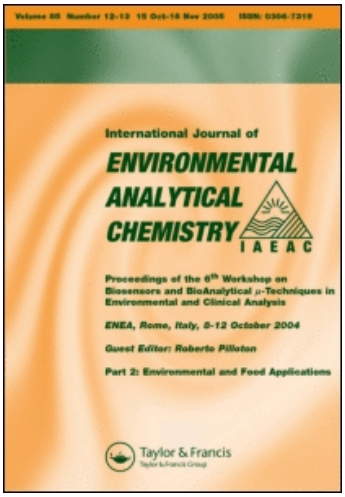

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On-line preconcentration and determination of nickel and zinc in natural water samples by flow injection-flame atomic absorption spectrometry using PTFE-turnings for column packing

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On-line preconcentration and determination of nickel and zinc in natural water samples by flow injection – flame atomic absorption spectrometry using PTFE-turnings for column packing[†]

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A rapid, sensitive and low cost, time-based flow injection atomic absorption spectrometric method was described for the determination of nickel and zinc upon on-line preconcentration on a micro-column packed with polytetrafluoroethylene-turnings material. The metals formed on-line complexes with ammonium pyrrolidine dithiocarbamate from acidified solutions (pH 2.0) in the flow manifold and retained in the column. The preconcentrated elements were subsequently eluted quantitatively with isobutylmethylketone and injected directly into the nebuliser for atomisation and measurement. The system offered improved flexibility, low backpressure and applicability. The enhancement factors were 170 and 65 for Ni(II) and Zn(II), respectively. The respective detection limits were 0.5 and 0.3 $\mu g\,L^{-1}$, and the precision, expressed as relative standard deviation, were 2.8% (at 5.0 $\mu g\,L^{-1}$) and 3.2% (at 2.0 $\mu g\,L^{-1}$), respectively. The accuracy of the developed method was sufficient and evaluated by the analysis of certified reference material and spiked environmental water samples.

Keywords: atomic absorption spectrometry; solid phase extraction; polytetrafluoroethylene; nickel; zinc

1. Introduction

Analytical monitoring of heavy metals in several environmental matrices like natural waters and wastewater is an important issue, given that the development of sensitive techniques to obtain adequate detection limits are in great demand. Nickel is a moderately toxic element as compared with other transition metals. However, it is the metal component of the enzyme unease and as such considered to be essential to plants. More attention has been focused on the toxicity of nickel in low concentrations, such as the fact that it can cause a skin disorder known as nickel-eczema. Zinc is an essential trace element for humans, animal and plants, playing a significant role in several biochemical processes. However, zinc can be toxic and, if it is in excess, it can affect significantly in the progression of some damages to the human body like disturbances in energy metabolism or increases in oxidative stress.

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To date, flame atomic absorption spectrometry (FAAS) continues to be one of the most extensively used techniques in most laboratories for trace element determination with adequate precision and accuracy. This fact is due to easy operation, high sample throughput and relative low operational and instrumental costs. However, there are some limitations to determine traces of heavy metals in environmental samples due to insufficient detection power or matrix interferences.

On-line flow injection (FI) solid phase extraction (SPE) has been shown to be efficient and effective in improving the sensitivity and selectivity of FAAS. In addition, on-line SPE has some extra advantages: large number of available sorbent materials, easy recovery of the solid phase, attainability of large preconcentration factors and facility for separation using various FI systems [1].

In recent years, a fast increasing number of FI analytical methods, which combine on-line micro-column preconcentration procedures with FAAS for metal determination, have been reported, reaching very low detection limits, comparable to that obtained with electrothermal atomic absorption spectrometry (ETAAS) [2,3].

On-line SPE has been performed by using several sorbent materials such as polystyrene–divinylbenzene polymer (PS–DVB) functionalised, Amberlite XAD-4 [4,5], XAD-2 [6]; octadecyl functional groups bonded on silica gel, C18 [7,8]; silica gel chemically modified with niobium (V) oxide (Nb_2O_5–SiO_2) [9]; cation-exchange resin SP Sephadex C-25 [10]; reversed-phase co-polymeric sorbent Oasis HLB [11]; polyurethane foam (PUF) [12–14]; polytetrafluoroethylene (PTFE) in the form of turnings [15–17], beads [18] or grafted fibres [19] and polychlorotrifluoroethylene (PCTFE) beads [20,21].

