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Simultaneous trace multielement determination by ICP-OES after solid phase extraction with modified octadecyl silica gel

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ABSTRACT

Multielement simultaneous determination of 35 trace elements in environmental samples was carried out by inductively coupled plasma emission spectrometry (ICP-OES) after preconcentration with octadecyl silicagel, modified with aurin tricarboxylic acid (Aluminon). Optimal experimental conditions including pH of sample solution, sample volume, sample and eluent flow rate, type, concentration and volume of eluent and foreign ions effect were investigated and established.

Trace element ions in aqueous solution were quantitatively adsorbed onto octadecyl silicagel modified with aurin tricarboxylic acid at pH 8.0 with a flow rate of 11.0 mL min^{-1}. The adsorbed element ions were eluted with 3–5 mL of 0.5 mol L^{-1} HNO_3 at a flow rate of 10.0 mL min^{-1} and analyzed by ICP-OES simultaneously.

The proposed method has at least preconcentration factor of 100 in water samples, which results high sensitive detection of ultra-trace and trace analysis. The present methodology gave recoveries better than 70% and RSD less than 16%.

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1. Introduction

Environmental problems are becoming one of the most human concern all over the world. The many industrial wastewater streams contain heavy metals, which can discharge to water and waste water or into surface waters. Some examples of such industrial wastewater are the following: (a) rinsing water in metal-working enterprises, containing Cu, Ni, Zn, Sn, Cd, Pd, Ag, Al, Au, Cr, Mo, etc.; (b) rinsing water in the semiconductor industry, containing Cu, Sn, Pb, Sb; (c) wastewater from the copper industry, containing As, Se and (d) other types of water in which the presence of toxic metals causes problems. As the number of ecological and health problems associated with environmental contamination continues to rise, the extraction and determination processes of trace metal ions or species from different matrices especially aqueous samples become paramount importance and received more and more attention [1,2]. Environmental pollution monitoring required determination of toxic heavy elements in trace levels.

Flame atomic absorption spectrometry (FAAS) is relatively simple and available technique in many laboratories for heavy metal determinations [12–14]. However the conventional determinations of elements at μg L^{-1} range by flame and furnace atomic absorption spectrometry frequently are not possible and there are a number of refractory elements such as vanadium, zirconium and molybdenum which cause problems in flame AAS.

With an inductively coupled plasma source, the sample experiences temperature estimated to be in the vicinity of 10,000 K. These results in atomization and excitation of even the most refractory elements with high efficiency so that detection limits for these elements with ICP-OES can be well over an order of magnitude better than the corresponding values for atomic absorption [3–6].

The inductively coupled plasma optical emission spectrometry (ICP-OES) technique which offers fast multi-elemental analysis suffers from a poor sensitivity, because the concentration of some metals in environmental samples are below the detection limit of ICP-OES. To solve this problem, preconcentration separation procedures have been proposed. Thus, preconcentration is a very important issue for achievement of low detection limits [14–17].

The preconcentration method provides lower detection limits and also helps to avoid the matrix interferences in the determination of heavy elements present in environmental samples like river water, tap water, and natural and spiked water samples. This drawback can be rectified by a combination of a suitable preconcentration technique with subsequent ICP-OES determination.

There are a lot of enrichment methods such as: co-precipitation, solvent extraction, electrolysis and solid phase extraction. Solid

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Table 1
Operation parameters of ICP-OES.

RF generator power	1300 W
Frequency of RF generator	27.12 MHz
Coolant gas flow rate	16 L min^{-1}
Carrier gas flow rate	0.65 L min^{-1}
Auxiliary gas	0.4 L min^{-1}
Max integration times (s)	15 s
Pump rate	50 rpm
Viewing configuration	Axial
Replicate	3
Flush time (s)	20

phase extraction is a very important place in preconcentration studies due to its simplicity, high preconcentration factors, environmental friendly, costs and time for sample preparation. Recently, solid phase extraction has been used for the separation and preconcentration of metal ions in water samples [7–11]. Most of them can be used for at most 10 elements. In this study we introduce a new method for enrichment of 35 elements.

