Preconcentration, Separation and Multi-Elements Determination in Seawater Using a Cellulose-Zinc Hydroxide System with Inductively Coupled Plasma Atomic Emission Spectrometry

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The use of a cellulose-zinc hydroxide mixture for the micro determination of Cd(II), Cr(III), Cu(II), Fe(III), Hg(II), La(III), Ni(II), Pb(II), Sn(IV) and vanadate ion in a seawater sample at different pH was carried out employing ICP technique. The effects of concentration of Zn(II), mass of the cellulose, shaking time and the pH value of the sample on the preconcentration were studied. The method is simple and rapidly applicable for the microdetermination of ten heavy metals at ppb level. The effect of alkali and alkaline earth cations on the preconcentration of the tested metal ions was examined. The distribution coefficient K_d is in the range of $10^{2.86} - 10^{6.31} \text{ cm}^3 \text{ g}^{-1}$.

Keywords Trace metals preconcentration, seawater, cellulose-zinc hydroxide, inductively coupled atomic emission spectrometry

The excellent performance of the ICP as a multi-elements source allows the rapid acquisition of data on samples introduced into a plasma.^{1,2} Some of the attractive features of the technique are its high power of detection, large dynamic range, relative freedom from interferences and ease of operation and of multi-elements simultaneous determination.³⁻⁵ Some metals are present in environmental samples such as seawater at very low levels that are difficult to detect by inductively coupled plasma-optical emission spectrometry (ICP-OES).

The various methods of preconcentration and separation procedures, such as ion-exchange, coprecipitation and sorption, can be used prior to the ICP-OES measurements.⁶⁻¹² The use of metal hydroxides such as those of iron(III), aluminum and indium as collectors for the trace elements in water samples normally produces bulky amorphous precipitates which are difficult to filter.¹³ Recently, cellulose-Hyphan (1-(2'-hydroxyphenylazo)-2-naphthol) was used for preconcentration of rare earth elements and noble metals from aqueous solutions.^{14,15}

In the present work, a cellulose-zinc hydroxide system was applied for the preconcentration and microdetermination of some metals in natural water.

Experimental

Reagents and solutions

Standard solutions ($1000 \mu\text{g cm}^{-3}$) of high purity (>99.99%) metals or salts were used. Zinc reagent (10 mg cm^{-3}) was prepared by dissolving $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in

doubly deionized distilled water. BDH cellulose and other reagents were used.

Apparatus

All the experiments were carried out ARL 3520-ICP

Table 1 Typical operation conditions for (ICP-OES) and equipment for spectral measurement

ICP system	ARL 3520 Switzerland
Power, RF generator	27.12 MHz, 2.5 kW
Argon plasma flow-rate	12 l min ⁻¹
Auxiliary gas flow-rate	0.8 l min ⁻¹
Nebulizer gas flow-rate	1 l min ⁻¹
Sample uptake rate	2 ml min ⁻¹
Nebulizer	glass concentric Meinhard type
Monochromator	Puschen-Range mounting (1 m radius) vacuum version with Ar
Spectral range	170 - 810 nm
Grating	1080 grooves mm ⁻¹ with reciprocal dispersion of 0.9 nm blazed at 600 nm
Speed	Displacement from one wavelength to any other wavelength is less than 1.5 s.
Entrance and exit slit widths	20 μm
Background correction limits	0.025 - 1 nm
Integration time	5 s

equipment; the important parameters of the operating conditions are listed in Table 1. A Beckman (Fullerton, CA, USA) digital pH meter was used.