Various chelating agents containing sulphur, nitrogen or oxygen donor atoms as weak Lewis bases were reported for metal determination. Ammonium pyrrolidine dithiocarbamate (APDC) has been proved to be suitable for metals determination by on-line SPE and FAAS [21].

In this work, an on-line time-based column preconcentration method for nickel and zinc determination by FAAS was developed. A mini-column packed with PTFE-turnings was used for metal-APDC complexes preconcentration. Due to the hydrodynamic properties of the PTFE in the form of turnings, the system was able to operate in high sample flow rates with low backpressure and consequently to achieve high enhancement factors. As far as we know, no other papers have been published using PTFE-turnings for on-line nickel and zinc determination. The proposed method is applicable to routine analysis of natural water samples, with very good analytical performance characteristics, and sensitivity comparable to that obtained by using ETAAS.

2. Experimental

2.1 *Instrumentation*

A Perkin–Elmer, Norwalk, CT, USA (http://www.perkinelmer.com) model 5100 PC flame atomic absorption spectrometer with deuterium lamp background corrector equipped with a nickel hollow cathode lamp (HCL) operated at 30 mA and a zinc electrodeless discharge lamp (EDL) operated at 6 W, was used as detection system. The analytical wavelengths were set at 232.0 nm (slit at 0.2 nm) for nickel and 213.9 nm (slit at 0.7 nm) for zinc. 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 isobutyl methyl ketone (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 nebuliser's free uptake rate was 5.3 mL min^{-1}. A flow spoiler was employed in the spray chamber for better nebulisation conditions. The spectrometer was set to work in the FI-FAAS mode coupled with the FIAS-400 system.

A Perkin–Elmer Norwalk, Connecticut, U.S.A. model FIAS-400 FI 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, while it was connected to the spectrometer's nebuliser, using a short PTFE capillary 20.0 cm length/0.35 mm i.d., in order to minimise the eluent dispersion. A special adapter, called flow compensation (FC) in 'T' form was used just before the nebuliser inlet, in order to compensate the nebuliser's free uptake flow rate when the eluent flow rate was much lower than it, as it has been reported in other work [21]. The benefit of FC unit was very good reproducibility of the recorded signal at elution flow rate lower than 2 mL min^{-1}. In addition, no gas bubbles were produced in the tubing, when the peristaltic pump P1 was off, as it is described in the procedure in Section 2.3. 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 Jour Research column 30 mm length/4.6 mm i.d. filled with 600 mg of PTFE-turnings was used for the SPE of the metals. PTFE turnings were mechanically produced in our laboratory by lathe as described in other work [17]. The image from PTFE turnings using an optical microscope has been given previously [15]. The turnings were washed thoroughly by ethanol followed by 1 mol L^{-1} HNO_3 and finally with de-ionised water. No frits or glass wool were necessary at either end to block the PTFE turnings. The column was initially flushed with de-ionised water and subsequently with IBMK. The performance of the column was stable at least for 1000 preconcentration cycles.

2.2 *Reagents and samples*

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 Ni(II) and Zn(II) were prepared by appropriate stepwise dilution of a 1000 mg L^{-1} stock standard solution (Titrisol, Merck) to the required microgram per litre levels and were made up to the working pH by 0.01 mol L^{-1} HNO_3.

The chelating reagent, 0.3% m/m APDC, was prepared daily by dissolving the appropriate amount of APDC in de-ionised water. IBMK was used, after saturation with de-ionised water, without any other purification.

Natural water samples (tap, lake and costal sea-water, from Northern Greece) and the industrial wastewater from treatment plant, were filtered through 0.45 μm membrane filters, acidified to 0.01 mol L^{-1} HNO_3 and stored at 4°C in acid-cleaned polyethylene bottles, in order to determine the 'dissolved metal' fraction. The standard reference material NIST CRM 1643e (National Institute of Standard and Technology, Gaithersburg, MD, USA, http://www.nist.gov/) containing trace elements in water, was analysed for accuracy study.

2.3 *Procedure*

The on-line FI-manifold with the main operation parameters is presented in Figure 1. The operation sequences and details of the FIAS-400 program are given in Table 1.

In the first step (Figure 1a, preconcentration), the injection valve was in the 'LOAD' position. Pump P2 fed sample solution mixed with complexing agent through the preconcentration column for an appropriate preconcentration time (PT) (60 or 30 s). The formed complexes were adsorbed on the surface of the PTFE-turnings. In the mean time, pump P1 remained inactive and the nebuliser of the FAAS aspirated air through the FC adapter.