2. Experimental

2.1. Apparatus

In this study, simultaneous ICP-OES, Thermo Scientific iCAP Series 6500, equipped with a charge injection device (CID) detector CETAC and Asx-520 Autosampler (England) has been used for the determination of elements. Control of the spectrometer is provided by PC based iTEVA software. The instrumental parameters are given in Table 1. A Metller pH meter (model E603) with a combined glass electrode was used for pH measurements.

2.2. Reagents

All the chemicals and reagents were of analytical grade from Merck (Darmstadt, Germany). Ultra-pure water obtained from a Milli-Q purification device (Millipore Co., Bedford, MA, USA). Standard labware and glassware were acid washed and rinsed with ultra-pure water. Multi-elemental standard solution for ICP-OES contains 35 elements of Ag, Al, As, Ba, Bi, Ca, Cd, Ce, Dy, Er, Eu, Ga, Gd, Hg, Ho, La, Lu, Mg, Na, Nd, P, Pb, Pr, Rb, Sc, Se, Sm, Sr, Tb, Th, Tl, Tm, U, Y and Yb (10 ppm, 26XSM80B.5L) and multi-elemental standard solution for ICP-OES contains 32 elements of Au, B, Be, Co, Cr, Cu, Fe, Ge, Hf, Ir, K, Li, Mn, Mo, Nb, Ni, Os, Pd, Pt, Re, Rh, Ru, Sb, Si, Sn, Ta, Te, Ti, V, W, Zn and Zr (10 ppm, 26XSM90C.5L), was obtained from MBH (London, England). The mixed standard solution was obtained by further diluted to desired concentration daily prior to use. Reagent grade ammonium salt of aurin tricarboxylic acid (Aluminon) prepared from Merck (Darmstadt, Germany). Sep-Pak C18 cartridges containing 500 mg octadecyl silica (50 mm particle size, 60 Å pore size) from Waters Associates Co. (MA, USA).

2.3. General procedure

In order to condition C18 cartridges, each cartridge was rinsed with 10 mL water following 5 mL HNO_3 (0.5 mol L^{-1}) and 5 mL methanol. After drying the cartridge by passing air through it for several minutes, cartridge was loaded with 2.0 mL of 500 mg L^{-1} of Aluminon and allowed to completely penetrate inside the solid phase. The solvent was evaporated at 80 °C for 15 min. The standard solutions of metal ions or real sample solutions were pipette into conical flasks. The solutions were adjusted to pre-fixed and passed through the modified cartridge at a flow rate that could be controlled with screw clamps. The cartridge was eluted with eluent and the desorbed ions were measured by ICP-OES simultaneously.

3. Results and discussion

The primarily study shows that the adsorption behavior of 67 elements on modified C18 with Aluminon are not quantitative and 35 elements retained on it. For this purpose 50 mL of solution containing 100 μg L^{-1} of 67 elements at desired pH, passed through the cartridge and collected. The results shows the elements of Al, Be, Bi, Ce, Cr, Cu, Dy, Er, Eu, Fe, Ga, Gd, Hf, Ho, Ir, La, Lu, Nd, Pr, Ru, Sc, Sm, Sn, Ta, Tb, Te, Th, Ti, Tm, U, V, Y, Yb, Zn and Zr adsorbed and other elements passed through modified cartridge.

3.1. Selection of eluent

According to aurin tricarboxylic acid chemical structure, acidic solution is need for desorption of ions from cartridge, thus HCl, HNO_3, H_2SO_4 were investigated. 50 mL of solution containing 100 μg L^{-1} of 67 elements at pH 8.0 passed through cartridge and eluted with 5 mL 0.5 mol L^{-1} of acids, separately. As you can see, the recovery of elements for HCl is a little better than HNO_3 and H_2SO_4 is not good (Table 2). Although, the recovery of elements for HCl is better than HNO_3 but we used HNO_3 as eluent, due to the risk of chloride interference. Thus HNO_3 was selected for further experiment.

