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Separation, preconcentration and inductively coupled plasma-mass spectrometric (ICP-MS) determination of thorium(IV), titanium(IV), iron(III), lead(II) and chromium(III) on 2-nitroso-1-naphthol impregnated MCI GEL CHP20P resin

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ABSTRACT

A simple and effective method is presented for the separation and preconcentration of Th(IV), Ti(IV), Fe(III), Pb(II) and Cr(III) by solid phase extraction on 2-nitroso-1-naphthol impregnated MCI GEL CHP20P resin prior to their inductively coupled plasma-mass spectrometric determinations. The influence of analytical parameters including pH of the aqueous solution, flow rates of sample and eluent solutions and sample volume on the quantitative recoveries of analyte ions was investigated. Matrix effects caused by the presence of alkali, earth alkali and some metal ions in the analyzed solutions were investigated. The presented solid phase extraction method was applied to BCR-144R Sewage Sludge (domestic origin), BCR-141R Calcareous Loam Soil, NIST 1568a Rice Flour and NIST 1577b Bovine Liver certified reference materials (CRMs) for the determination of analyte ions and the results were in good agreement with the certified values. The separation procedure presented was also applied to the various natural water samples collected from Turkey with satisfactory results.

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1. Introduction

It is an important necessity to find accurate determination for trace heavy metals in environmental samples including natural water and soil samples, because they are sensitive indicators of environmental pollutions due to traffic and human activities [1–5]. High level of alkali and earth alkali ions in the environmental samples is a main problem in the instrumental detection of heavy metal ions including inductively coupled plasma-mass spectrometry and atomic absorption spectrometry [6–10]. Separation–preconcentration systems including precipitation [11,12], liquid–liquid extraction [13–15], cloud point extraction [16,17], membrane filtration [18,19] and electroanalytical systems [20,21] are used to solve this problem. Separation and preconcentration of trace metal ions by solid phase extraction are also widely used for that purpose [22–24], due to its some important advantages like simplicity, fast analyzing time and simple adaptation to automation systems [25–28].

Synthetic and natural solid materials as sorbents have been used for the solid phase extraction of trace heavy metal ions. In the solid phase extraction studies, the sorbent should have some properties: the possibility for extracting lots of metal ions in a wide pH range, high surface area, fast and quantitative adsorption and easy elution, ultra pure, repeated usability and accessibility [29–32]. To obtain quantitative recoveries of analyte ions, in the solid phase extraction studies, a suitable chelating agent was generally used [33–36].

Impregnated resins have been widely used for the preconcentration–separation of trace heavy metal ions on the environmental samples including natural water [37–39]. No data were obtained on impregnation of 2-nitroso-1-naphthol on MCI GEL CHP20P resin for the preconcentration of thorium(IV), titanium(IV), iron(III), lead(II) and chromium(III) in environmental samples in our literature scanning.

In the present work, a solid phase extraction procedure for the separation–preconcentration of ultratraces of Th(IV), Ti(IV), Fe(III), Pb(II) and Cr(III) in environmental samples on 2-nitroso-1-naphthol impregnated MCI GEL CHP20P resin is presented prior to their inductively coupled plasma-mass spectrometric (ICP-MS) determination.

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Table 1
Operating conditions of ICP-MS.

Nebulizer	Babington
Spray chamber	Quartz, double pass
RF power	1260 W
Carrier gas flow rate	1.15 L min^{-1}
Sample uptake rate	0.3 mL min^{-1}
Detector mode	Auto
Integration time	0.10 s
Number of replicates	3
Analytical masses	^{47}Ti, ^{53}Cr, ^{208}Pb, ^{57}Fe, ^{232}Th

2. Experimental

2.1. Instrumentation

An Agilent model 7500a ICP-MS (Agilent Technologies, Tokyo, Japan) was used for the determination of Th(IV), Ti(IV), Fe(III), Pb(II) and Cr(III). The instrument was optimized daily before measurement and operated as recommended by the manufacturers. The conditions are given in Table 1. A pH meter, WTW Inolab Level 3 Model glass-electrode was employed for measuring pH values in the aqueous phase. The water was purified in Millipore Synergy 185.