During step 2, the injection valve was turned in the 'ELUTE' position, pump P2 was inactive while pump P1 was activated propelling the eluent solvent IBMK through the column. The eluted complexes were delivered directly to the nebuliser for atomisation and measurement. In order to keep the dispersion as low as possible, IBMK flows through

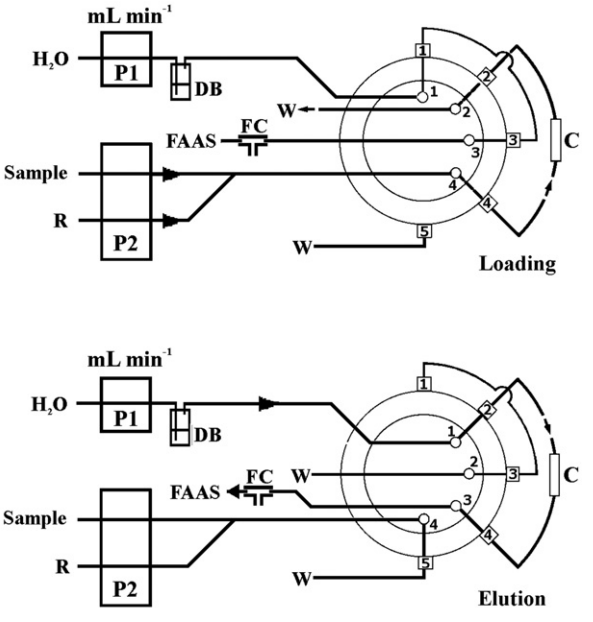

Figure 1. Schematic diagram and operation sequences of the FI on-line SPE system for nickel and zinc determination by FAAS. *R*, 0.2% m/v APDC; FC, flow compensation; P1, P2, peristaltic pumps; DB, displacement bottle for IBMK; C, mini-column packed PTFE-turnings; W, waste.

Table 1. Operation sequences of the FI on-line SPE system for nickel and zinc determination.

		Pumps					
Step	Valve position	P1	P2	Delivered medium	Flow rate ($mL\,min^{-1}$)	Time (s)	Operation
1	Load	OFF	ON	Sample 0.6% m/v DDPA	13.5/9.0 0.8	60/30	Ni(II)/Zn(II) Preconcentration
2	Elute	ON	OFF	IBMK	2.8	40	Elution/measurement

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.

3. Results and discussion

Both chemical and flow variables were thoroughly studied using the manifold shown in Figure 1, in order to improve the performance characteristics of the method for each analyte separately. Mixed standard solution containing 20.0 μg L^{-1} Ni(II) and 5.0 μg L^{-1} Zn(II) were employed for optimisation studies.

3.1 *Effect of pH*

In on-line SPE preconcentration, the complex formation and its retention on the sorbent surface are affected significantly by pH of the reaction medium. The effect of the pH on the absorbance was studied within the range of 0.5–5.0 (adjusted with dilute HNO_3). The waste and the sample solution had the same pH value, indicating that the effect of the APDC solution on the pH was negligible. Maximum absorption signal obtained within the pH range of 1.2–3.1 and 2.0–4.0 for Ni(II) and Zn(II), respectively, as can be seen in Figure 2. Thus, the pH 2.0 (or 0.01 mol L^{-1} HNO_3) was used for every analyte. This fact enables the use of the method directly in various aqueous samples after common acid preservation at pH ≈2.0.

3.2 *Effect of APDC concentration*

The effect of APDC concentration on the peak height was tested from 0.01 to 0.6% m/v. The flow rate of APDC was fixed at 0.8 mL min^{-1}. The results showed that the absorbance