3.2. Effect of the pH

The pH value plays an important role in adsorption of different ions on the modified cartridge. The acidity of a solution has two effects on metal adsorption. First, protons in an acidic solution can protonate the binding sites of the chelating molecules. Secondly,

Table 2
Effect of eluent type on desorption of elements from modified cartridge.

Analyte	% Recovery		
	HCl (0.5 mol L^{-1})	HNO_3 (0.5 mol L^{-1})	H_2SO_4 (0.25 mol L^{-1})
Al	82.4	92.1	78.4
Be	100	100	100
Bi	100	97.5	65.3
Ce	91	77.5	85.1
Cr	92.9	96.6	104.9
Cu	93.1	95.2	97.1
Dy	92.6	80.6	86.1
Er	96.4	82.9	90.2
Eu	89.1	76.9	83.6
Fe	70.1	97.1	73.3
Ga	84.9	74.1	82.1
Gd	95.4	81.5	90.9
Hf	35.7	72.3	33.1
Ho	90.9	84.1	86.6
Ir	66.4	70.1	68.7
La	95.4	80.9	88.9
Lu	100.4	87.9	96
Nd	89.1	83.8	86.5
Pr	89.5	67.4	88.3
Ru	56.6	78.2	35.8
Sc	96.3	91.1	85.7
Sm	62.9	84.4	42.4
Sn	67.8	100	60.6
Ta	70.6	70.1	40.9
Tb	93.4	83.2	90.8
Te	87.1	100	24.2
Th	99.7	76.3	33.6
Ti	84.3	79.1	48.6
Tm	96.8	77.2	86.8
U	91.9	84.8	80.2
V	100.4	90.7	99.2
Y	94.9	83	89.9
Yb	94.7	83.4	89.9
Zn	94.3	96.4	87.8
Zr	56.3	82.8	35.4

Table 3
Effect of pH of sample solution for adsorption on modified cartridge.

Analyte	The studied pH range	Appropriate pH	% Recovery at optimum pH (8.0)
Al	1.2–12.4	6.0–7.0	87.3
Be	1.2–12.4	6.0–8.4	100
Bi	1.2–12.4	6.5–8.0	100
Ce	1.2–12.4	6.5–8.4	96.8
Cr	1.2–12.4	6.5–8.4	100
Cu	1.2–12.4	6.0–8.0	100
Dy	1.2–12.4	6.5–8.0	95.4
Er	1.2–12.4	6.5–8.5	92.5
Eu	1.2–12.4	6.5–8.5	95.8
Fe	1.2–12.4	5.5–7.0	85.2
Ga	1.2–12.4	6.0–12.0	97.7
Gd	1.2–12.4	6.0–12.0	91.6
Hf	1.2–12.4	6.7–8.0	100
Ho	1.2–12.4	6.7–8.0	95.5
Ir	1.2–12.4	6.7–9.0	89.2
La	1.2–12.4	6.0–10.0	95.5
Lu	1.2–12.4	6.6–10.0	97.7
Nd	1.2–12.4	6.0–10.0	96.6
Pr	1.2–12.4	6.0–10.0	97.5
Ru	1.2–12.4	6.0–12.0	90.7
Sc	1.2–12.4	7.0–9.0	90.4
Sm	1.2–12.4	8.0–9.0	100
Sn	1.2–12.4	6.5–9.0	98.2
Ta	1.2–12.4	8.0–10.0	91.3
Tb	1.2–12.4	6.0–10.0	92
Te	1.2–12.4	6.0–10.0	92.7
Th	1.2–12.4	6.0–10.0	100
Ti	1.2–12.4	6.5–10.0	88
Tm	1.2–12.4	6.0–11.0	96.1
U	1.2–12.4	6.0–11.0	99.5
V	1.2–12.4	6.0–9.0	87.5
Y	1.2–12.4	6.0–10.0	99.9
Yb	1.2–12.4	6.0–10.0	99.6
Zn	1.2–12.4	6.0–8.0	100
Zr	1.2–12.4	5.0–8.0	88.6