2.2. Reagents and solutions

High purity reagents were used for all standard and sample solutions. Stock solutions of Th(IV), Ti(IV), Fe(III), Pb(II) and Cr(III), 1000 mg L^{-1} (Sigma, St. Louis) were diluted daily for obtaining working solutions. The standard solutions used for the calibration procedures were prepared before use by dilution of the stock solution with 1 mol L^{-1} HNO_3. Stock solutions of diverse elements were prepared from the high purity compounds (99.9%, E. Merck, Darmstadt). 1 M HCl and 1 M NH_3 were used in the pH adjustments.

A solution of 2-nitroso-1-naphthol (1.0×10^{-2} M) was prepared by dissolving 0.044 g of 2-nitroso-1-naphthol (E. Merck, Darmstadt) in 5 mL of ethanol and diluting to 25 mL with water. MCI GEL CHP20P is a styrene-divinylbenzene polymer that was purchased from Sigma Chem. Co., St. Louis, USA (Supelco no.: 13630-U). Its surface area is 500 m^2 g^{-1} [41].

The preparation of 2-nitroso-1-naphthol impregnated MCI GEL CHP20P resin is based on the procedure reported in literature [37,39]. MCI GEL CHP20P (2.0 g) resin was added to 25 mL of 2-nitroso-1-naphthol solution with continuous stirring for 12 h. Afterwards 2-nitroso-1-naphthol impregnated MCI GEL CHP20P was filtered off, washed with water and dried over night at 100 °C. The amount of 2-nitroso-1-naphthol deposited/adsorbed on MCI GEL CHP20P resin was estimated by spectrophotometric measurements at 262 nm from the residual amount of 2-nitroso-1-naphthol in the solution. It was found that 98.8% of 2-nitroso-1-naphthol was retained on the resin.

All solutions were delivered to pass through the home made PVC mini column (0.4 mm i.d., 4.0 cm long) dry-packed with 190 mg of 2-nitroso-1-naphthol impregnated MCI GEL CHP20P resin by a four-channel variable speed peristaltic pump (Rainin Dynamax Model RP-1). A small amount of glass wool was placed at both ends of the column to prevent the loss of resin when the sample solution passed through the MCI GEL CHP20P column. Before the passage of each sample solution through the column, a blank solution was passed through the column. After each elution, the column was washed with 1 mol L^{-1} HNO_3 to clean the resin and double distilled water. The other parts of the system connected with Tygon tubings (1.3 mm i.d.) and 2 two-way valves from Ismatec, Switzerland, were employed to propel the sample, reagent and eluent.

2.3. Preconcentration procedure

The complete cycle of separation and enrichment of trace metal ions at pH 7 on 2-nitroso-1-naphthol impregnated MCI GEL CHP20P column consisted of two steps: loading (step 1) and elution (step 2). In step 1, 10–100 mL of the solution containing 2–5 μg of each metal ion was brought to the desired pH 7. The column was preconditioned with 10–15 mL of the water brought to the same working pH. The metal solution was passed through the 2-nitroso-1-naphthol impregnated MCI GEL CHP20P column at a 3 mL min^{-1} flow rate. In this step trace metal ions were adsorbed on the 2-nitroso-1-naphthol impregnated MCI GEL CHP20P column. In step 2, the metal ions retained on the column were eluted with 5 mL of 1 M HNO_3 at 3 mL min^{-1} of flow rate into a smaller beaker. The metal concentration in the solution was determined by ICP-MS.

2.4. Analysis of real samples

Four CRMs analyzed by the presented method were BCR-144R Sewage Sludge (domestic origin), BCR-141R Calcareous Loam Soil, NIST 1568a Rice Flour and NIST 1577b Bovine Liver. 0.1 g of each CRM was digested with aqua regia (12 mL concentrated HCl and 4 mL of concentrated HNO_3) at room temperature then it was heated at 95 °C. After the evolution of NO_2 fumes had ceased, the mixture was evaporated almost to dryness on a sand-bath and mixed with 8 mL of aqua regia. The mixture is then again evaporated to dryness [27]. After evaporation 8–9 mL of distilled water was added. The resulting mixture was filtered through a blue band filter paper. The filtrate was diluted to 25 mL with distilled water. The pH of this solution was adjusted to 7.0 by the addition of appropriate amount of 1 mol L^{-1} NH_3. Then the preconcentration procedure given above was applied.