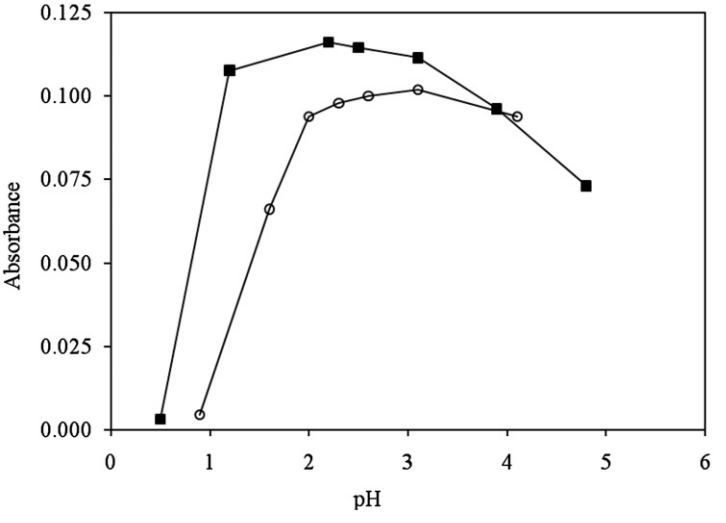

Figure 2. Effect of pH on the absorbance of 20.0 μg L^{-1} Ni(II) (■) and 5.0 μg L^{-1} Zn(II) (⊖). Sample flow rate 11.0 and 9.0 mL min^{-1} for Ni(II), and Zn(II), respectively. All other parameters are as given in Table 1.

rose when APDC concentration changed from 0.01% to 0.1% m/v and the absorbance remained constant for higher APDC concentrations up to 0.6% m/v. Therefore, 0.2% m/v APDC was selected for further study. In the absence of chelating agent, no detectable amounts of the two analytes could be retained in the column.

3.3 *Choice of eluent*

Aqueous and acidic solutions were proved less effective as eluents at on-line SPE preconcentration systems, than organic ones [20]. On the other hand, IBMK is considered to be a better eluent for FAAS than low molecular weight alcohols (e.g. ethanol or methanol), or halogenated hydrocarbons (e.g. chloroform, tetra-chloromethane) solvent offering higher enhancement factors. This is due to the fact that IBMK is practically immiscible in water with sufficient polarity and hydrophobicity than other organic solvents producing lower dispersion and quantitative elution of the complexes. In addition, IBMK contributes in the increment of the flame temperature and the atomisation process instead of halogenated hydrocarbons that affect negatively the atomisation properties of the flame due to halogens. Preliminary experiments between ethanol, methanol and IBMK as eluents showed that IBMK produced higher and sharpest signals. Thus, IBMK was chosen as eluent.

3.4 *Effect of sample flow rate*

The effect of the sample flow rate in the proposed manifold was investigated in the range from 4.0 to 16.0 mL min^{-1}, by varying the interior diameter of the peristaltic-pump tubing or adjusting the rotation rate (rounds per minutes, rpm) of the peristaltic pumps. As it is shown in Figure 3, the absorbance was increased almost linear up to flow rate 13.5 mL min^{-1} for Ni(II) and up to 9.0 mL min^{-1} for Zn(II) for 60 and 30 s PT, respectively. For higher flow rates the absorbance was increasing at a lower rate. This fact is a very useful feature of the method, because it permits the establishment of various sample flow rates in order to improve the required preconcentration. Therefore, flow rate of 13.5 mL min^{-1} for Ni(II) and up to 9.0 mL min^{-1} for Zn(II) was selected as a compromise between high sensitivity and low sample consumption.

3.5 *Effect of elution flow rate*

The effect of elution flow rate was studied in the range of 1.2–5.4 mL min^{-1}. The flame composition of the FAAS, adjusted properly according to the elution rate during the study, as it was described above. The best analytical signals were achieved within the range 2.6–2.9 mL min^{-1}. At low flow rates the signals decrease, probably due to significant dispersion produced from the high difference between elution flow rate and nebuliser free uptake. Above 2.9 mL min^{-1} the absorbance decreases, mainly due to insufficient contact time. Thus, 2.8 mL min^{-1} elution flow rate was employed throughout this work.

3.6 *Effect of PT*

The PT was studied in the range from 10 to 120 s. The absorption was increased linearly up to 120 s for Ni(II) and up to 30 s for Zn(II). For longer time, the analytical signals

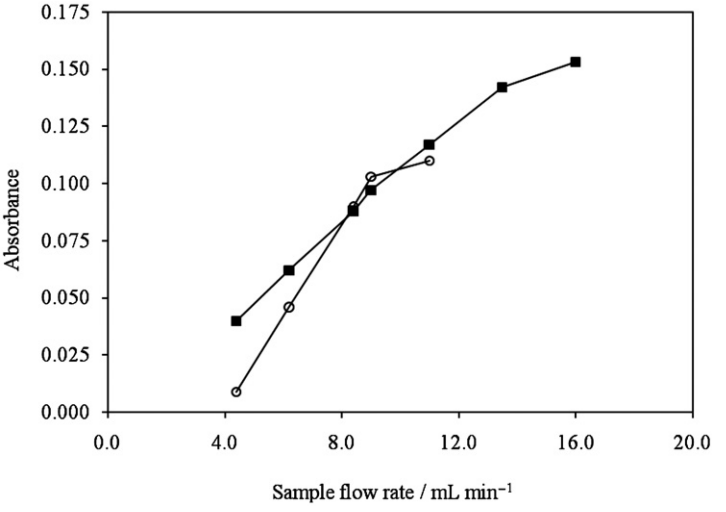

Figure 3. Effect of flow rate on the absorbance of 20.0 μg L^{-1} Ni(II) (-■-) and 5.0 μg L^{-1} Zn(II) (-⊖-). All other parameters are as given in Table 1.

