytes retained on the column.

RESULTS AND DISCUSSION

Stability of the Sorbent

The stability of the PAN doped on silica gel was checked by repeatedly eluting the PAN/SiO_2 column with 10 ml of 1.0-M HCl. The eluent was determined by spectrophotometric technique for the determination of leached dye in the eluting. The results showed that PAN/SiO_2 could tolerate at least 50-fold washing and that the PAN was not washed by the mobile phase and was stable on the surface of silica gel.

Optimization of the FI Online Preconcentration System

To optimize the system, the main efforts were focused on the conditions for sample loading (sample acidity, sample loading time and rate) and Pb (II) eluting from the column (wash medium, elution rate, and eluent concentration) in order to obtain highly sensitive, accurate, and reproducible results.

The influence of sample acidity on the preconcentration efficiency of Pb (II) was examined in pH values of 1.3–11.0 (adjusted with diluted HNO_3, NaOH for pH 1–2, NaOH and potassium hydrogen phthalate solution for pH 3–6, and boric acid and sodium hydroxide for pH 7–11) with an ionic strength of 0.3 mmol, at a sample loading rate of 4.5 mL min^{-1} with 60-s preconcentration for 20-µg-L^{-1} Pb. Fig. 2 describes the relationship between the peak height absorbance signal of lead and the pH of the sample. Clearly, the optimum pH of the sample range was quite wide, ranging from 2.5 to 5.0. The lower absorbance signal may result from the decrease in the formation constant of Pb(II)–PAN complex owing to the protonation of PAN in a lower pH values ($pH < 2$) solution, and the reaction of Pb (II) with hydroxyl ions at higher pH values ($pH > 6$). For the work, a pH of 3.5 in the sample was selected.

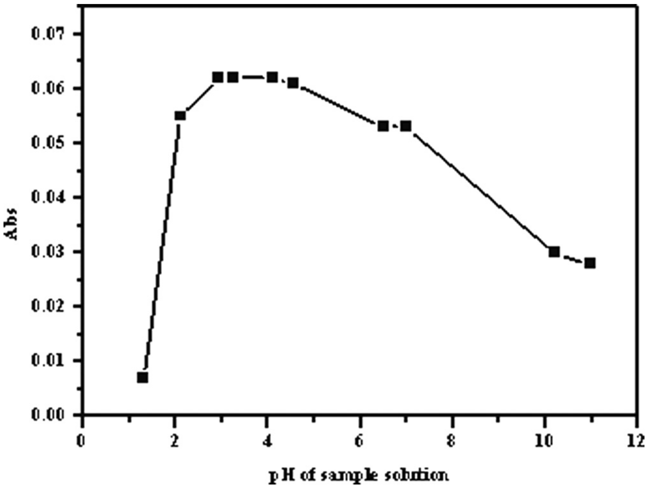


FIGURE 2 Effect of sample acidity. Abs, absorbance. Operation conditions: 20 µg L^{-1}. Lead (II); 4.5 mL · min^{-1} preconcentration flow rate: 60 s preconcentration time and 4.3 mL · min^{-1} eluent (0.8 mol L^{-1} HCl) elution flow rate.

The effect of sample loading rate was tested using a standard solution of 20-µg-L^{-1} Pb with 60-s preconcentration. Peak height absorbance was found to increase linearly with the sample loading rate up to at least 6.9 mL min^{-1}. This indicates that the kinetic property of PAN/SiO_2 is sufficiently favorable to allow easy retention of the analyte. In the next part of the experiments, 6.5 mL min^{-1} was selected as the optimized sampling rate. Under the optimized sampling rate, a linear increase in peak height for 20-µg-L^{-1} Pb was observed with increasing sample loading time up to at least 110 s. It is worthwhile to note that the present column preconcentration system permits the use of high sample loading rates to achieve high enrichment factors within a defined time period due to its favorable kinetics and low hydrodynamic impedance. Higher sensitivity enhancements could also be obtained through increasing the sample loading time; however, the loading time selected in the experiment was 60 s in order to achieve a high sampling frequency with a reasonable degree of sensitivity.

The choice of a suitable eluent with an appropriate concentration and flow rate is important for the analytical performance of the FI online preconcentration AAS system. In a preliminary study for this work, 0.5-mol-L^{-1} HCl, HNO_3, and H_2SO_4 solutions (as the adsorption of Pb at $pH < 1$ can be negligible) at a flow rate of 4.3 mL min^{-1} were used for desorption of the retained Pb from the microcolumn, respectively. The results showed that the optimal elution was HCl. Therefore, HCl was selected for the further experiments. Various concentrations and flow rates of HCl were used for the check of the