the hydroxide ion in a basic solution may complex and precipitate many metals. Therefore, the pH of a solution is the first parameter to be optimized. In order to evaluate the effect of pH, the pH values of sample solutions were adjusted to a range of 1.2–10.4 with HCl/NH_4OAC or $NaOH/NH_4OAC$, and solutions containing cations were passed through the cartridge. The results of the pH on the recoveries of elements are shown in Table 3. For pHs lower than 6.0, a competition between protons and the analyte for the adsorption sites is shown, and quantitative recovery (>87%) was found at pHs higher than pH 7.0 for the studied elements. A pH of 8.0 was selected as the compromise condition.

3.3. *Effect of eluent volume*

The volume of eluent has influence on preconcentration factor. The volume of the eluent must be as low as possible to achieve the highest enrichment factor. For this purpose, 50 mL of solution containing 100 $\mu g\,L^{-1}$ of 67 elements at pH 8.0 passed through cartridge and eluted with 1–6 mL 0.5 mol L^{-1} HNO_3 separately. The results are shown in Fig. 1. As you can see, 2 mL of 0.5 M HNO_3 desorbed elements of Be, Bi, Ce, Cr, Cu, Dy, Er, Eu, Ga, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Sn, Ta, Tb, Te, Tm, U, V, Y, Yb quantitatively and for elements of Al, Fe, Hf, Ir, Ru, Th, Ti, Zn, and Zr larger volume is necessary (at least 5 mL).

3.4. *Effect of flow rates*

Two important factors for the quantitative recoveries and desorption of metal chelates on the solid phase extraction studies are flow rates of the sample and eluent solutions. The effect

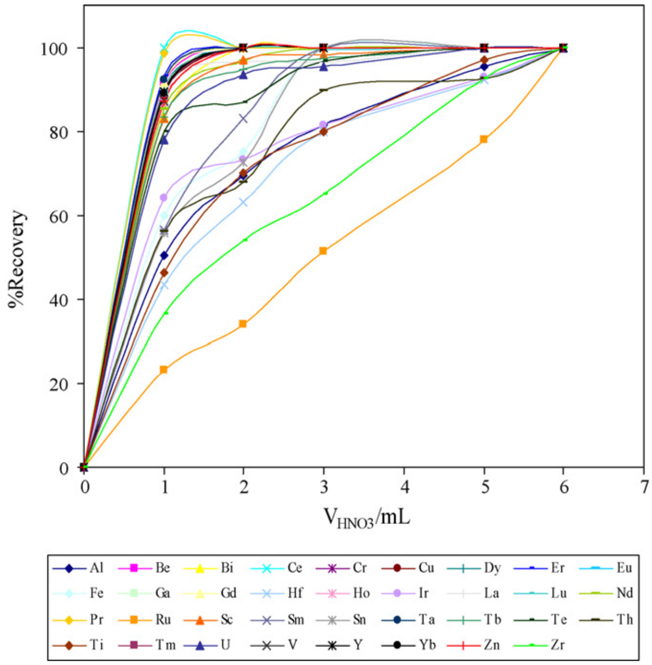

Fig. 1. Effect of amount of HNO_3 on percent recovery of 35 elements. Conditions: sample volume: 50 mL, concentration of each element added: 100 $\mu g\,L^{-1}$ the amount of Aluminon: 1.0 μg, sample flow rate: 11 mL min^{-1}, eluant flow rate: 10 mL min^{-1}, concentration of eluant: 0.5 mol L^{-1}, pH of solution: 8.0.

Table 4
Analytical figures of merit of the off-line solid phase extraction coupled with ICP-OES.