Eight natural water samples from different locations in Turkey were also analyzed. Each water samples was filtered through a cellulose membrane filter (Millipore) of 0.45 μm pore size. 100 mL of water sample was transferred to a beaker. The pH of these solutions was adjusted to 7.0. Then the procedure given in Section 2.3 was applied.

3. Results and discussion

3.1. Effect of pH

pH is a very important factor for efficient recoveries of analyte ions on the solid phase extraction studies [42–44]. Therefore, the effects of pH of aqueous solution on the retentions of Th(IV), Ti(IV), Fe(III), Pb(II) and Cr(III) ions on 2-nitroso-1-naphthol impregnated MCI GEL CHP20P resin were examined at the pH range of 2.0–10.0. The pH was adjusted using 1 M HCl and/or 1 M NH_3. The results are depicted in Fig. 1.

All the analyte ions were quantitatively recovered in the pH range of 6.0–8.0. Therefore, in the light of these results, for all subsequent works, pH 7.0 was fixed as optimum for the quantitative separation–preconcentration.

3.2. Effect of eluent type

The influence of eluent type on desorption of the analytes from the column was investigated. Various eluents given in Table 2 were used for elution of retained analyte ions on the 2-nitroso-1-naphthol impregnated MCI GEL CHP20P column. The recoveries with some eluents were not quantitative, for example with 2 mol L^{-1} H_2SO_4. The lower recoveries with 2 M H_2SO_4 and others in Table 2 may source from the strong interaction between metal and sorbent. It is not possible to break down to these interactions with 2 mol L^{-1} H_2SO_4 and others in Table 2. Quantitative

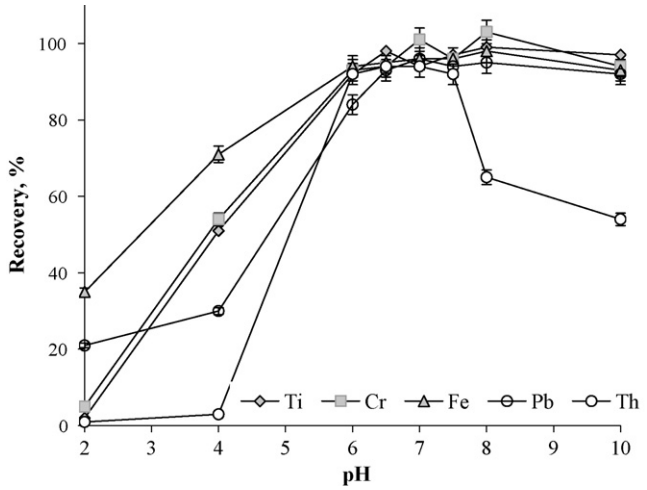

Fig. 1. Effect of pH on the recoveries of analyte ions (sample volume: 25 mL, amount of analytes: 2–5 μg, $N = 3$).

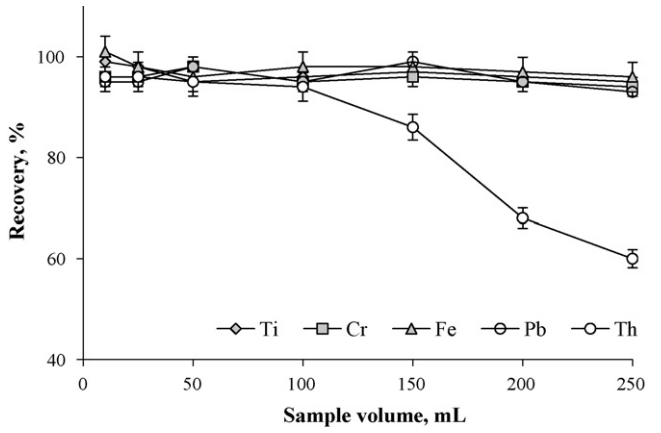

Fig. 2. Effect of sample volume on the recoveries of analytes (pH = 7, amount of analytes: 2–5 μg, $N = 3$).

recovery was obtained using 5 mL of 1 mol L^{-1} HNO_3. It seems that oxidation capability of HNO_3 is the reason for quantitative recoveries of the analyte ions, as the concentration of hydronium ion in HCl (1 mol L^{-1}) and HNO_3 (1 mol L^{-1}) is the same. Under optimized conditions, for all further works, 5 mL of 1 mol L^{-1} HNO_3 was used.