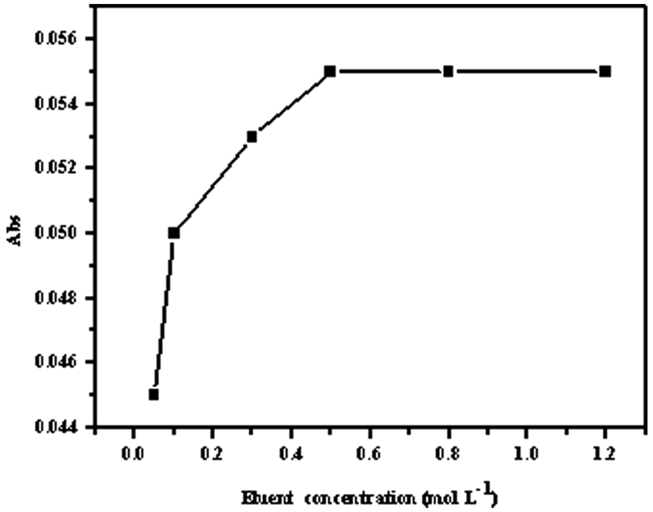


FIGURE 3 Effect of eluent concentration. Operation conditions: The sample pH was 3.5. Other conditions were the same as in Figure 2.

influent of eluent concentration and flow rate (the results are shown in Fig. 3 and Fig. 4). It was found that the peak height absorbance of lead increased significantly, and no stable absorbance was obtained as the concentration of HCl incremented from 0.1 to 0.5 mol L^{-1} (as shown in Fig. 3). However, a plateau in absorbance reached with a further increase in HCl concentration. A sampling rate of 0.8-mol-L^{-1} HCl was selected. The influence of eluent flow rate was checked in the range of 2.5–10.8 mL min^{-1}. The results showed (Fig. 4) that the peak height absorbance of lead increased in the initial stage owing to the increase in the Pb (II) desorbed from the sorbent. A plateau in absorbance was also obtained at the flow rate of 4.0–6.2 mL min^{-1}. Nevertheless, a decreasing trend in absorbance of lead appeared at the higher flow rate. Low absorbance of lead at high eluent flow rate could result from the dilution of analyte by the large amount of eluent. So, a flow rate of 4.3 mL min^{-1} was selected for the elution of retained Pb (II). Under optimized conditions, the column can be reused for at least 20 instances of preconcentrations and elutions without decreasing the enrichment factor of the solid phases. It was noted that the use of strong acid HCl as eluent may cause some problems such as the corrosion of the injection valve or the nebulizer, so timely and thorough washing of the valve and nebulizer with DDW after experiments is strongly recommended.

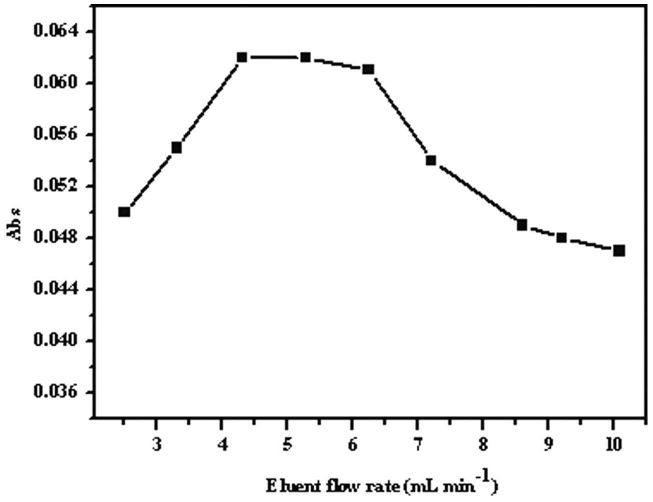


FIGURE 4 Effect of eluent flow rate. Operation conditions were the same as in Figure 3 except eluent flow rate.

Interference Studies

The influence of matrix ions in water samples on the recovery of Pb (II) ions was also investigated. No significant interferences from large amounts of alkaline or alkaline earth metal ions (1000-fold) were observed under the optimized conditions given in Table 1 and Fig. 1. The tolerable concentrations of transition ions such as Cd(II), Cu(II), Fe(III), Fe(II), Co(II), Ni(II), Mn(II), Ag(I), and Zn(II) for the determination were found to be 5.0, 5.0, 1.0, 3.0, 3.0, 5.0, 5.0, 4.0, and 6.0 mg L^{-1}, respectively.

Performance of the FI Online Preconcentration System and Application to the Sample Analysis

The analytical characteristic performance data for the FI online SPE coupled with FAAS system were

TABLE 2 Analytical Performance of FI Online Preconcentration System Under the Conditions in Table 1

Parameter	Performance
Preconcentration time (s)	60
Enhancement factor (samples hr^{-1})	101
Sampling frequency (hr^{-1})	45
Sample consumption (mL)	6.5
Eluent flow rate ($mL \cdot min^{-1}$)	4.3
Precision (RSD, $n = 11$) (%)	2.2 (20 $\mu g \cdot L^{-1}$) and 1.2 (40 $\mu g\, L^{-1}$)
Detection limit (3σ) ($\mu g \cdot L^{-1}$)	0.24
Range of calibration graph ($\mu g \cdot L^{-1}$)	1.0–60
Calibration function (n = 6) (*A*, peak height absorbance, *C* in $\mu g \cdot L^{-1}$)	$A = 0.0014 + 0.0031 \times C$
Correlation coefficient	0.9993