Procedure

Batch experiments. Transfer 5 cm³ of a mixture of the 10 heavy metals 10 µg cm⁻³ each, to a 50 cm³ beaker. To this solution 5 cm³ of zinc reagent was added and the pH was adjusted in the range 3–12 using a 5 mol dm⁻³ NaOH and or 1.0 mol dm⁻³ nitric acid. The contents were transferred to a 100 cm³ conical flask and 0.1 g cellulose was added to each solution. These solutions were then stirred for 20 min with a mechanical shaker. The precipitate was filtered through sintered glass (0.45 µm membrane), washed with 10 cm³ of 0.2 mol dm⁻³ NaOH and doubly distilled water. The formed precipitate was dissolved in 10 cm³ hot 0.5 mol dm⁻³ nitric acid and the resulting solution was adjusted to 50 cm³ volume and directly aspirated into ICP-OES equipment. The atomic emission intensities for the elements at each pH value were measured. After those procedures, the effects of the masses of cellulose (0.005–0.1 g) and zinc sulfate (1–200 mg) were also studied.

Determination of trace metals in seawater. One cubic decimeters of seawater, was filtered off through sintered glass (0.45 µm membrane), then 1 cm³ of concentrated nitric acid, 5 cm³ of zinc reagent and 0.1 g cellulose were added. The pH was adjusted to a value of 9. The reaction mixture was shaken for 20 min, the solid material was filtered off and the precipitate was then washed with 0.2 mol dm⁻³ NaOH solution. The precipitate was dissolved in hot 0.5 mol dm⁻³ nitric acid and the concentration of each element was measured.

The calibration curves used for the determination of heavy metals by ICP-OES were done using standard solutions for the studied metal ions in the range 0.1–10 µg cm⁻³, with the exception of vanadate ion: Pb²⁺, Hg²⁺ and La³⁺ which have a range of 0.2–20 µg cm⁻³.

Results and Discussion

Analytical lines and calibration curves

The chosen wavelengths of the analytical lines are given in Table 2. The concentrations tested in this investigation follow exactly a linear relationship between $\Delta Y_{x,0} = \log(I_x/I_0)$, where I_x is the intensity of the analytical lines and I_0 is the intensity of the background^{16,17}, and the range of concentration: in µg cm⁻³, this extends from 0.1 up to at least 10 µg cm⁻³ of the tested multi-elements in the presence of Na⁺+Mg²⁺ (in the concentration level of seawater (*cf.* Table 2)). The instrumental detection limit of the studied heavy metal ions was calculated employing this equation:¹⁸

$$C_L = \frac{0.01 \times K \times (RSD)_B \times C_0}{SBR}$$

Table 2 Analytical lines, analytical detection limits, C_L ng dm⁻³, relative standard deviation in concentration, RSD and linear regression coefficient, r

Element ^a	Wavelength/ nm	C_L / ng dm ⁻³	RSD ^b	r	η
Cd(I)	228.80	2.6	0.02	0.9998	1.03
Cr(II)	205.55	14.1	0.08	0.9991	1.00
Cu(I)	324.75	5.5	0.10	0.9996	1.02
Fe(II)	238.20	4.2	0.18	0.9994	1.00
Hg(II)	194.23	3.5	0.02	0.9986	1.01
La(II)	379.48	0.80	0.02	0.9999	1.02
Ni(II)	231.60	0.60	0.09	0.9989	1.00
Pb(II)	220.35	0.40	0.06	0.9975	0.67
Sn(II)	189.98	0.10	0.01	0.9994	1.08
V(II)	309.31	0.90	0.08	0.9996	0.96

η : slope of calibration curve.

a. In the present study, a mixture of 1 mol dm⁻³ Na⁺ ion+1.2 mol dm⁻³ Mg²⁺ ion was used as matrix.

b. The concentration of all the studied metal ions was 100 µg dm⁻³.

where (RSD)_B is the present relative standard deviations of the background, SBR is the signal to background ratio, C_0 is the analyte concentration at which the SBR is measured and K is 2. The detection limits are very impressive for most studied elements. The analytical detection limits were calculated by dividing instrumental detection limits by each preconcentration factor. The detection limits of these elements ranged between 0.1 and 14.1 ng dm⁻³. The analytical detection limits (C_L), ng dm⁻³, relative standard deviation (RSD), linear regression coefficient and the slope (η), are summarized in Table 2.