3.3. Flow rate of sample and eluent solutions

The influence of the flow rates of sample and eluent solutions on the recoveries of the analyte ions was investigated in the range of 1–5 mL min^{-1}. The quantitative recovery values were obtained in the flow rate range of 1–4 mL min^{-1} for sample and for eluent solution. After 4 mL min^{-1} of sample solution, the recovery values of analyte ions were below 95%. Three milliliters per minute was selected as a flow rate for both sample and eluent solutions.

Table 2
Recovery values for analyte ions with different eluents ($N = 3$).

Eluent	Recovery (%)				
	Ti	Cr	Fe	Pb	Th
1 mol L^{-1} HCl	85 ± 3	88 ± 4	99 ± 2	96 ± 3	64 ± 2
2 mol L^{-1} HCl	94 ± 2	85 ± 3	94 ± 4	97 ± 2	58 ± 4
1 mol L^{-1} H_2SO_4	96 ± 1	97 ± 2	102 ± 3	96 ± 2	72 ± 3
2 mol L^{-1} H_2SO_4	78 ± 2	80 ± 2	90 ± 3	85 ± 3	52 ± 3
1 mol L^{-1} HNO_3	98 ± 1	99 ± 2	97 ± 2	96 ± 1	95 ± 2
2 mol L^{-1} HNO_3	94 ± 3	92 ± 3	96 ± 4	92 ± 2	86 ± 3

3.4. Sample volume and preconcentration factor

The influence of sample volume on the recoveries of analyte ions on the solid phase was also examined, due to its importance to obtain high preconcentration factor [45–47]. The results were given in Fig. 2. Ti(IV), Fe(III), Pb(II) and Cr(III) ions were quantitatively (>95%) recovered at volume range of 10–250 mL. The recoveries of Th(IV) ions were at range of 10–100 mL. The recovery values of Th(IV) decreased probably due to the excess analytes loaded over the column capacity with increasing sample volume above 100 mL. Therefore, 10–100 mL of sample solution range was adopted for the separation/preconcentration of analyte ions. The adsorbed metal ions can be eluted with 5.0 mL of 1 mol L^{-1} HNO_3 and a preconcentration factor of 20.

3.5. Effect of foreign ions

The problematic effects of alkali, earth alkali and transition metal ions at high levels are known as "matrix effects" in the spectroscopic determination of metal ions in environmental samples [45,46]. Therefore, the influence of some ions given in Table 3 on the recoveries of analyte ions was investigated in the present work. The tolerance limit is defined as the ion concentration causing a relative error smaller than ±5% related to the preconcentration and determination of analytes. There is no interference in the presence of large amounts of alkali, earth alkali and transition metals with some exceptions. Thorium recoveries were affected in the presence of sodium ions at 10 000 mg L^{-1} while the recoveries were quantitative at 2500 mg L^{-1} of sodium ions.

Table 3
Influences of some alkali, earth alkali and transition metal ions on the recoveries of analyte ions (pH = 7, amount of analytes: 2–5 μg, V_{sample}: 100 mL, V_{eluent}: 5 mL, $N = 3$).