TABLE 3 **Analytical Results (Mean ± s, n = 3) for the Determination of Trace Lead in Real Samples**

Sample	Unit	Concentration			Recovery (%)
		Certified	Determined	Added	
GBW 07602	µg g^{-1}	7.1 ± 1.1	7.0 ± 1.0	10	99
GBW07605	µg g^{-1}	4.4 ± 0.3	4.2 ± 0.2	5	102
Tap water	µg L^{-1}	—	1.6 ± 0.7	2	103
Mineral water	µg L^{-1}	<1000	4.21 ± 0.33	5	97
Ground water	µg L^{-1}	—	7.76 ± 0.78	5	99

presented in Table 2. With a sample loading time of 60 s at a sample loading flow rate of 6.5 mL min^{-1}, the enhancement factors were 101 at a sample throughput of 45 hr^{-1} compared with the conventional FAAS method. The detection limits (3σ) were 0.24 µg L^{-1}. The precision (RSD, n = 11) were found to be 2.2% and 1.2% at the level of 20 µg L^{-1} and 40 µg L^{-1} of Pb(II), respectively.

To evaluate the accuracy and the application performance of the developed method, the CRMs, GBW07602 and GBW07605, and three water samples were analyzed. As is shown in Table 3, the concentrations of lead in the CRMs determined by the present method using simple aqueous standards for calibration were in good agreement with the certified value. And the recoveries of lead spiking for the CRMs and water samples were in the range of 97–103%.

CONCLUSION

The inexpensive and facile material 1-(2-pyridylazo)-2-naphthol doped silica gel (PAN/SiO$_2$)

TABLE 4 **Comparisons of Some Parameters for Online Preconcentration and Determination of Lead (II) Using Other Sorbents**

Sorbent	Spectrometer model and manufacturer and its location	Sample	EF	DL (µg L^{-1})	F (h^{-1})
PAN chelate in a knotted reactor[20]	Varian AA 220 (Mulgrave, Victoria, Australia)	Environmental samples	26.5	0.43	48
Lead-selective chromatographic resin[34]	Shimadzu AA-6400 (Shimadzu corporation, Kyoto, Japan)	River-water and seawater	—	0.05	—
Pyrogallol red loaded activated carbon[35]	Perkin-Elmer AA 2380 (Perkin-Elmer Life and Analytical Sciences, Shelton, CT, USA)	Natural water	100	1.0	—
Poly (aminophosphonic acid)[36]	Perkin-Elmer AA 5000	Natural water	—	3.1	48
2-(2-Benzothiazolylazo)-2-p-cresol modified polyurethane foam (PUF)[37]	Varian AA 220	Seafood samples	26	1	48
Ammonium O,O-diethyldithiophosphate chelatecombined with AC and PUF[38]	Varian AA 179	Water	63 and 294	3 and 0.8	—
Dithiocarbamate functionalized or surface sorbed Merrifield resin beads[39]	Perkin-Elmer AA 100	Natural water	48 and 27	1.3 and 1.44	—
AC loaded with xylenol orange[40]	Perkin-Elmer AA 2380	Water samples	200	0.4	—
Multiwall carbon nanotubes[41]	Shimadzu AA-6800	Water samples	44.2	2.6	14
Polychlorotrifluoroethylene[42]		Water	—	2.7	30
Immobilized salen (N, N′-bis (salicylidene) ethylenediamine)[43]	Buck Scientific AA 210 VGP (Buck Scientific Co., CI, USA)	Water samples, multivitamin tablet, and standard reference alloys	75	2.6	—
Amberlite XAD-2 loaded with PAN (off-line)[44]	Perkin-Elmer AA 3110	River water samples	50	23.2	—
Dibenzyldithiocarbamate chelates on Dowex Optipore V-493[45]	Perkin-Elmer AA 700	Environmental samples	50	0.65	—
Multiwalled carbon nanotubes[46]	Perkin-Elmer AA 700		80	0.30–0.60	—
PAN-doped silica gel [this work]	Purkinje General TAS 990	Water and biological samples	101	0.24	45

Note. EF = Enrichment factor, DL = detection limit, F = sampling frequency.

was demonstrated as a new sorbent for flow injection online microcolumn preconcentration and FAAS determination of trace Pb (II) in environmental and biological samples. The PAN-doped silica gel showed fast sorption/desorption kinetics and reusability. Also, the FI online SPE coupled with FAAS system showed a relatively high tolerance of the matrix elements. Compared with the data from recent articles on the online preconcentration and determination of trace Pb (II) (summarized in Table 4), the detection limit of the determinations in the present work was lower than those of some other methods[20,34–46] with a relatively high enrichment factor and sampling frequency.

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