Analyte	Analytical wavelength (nm)	Equation	Correlation coefficient	LOD (ppb)
Al	396.152	$y = 44388x + 158$	0.991	0.1
Be	313.042	$y = 308860x + 67$	0.9999	0.003
Bi	190.241	$y = 199x + 2.2$	0.9905	0.03
Ce	404.076	$y = 5876x - 5.5$	0.9998	0.006
Cr	267.716	$y = 5276x + 123$	0.977	0.005
Cu	324.757	$y = 1743x + 2.1$	0.9997	0.005
Dy	353.17	$y = 17033x + 0.8$	0.999	0.01
Er	323.058	$y = 5999x + 27$	0.999	0.008
Eu	381.967	$y = 74642x + 21$	0.999	0.01
Fe	259.94	$y = 4701x + 376$	0.9926	0.1
Ga	287.424	$y = 853x + 9$	0.998	0.02
Gd	335.047	$y = 7931x - 19$	0.98	0.05
Hf	232.247	$y = 8715x + 91$	0.9994	0.002
Ho	345.6	$y = 20237x + 0.05$	1	0.01
Ir	212.681	$y = 1780x - 21$	0.996	0.01
La	412.323	$y = 14177x - 3.4$	0.9871	0.3
Lu	261.542	$y = 35868x + 5$	0.9994	0.005
Nd	401.225	$y = 11172x - 4.4$	0.997	0.04
Pr	414.311	$y = 4018x + 4.2$	0.996	0.05
Ru	240.272	$y = 910x + 1.3$	0.9998	0.006
Sc	361.384	$y = 113258x + 19$	0.9993	0.005
Sm	330.639	$y = 5047x - 13.8$	0.998	0.009
Sn	283.999	$y = 301x + 12.5$	0.998	0.05
Ta	268.517	$y = 744x + 2.2$	0.993	0.03
Tb	350.9	$y = 10585x - 21$	0.99	0.009
Te	214.281	$y = 360x + 2$	0.9997	0.01
Th	283.73	$y = 1341x - 6$	0.9989	0.02
Ti	334.941	$y = 332x + 0.82$	0.9989	0.005
Tm	313.126	$y = 10145x - 99$	0.999	0.02
U	385.958	$y = 60936x - 1.4$	0.9997	0.09
V	309.311	$y = 30502x + 17$	0.9875	0.2
Y	371.03	$y = 115874x + 21$	0.996	0.002
Yb	328.937	$y = 84251x + 14$	0.999	0.002
Zn	213.856	$y = 3460x + 10$	0.9998	0.04
Zr	339.198	$y = 26161x - 16$	0.9984	0.008

Table 5
Determination of 35 elements in tap water by SPE-ICP-OES[a].

Element	Concentration of each element in tap water (μg L^{-1})	Added (μg L^{-1})	Found (μg L^{-1})	Recovery (RSD%[b])
Al	2.8	5	6.9	68.0 (3.6)
Be	<LOD	5	4.2	84.0 (5.1)
Bi	<LOD	5	4.2	84.0 (6.2)
Ce	<LOD	5	3.7	74.0 (7.8)
Cr	<LOD	5	4.1	82.0 (6.2)
Cu	11.1	5	16.5	108.0 (2.1)
Dy	<LOD	5	4	80.0 (3.4)
Er	<LOD	5	4	80.0 (7.5)
Eu	<LOD	5	3.9	78.0 (10.2)
Fe	106	5	102	91.8 (5.7)
Ga	<LOD	5	4.6	92.0 (4.5)
Gd	<LOD	5	4.2	84.5 (5.2)
Hf	<LOD	5	3.2	64.0 (3.9)
Ho	<LOD	5	4	80.2 (8.2)
Ir	<LOD	5	3.4	67.4 (4.6)
La	<LOD	5	3.5	70.0 (11.3)
Lu	<LOD	5	4	80.3 (9.6)
Nd	<LOD	5	4.2	83.5 (8.3)
Pr	<LOD	5	3.6	72.8 (7.5)
Ru	<LOD	5	3.2	63.3 (10.3)
Sc	<LOD	5	3.5	70.7 (10.1)
Sm	<LOD	5	2.7	54.0 (12.3)
Sn	<LOD	5	3.9	77.5 (5.8)
Tb	<LOD	5	4	79.1 (14.1)
Te	<LOD	5	2.7	54.0 (13.2)
Th	<LOD	5	3.9	77.5 (9.4)
Ti	<LOD	5	2.9	58.0 (11.5)
Tm	<LOD	5	4.2	84.3 (8.9)
U	<LOD	5	3	59.6 (8.7)
V	<LOD	5	6.2	112.2 (5.6)
Y	<LOD	5	4	76.5 (6.5)
Yb	<LOD	5	3.9	77.1 (3.6)
Zn	203.4	5	231.8	111.3 (3.5)
Zr	<LOD	5	1.8	30.2 (16.2)