	Added as	Concentration (mg L^{-1})	Recovery (%)				
			Ti	Cr	Fe	Pb	Th
Na^+	NaCl	10 000	99 ± 3[a]	96 ± 2	105 ± 4	99 ± 3	[a]
K^+	KCl	2 500	99 ± 1	98 ± 2	102 ± 4	98 ± 2	93 ± 3
Ca^{2+}	$CaCl_2$	2 500	95 ± 2	94 ± 2	102 ± 3	96 ± 1	93 ± 2
Mg^{2+}	$MgCl_2$	2 500	96 ± 1	94 ± 2	100 ± 2	98 ± 2	93 ± 2
SO_4^{2-}	Na_2SO_4	1 000	95 ± 2	98 ± 1	97 ± 2	96 ± 3	94 ± 1
NO_3^-	KNO_3	1 000	98 ± 2	96 ± 4	99 ± 2	94 ± 3	92 ± 4
CO_3^{2-}	Na_2CO_3	500	93 ± 2	94 ± 3	97 ± 3	94 ± 2	93 ± 2
Al^{3+}	$Al_2(SO_4)_3{\cdot}18H_2O$	10	96 ± 4	96 ± 1	98 ± 2	94 ± 3	93 ± 3
Zn^{2+}	ZnI_2	10	94 ± 2	96 ± 2	95 ± 1	95 ± 2	92 ± 3
Ni^{2+}	$NiCl_2{\cdot}6H_2O$	10	96 ± 2	93 ± 2	97 ± 4	99 ± 3	93 ± 2
Co^{2+}	$CoCl_2{\cdot}6H_2O$	10	94 ± 1	98 ± 1	94 ± 2	98 ± 2	95 ± 3

[a] Thorium was quantitatively recovered at 1000 mg L^{-1} of sodium ion.

Table 4
Limit of detection values for the analyte ions ($N = 15$).

Element	Limit of detection[a] ($\mu g\,L^{-1}$)
Ti	0.11
Cr	0.04
Fe	0.60
Pb	0.28
Th	0.03

[a] $(x_{blank} + 3s_{blank})/PF$ [48,49], PF: preconcentration factor.

3.6. Analytical performances

The limits of detection (LOD) of the proposed method for the determination of analyte elements were studied under the optimal experimental conditions. The detection limits based on three times the standard deviations of the blank for analyte ions are given in Table 4.

The analytical performance of the procedure can be calculated from the results of ICP-MS. The reproducibility of the method was evaluated by a 25 mL of solution containing analyte ions at 80–200 $\mu g\,L^{-1}$ concentration range ($N = 10$). The relative standard deviations (RSD) of these determinations were in the range of 1.6–3.2%.

An addition/recovery test using the presented method was performed to spring water sample from Nigde Çiftehan to estimate the accuracy of the procedure. The results are given in Table 5. Good agreement is obtained between the added and found analyte content using the recommended procedure. The recovery values for the analyte ions are quantitative and show that the presented method can be applied for the separation/preconcentration of analyte ions in natural waters.

3.7. Applications

The validation of the presented procedure is performed by the analysis of four CRMs. The certified and observed values for CRMs are given in Table 6. The results found were in good agreement with the certified values of CRMs.

Table 5
Test of addition/recovery for a spring water from Nigde Çiftehan (V_{sample}: 100 mL, V_{final}: 5 mL, $N = 4$).

Element	Added (μg)	Found (μg)	Recovery (%)
Ti	0	BDL	–
	2.50	2.36 ± 0.05	94 ± 2
	5.00	4.72 ± 0.28	94 ± 6
	7.50	7.15 ± 0.23	95 ± 3
Cr	0	0.09 ± 0.02	–
	2.50	2.44 ± 0.05	94 ± 2
	5.00	4.80 ± 0.14	94 ± 3
	7.50	7.09 ± 0.09	93 ± 2
Fe	0	8.28 ± 0.80	–
	2.50	10.90 ± 0.16	105 ± 7
	5.00	13.25 ± 0.30	99 ± 6
	7.50	16.11 ± 0.26	104 ± 4
Pb	0	0.46 ± 0.16	–
	2.50	2.83 ± 0.05	95 ± 2
	5.00	5.21 ± 0.10	95 ± 2
	7.50	7.51 ± 0.15	94 ± 2
Th	0	0.07 ± 0.03	–
	1.00	1.02 ± 0.01	95 ± 1
	2.00	1.99 ± 0.03	96 ± 2
	4.00	3.81 ± 0.14	94 ± 3

BDL: below the detection limit.

Table 6
Analysis of CRMs by the presented method ($N = 5$).