of Zn(II) levelled off probably due to the partial leaching of the complex, showing the breakthrough of the column. Finally, a PT of 60 and 30 s was chosen for Ni(II) and Zn(II), respectively, as a compromise between sample consumption, high sensitivity and sufficient sampling frequency.

3.7 *Interference studies*

In order to evaluate the selectivity of the proposed on-line preconcentration system the interference of various elements was investigated on the determination of 10 μg L^{-1} Ni(II) and 5.0 μg L^{-1} Zn(II), taking as a criterion for an interference the deviation from the quantitative recovery of 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 cause any interference. Also NaCl did not interfere at concentrations up to 30 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), Mn(II) and Zn(II) was 25 mg L^{-1}, of Co(II) and Pb(II) was 1.0 mg L^{-1} and of Cu(II), Cd(II) and Hg(II) was 0.5 mg L^{-1} for the determination of nickel. Concerning zinc, the tolerable concentrations of Al(III), Cr(III), Fe(III) and Mn(II) was 5 mg L^{-1}, of Co(II), Pb(II) and Ni(II) was 1.0 mg L^{-1} and of Cu(II), Cd(II) and Hg(II) was 0.5 mg L^{-1}.

3.8 *Analytical features*

Under the optimised conditions, the performance characteristic of the on-line preconcentration method for FAAS determination of nickel and zinc are summarised in Table 2. Peak height absorption signals were used for the calculation of the calibration curve and the precision of the method. The detection limit was calculated by the 3s criterion, as the

Table 2. Analytical performance of the FI on-line SPE method for nickel and zinc determination.

Features	Nickel	Zinc
PT (s)	60	30
Sampling frequency (h^{-1})	36	51
Enhancement factor	170	65
Linear range ($\mu g\,L^{-1}$)	1.3–45	1.0–15
Regression equation (12 standards, $n=5$; [M]/$\mu g\,L^{-1}$)	$A = 0.002 + 0.0069$ [Ni(II)]	$A = 0.0025 + 0.0208$ [Zn(II)]
Correlation coefficient	$r = 0.9994$	$r = 0.9993$
Detection limit (3s) ($\mu g\,L^{-1}$)	0.5	0.3
Precision (RSD, $n=10$)/%	2.8% (5.0 $\mu g\,L^{-1}$)	3.2% (2.0 $\mu g\,L^{-1}$)

Table 3. Analytical results for the determination of nickel and zinc in water samples (determination in dissolved metal fraction).

		Nickel			Zinc		
Sample	Certified value ($\mu g\,L^{-1}$)	Added ($\mu g\,L^{-1}$)	Found[a] ($\mu g\,L^{-1}$)	R (%)	Added ($\mu g\,L^{-1}$)	Found[a] ($\mu g\,L^{-1}$)	R (%)
CRM 1643e	Ni: 62.41 ± 0.69 Zn: 78.5 ± 2.2		60.2 ± 1.8	96		76.2 ± 3.1	97
Bottled water		–	1.5 ± 0.1		–	1.5 ± 0.2	
		5.0	6.4 ± 0.5	98	5.0	6.3 ± 0.5	96
Underground water		–	1.1 ± 0.1		–	2.5 ± 0.2	
		5.0	5.9 ± 0.4	96	5.0	7.3 ± 0.5	96
River water		–	8.2 ± 0.6		–	9.4 ± 0.7	
		5.0	13.1 ± 0.6	98	5.0	14.2 ± 0.6	96
Seawater		–	1.2 ± 0.08		–	8.8 ± 0.4	
		5.0	5.9 ± 0.6	94	2.0	10.7 ± 0.6	95
Wastewater		–	4.4 ± 0.5		–	10.4 ± 0.2	
		5.0	9.5 ± 0.8	102	2.0	12.3 ± 0.7	95

Notes: [a]Mean value ± standard deviation based on three replicate determinations.
R, Recovery obtained from spiked samples.