Distribution coefficients K_d for ten heavy metal ions

The distribution coefficients are calculated by the equation

$$K_d = \frac{C_{i,ex} (\mu\text{g g}^{-1})}{C_{sol} (\mu\text{g cm}^{-3})}$$

where $C_{i,ex}$ is the concentration of the metal ions in cellulose and C_{sol} is that in solution. The distribution coefficients, K_d for the studied metal ions on cellulose–zinc hydroxide system as a function of pH are given in Table 3. In the concentration range 0.1–10 µg cm⁻³, the K_d values are practically independent of the trace elements concentration. Figures 1a and 1b summarize the relation between recovery % and pH values for the studied metal ions. It is clear that the pH has a great effect on the metal-distribution between cellulose–zinc hydroxide system and solutions. Better recoveries between pH range (8–9) can be achieved, as is given in Table 3. The high distribution coefficients for the heavy metals on cellulose–zinc hydroxide system facilitate the separation of these metals from one sample

Table 3 Logarithmic distribution coefficient, K_d , and percent recovery, $R\%$ at different pH values for multi-elements (50 mg of Zn^{2+} ion and 0.1 g of cellulose)

Element	pH	$\log K_d$	$R\%$
Cd	9 ^a	3.90	97.5 ^a
	8	2.86	78.0
Cr	9	3.64	95.5
	8	3.64	95.5
Cu	9	4.13	98.5
	8	4.11	98.4
Fe	9	3.90	97.5
	8	4.31	99.0
Hg	9	4.11	98.0
	8	3.44	93.5
La	9	4.12	98.3
	8	3.62	95.2
Ni	9	3.27	90.1
	8	3.03	84.0
Pb	9	3.82	96.0
	8	6.29	99.9
Sn	9	3.90	97.5
	8	4.13	98.5
V	9	3.64	95.5
	8	6.29	99.9

a. Without cellulose as collector.

Fig. 1a Effect of change of pH on recoveries of Cd, Cr, Cu, Fe and Hg (mass of cellulose 0.1 g and 50 mg of Zn^{2+}).

Fig. 1b Effect of change of pH on recoveries of La, Ni, Pb, Sn and V (mass of cellulose 0.1 g and 50 mg of Zn^{2+}).

solution by shaking with small amounts of the collector. The recovery of one-stage separation is given by^{14,15}

$$P = \frac{K_d m_{czn}}{K_d m_{czn} + V_L}$$

where m_{czn} is the mass of cellulose and zinc sulfate and V_L is the volume of solution (50 cm³). The recovery depends on the pH values of solutions. At the maximum values of K_d the following recoveries are obtained: 97.5% Cd, 95.5% Cr, 98.5% Cu, 99.0% Fe, 98.0% Hg, 98.3% La, 90.1% Ni, 99.5% Pb, 99.8% Sn and 99.99% V. In case of Cd, Cu, Fe, Hg, Pb, Sn and V, the high yield may be due to the high adsorption of metal hydroxides on the system used (Table 3). This is also in agreement with the charge densities of metal ions. Thus these elements can be separated quantitatively according to a single-stage batch procedure.¹⁹

Effects of mass of cellulose and concentration of zinc on the coprecipitation and time of stirring