[a] 250 mL of each water sample was taken.
[b] %RSD for three determinations.

of the flow rate of sample solution was examined from 5 to 25 mL min^{-1}. It was found that the flow rate up to 11 mL min^{-1} has no effect on recovery of cations and in higher speed the recovery decreased. Thus, 11 mL min^{-1}has been selected for optimal condition.

The effect of elution flow rate on desorbtion of analytes was investigated by keeping the elution volume of 0.5 mol L^{-1} HNO_3. The result indicates that the analytes can be desorbed quantitatively at flow rate range of 1.0–10.0 mL min^{-1}. Hence, elution flow rate of 10.0 mL min^{-1} was selected in this study.

3.5. Effect of foreign ions and breakthrough of volume

For the study of interference by other coexisting ions, such as K^+, Ag^+, Au^+, As^{5+}, B^{5+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Li^+, Na^+, Hg^{2+}, Mn^{2+}, Mo, Ni^{2+}, Pb^{2+}, Pd^{2+}, Pt^{2+}, Rb^+, Cs^+, Sb^{5+}, Sr^{2+} and Si^{4+} (all 10 mg L^{-1}) on the preconcentration and recovery of analytes were examined under the optimum conditions. The obtained results shown did not have any adverse effects on the extraction efficiency.

In the analysis of real samples, the sample volume is one of the most important parameters influencing the preconcentration factor. In order to achieve a high enrichment factor for sample with very low analyte concentration, a large volume of samples solution is required. Therefore, the effect of sample volume on the retention of elements was investigated. For this purpose, 50, 100, 150, 250, and 500 mL of sample solutions containing 0.25 μg of each element were passed through the cartridge. The results indicate that the recoveries of all elements were close to quantitative up to a sample volume of 500 mL. The enhancement factors calculated as the ratio of the slopes of the calibration curves obtained by this SPE method for 3 and 5 mL eluent and by usual nebulization ICP-OES were 170 and 100, respectively.

3.6. Analytical performance and application of the method for tap water

Calibration graphs were obtained using 250 mL of the standard solutions of multielement ions buffered at pH 8.0 at optimal conditions. The analytical figures of merit of the present multielement preconcentration method determination by ICP-OES were evaluated under optimal experimental conditions. According to the IUPAC definition, the detection limit (3σ) was calculated. The results are shown in Table 4. The method was applied for determination of trace elements (35 elements) in tap water. The results were in good agreement with add-found method (Table 5).

4. Conclusion

Compromise conditions for different variables affecting the metal-Aurin formation and the adsorption on and elution from the modified C18-Silica allow the simultaneous solid phase extraction of 35 elements from aqueous samples. The optimized solid phase extraction is fast (simultaneous solid phase extraction) and at least a preconcentration factor of 100 can be achieved. Our Methodology was shown to be an effective approach for improving the sensitivity of ICP-OES for 35 elements. The system is very simple, rapid, easy to use, selective and with a good sensitivity for the determination of 35 elements.

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