concentration that gives a response equivalent to three times the standard deviation of the blank ($n=12$). The quantification limit was calculated as the concentration that gives a response equivalent to 10 times the standard deviation of the blank ($n=12$), and define the lower limit of the linear range. The calculation of the enhancement factor was based on the ratio of the slopes of the calibration curves, obtained with and without preconcentration, using FAAS. The detection limits were 0.5 $\mu g\,L^{-1}$ for nickel and 0.3 $\mu g\,L^{-1}$ for zinc. The precision (RSD, $n=10$) was found to be 2.8% for 5.0 $\mu g\,L^{-1}$ Ni(II) and 3.2% for 2.0 $\mu g\,L^{-1}$ Zn(II).

The accuracy of the proposed method was tested by determining the nickel and zinc concentration of a certified reference material NIST SRM 1643e (National Institute of Standard and Technology, Trace elements in water). For nickel the certified concentration

Table 4. Comparison of the performance characteristics among selected on-line SPE methods and the developed one for Ni(II) and Zn(II) determination with FAAS.

Ref.	Analyte	Sorbent material	Reagent	Eluent	PT (s)	SC (mL)	f (h^{-1})	c_L ($\mu g\,L^{-1}$)	s_r (%)	EF
**	Ni	PTFE-turnings	APDC	IBMK	60	13.5	36	0.5	2.8	170
[4]		XAD-4 functionalised	2,6-diacetylpyridine	HNO_3	30	0.4	–	4.8	–	–
[5]		XAD-4 functionalised	2-aminothiophenol	HCl	180	21.0	18	0.8	1.9	43
[6]		XAD-2 loaded	BTAC	HCl	60	7.0	48	1.1	5.0	30
[7]		C18-silica gel	5,7-dichlorooxine	MeOH ($pH \geq 2$)	60	7.0	30	1.0	7.2	80
**	Zn	PTFE-turnings	APDC	IBMK	30	9.0	51	0.3	3.2	65
[7]		C18-silica gel	5,7-dichlorooxine	MeOH ($pH \geq 2$)	60	7.0	30	0.5	6.5	60
[8]		C18-silica gel	TAN	MeOH ($pH \geq 2$)	60	–	30	0.15	2.5	120
[9]		Silica gel modified	Nb_2O_5–SiO_2	HCl	95	10.0	27	0.77	1.5	77
[12]		PUF loaded	Me-BTABr	HCl	60	6.0	48	0.37	5.9	23
[14]		PUF	KSCN	Acetone in HNO_3	60	6.7	17	0.85	6.0	15

Notes: **This work; BTAC: 2-(2-benzothiazolylazo)-2-*p*-cresol; TAN: 1-(2-thiazolylazo)-2-naphthol; Me-BTABr: 2-[2′-(6-methyl-benzothiazolylazo)]-4-bromophenol; PUF: polyurethane foam; PT: preconcentration time; SC: sample consumption; f: sampling frequency; c_L: detection limit; s_r: precision (relative standard deviation); EF: enhancement factor.

was $62.41 \pm 0.69\,\mu g\,L^{-1}$ and the obtained recovery was 96.5% ($60.22 \pm 1.81\,\mu g\,L^{-1}$, $n = 5$). For zinc the certified concentration was $78.5 \pm 2.2\,\mu g\,L^{-1}$ and the recovery was 97.1% ($76.2 \pm 3.1\,\mu g\,L^{-1}$, $n = 5$).

The proposed method was applied also to the analysis of local natural water samples as well as wastewater and 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 concentration found in 'not spiked' samples. The obtained results are presented in Table 3, and the recoveries were varied in the range 94–102% for nickel and 95–97% for zinc showing the good performance of the method in all types of the examined samples.

For comparative purposes, the performance characteristics of the proposed method and other selected on-line SPE preconcentration FAAS methods reported in the literature are given in Table 4. The proposed method shows good sensitivity (c_L) and precision (s_r) with reasonable PT over other on-line preconcentration methods.

4. Conclusions

The results obtained in the present work, testify to the applicability of PTFE-turnings packed column in FI on-line sorbent extraction preconcentration system coupled with FAAS for nickel and zinc determination in water samples. The proposed method is simple and fast with reasonable performance characteristics and sample throughput.

The hydrophobic nature and excellent chemical inertness of the proposed sorbent material make it very attractive for on-line column preconcentration systems. It was also indicated that samples with difficult matrices like seawaters could be analysed successfully by the proposed method.

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