	Concentration (mg/kg)		
	Analyte	Certified value	Determined values*
BCR-144R Sewage Sludge (domestic origin)	Cr	138 ± 5	132 ± 7
	Pb	51 ± 2	54 ± 4
BCR-141R Calcareous Loam Soil	Cr	90 ± 6	95 ± 5
	Pb	96 ± 2	92 ± 3
NIST 1568a Rice Flour	Fe	7.4[a]	6.7 ± 0.7
NIST 1577b Bovine Liver	Fe	184[a]	152 ± 8
	Pb	0.129[a]	0.114 ± 0.006

[a] Not certified.
* P: 0.95; $\bar{X} \pm ts/\sqrt{N}$.

Table 7
Results for some water samples from Anatolia, Turkey (V_{sample}: 100 mL, V_{final}: 5 mL, $N = 5$).

	Concentration ($\mu g\,L^{-1}$)				
	Ti	Cr	Fe	Pb	Th
Afyon Ihsaniye Kızılay spring water	BDL	BDL	5.43 ± 0.58	0.48 ± 0.07	BDL
Bursa Uludağ spring water	0.15 ± 0.05*	3.56 ± 0.95	6.17 ± 0.80	0.60 ± 0.14	0.06 ± 0.03
Bolu Yeniçağ Anatolya spring water	BDL	0.12 ± 0.04	5.09 ± 0.83	1.56 ± 0.21	0.25 ± 0.04
Aydın Bozdoğan Pınar Madran spring water	BDL	0.17 ± 0.06	0.48 ± 0.07	2.79 ± 0.87	BDL
Üçpınar Tap water	0.19 ± 0.07	2.84 ± 0.20	7.33 ± 0.60	2.06 ± 0.33	BDL
Nigde Narlıgöl hot spring water	0.21 ± 0.09	0.12 ± 0.03	57 ± 13	0.88 ± 0.12	0.19 ± 0.04
Water from out of treatment plant of Balikesir	1.28 ± 0.23	23.4 ± 4.4	335 ± 30	2.09 ± 0.28	BDL

BDL: below the detection limit.
* P: 0.95; $\bar{X} \pm ts/\sqrt{N}$.

Table 8
Comparative data from recent papers on 2-nitroso-1-naphthol and other naphthols as chelating agent on solid phase extraction studies.

Analytes	Method and instrumental detection	PF	Detection limit ($\mu g\,L^{-1}$)	Relative standard deviation (%)	References
Co(II)	Silica gel loaded with 1-nitroso-2-naphthol/ICP-MS	100	1.81	<10	[50]
Co(II)	Surfactant-coated alumina/AAS	100	–	1.4–4.0	[51]
Co(II)	2-Nitroso-1-naphthol immobilized on surfactant-coated alumina/AAS	125	0.02	1.7	[40]
Cu(II), Cd(II), Pb(II)	SPE on Amberlite XAD-2/AAS	50	0.8–23.2	<5	[52]
Co(II)	1-Nitroso-2-naphthol/C18 microcolumn/AAS	17.2	3.2	1.6	[53]
Th(IV), Ti(IV), Fe(III), Pb(II), Cr(III)	2-Nitroso-1-naphthol impregnated MCI GEL CHP20P/ICP-MS	20	0.03–0.60	1.6–3.2	Present work

PF: preconcentration factor.

The presented method was applied to different water samples from Anatolia, Turkey prior to their ICP-MS determinations. The results are given in Table 7.

4. Conclusions

A simple, fast and economic solid phase extraction procedure for ICP-MS determination of Th(IV), Ti(IV), Fe(III), Pb(II) and Cr(III) has been established in the present work. The comparative data from recent papers on 2-nitroso-1-naphthol and other naphthols as chelating agent on solid phase extraction studies were given in Table 8. The preconcentration factors of investigated elements are superior to those of some preconcentration/separation techniques for analyses. The solid phase extraction studies with 2-nitroso-1-naphthol were generally single element works [40,50,51,53]. Our procedure is multi-elemental. The matrix effects with the method were reasonably tolerable. The solid phase filled to PVC column could be used 20 times without any loss of its adsorption properties for analyte ions. Also the presented method is relatively rapid as compared with previously reported procedures for the enrichment of analytes of trace heavy metal ions in real samples [42–46,54,55]. The analyte determinations were performed in some CRMs and natural water samples from Anatolia, Turkey.

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