The effects of changes of both the mass of cellulose and the zinc reagent concentration on the coprecipitation of the trace amounts of heavy metals were studied. The recoveries of the metals at pH=9 were examined by changing cellulose mass and the concentration of zinc independently. The effects of changes of cellulose mass and of concentration of zinc on recovery of the metals are shown in Figs. 2 and 3. It is quite clear that cellulose plays an important role in the coprecipitation process, because it facilitates and accelerates the process of filtration and acts as a good carrier for the coprecipitation of both zinc hydroxide and heavy metal ions. Small quantities of cellulose were enough to give maximum recoveries for Cr, La, Ni and V, which were not affected by higher quantities of cellulose. Cu, Fe, Hg, Pb and Sn were slightly affected by the increase of cellulose mass and can generally exceed 95% coprecipitated with 0.1 g of cellulose. Cadmium has maximum recovery when the zinc reagent is used alone in the coprecipitation process. The efficiency of the coprecipitation process of heavy metal ions- $Zn(OH)_2$ precipitate on cellulose, depends upon the positive nuclear charge of such ions and increases with increasing the latter. Since Cd^{2+} , Hg^{2+} , Sn^{2+} and Fe^{3+} ions have completely filled or half-filled n-1d sub-shells, these lead to the shielding of the nuclear charges of such ions and to decreasing the adsorption phenomena on cellulose and consequently to lowering their recovery percentage. The coprecipitation of Cu, Cd, Ni, Hg and Sn deteriorated rapidly when the concentration of zinc was greater than 100 mg per 50 cm³ solution of the heavy metals. The recoveries of La and V, on the other hand, were independent of the zinc concentration, when the concentration of the latter was greater than 50 mg. The effect of time of stirring on the recovery at constant mass of cellulose (0.1 g) and constant zinc concentration (50 mg) was studied in the range of 10 – 120 min (Fig. 4). Most metals were recovered

Fig. 2 Effect of changes of mass of cellulose on the coprecipitation of heavy metal at pH=9 and 50 mg of Zn^{2+} .

Fig. 3 Effect of change of concentration of zinc on the coprecipitation method at pH=9, stirring time=20 min (mass of cellulose 0.1 g).

after stirring times of 20 min; Cd, Cr and Ni were recovered after 10 min only.

Analytical applications

Analytical separation procedures for trace elements can be strongly interfered with matrix constituents *e.g.* alkali and alkaline earth elements. For this reason, the reliability of the tested preconcentration method is examined in the presence of the possible matrix elements. The recoveries of the heavy metals on cellulose-zinc

hydroxide in the presence of Li^+ , K^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Sr^{2+} and Be^{2+} (10 or 100 mg dm^{-3}) were studied. The results indicate that the matrix ions have little effect on the recovery percentage of the metals studied. However, the Mg^{2+} ion (3.0 g dm^{-3}) has a great effect on the recovery percentage (2 – 12%). The effect of Ca^{2+} in sea level (1.0 g dm^{-3}) concentration has slight interference. The analytical results of seawater collected at coastal area (Dubai, UAE) at Gulf and Lake in Dubai (waste water) are shown in Table 4. On the other hand, the

Fig. 4 Effect of stirring time on the coprecipitation of the ten heavy metals (pH=9, mass of cellulose=0.1 g and amount of zinc in solution=50 mg).

Table 4 Multi-elements analysis of seawater in the Gulf (Dubai Coast, UAE), concentration, $\mu\text{g dm}^{-3}$, mean values $\pm$ SD and relative standard deviation (%)

	Open Gulf		Lake Dubai (waste water)	
Cd	0.09 $\pm$ 0.01 (0.05–4.3)	0.11%	0.15 $\pm$ 0.02	0.13%
Cr	0.17 $\pm$ 0.02 (0.15–9.0)	0.12	0.38 $\pm$ 0.05	0.13
Cu	0.90 $\pm$ 0.04 (0.01–5.3)	0.04	1.29 $\pm$ 0.05	0.04
Fe	1.01 $\pm$ 0.03 (0.80–70.0)	0.03	1.26 $\pm$ 0.02	0.02
Hg	0.05 $\pm$ 0.005 (0.04–0.05)	0.10	0.10 $\pm$ 0.01	0.10
La	0.29 $\pm$ 0.03 (0.3)	0.10	0.35 $\pm$ 0.04	0.11
Ni	0.28 $\pm$ 0.04 (0.73–8.2)	0.14	0.61 $\pm$ 0.05	0.08
Pb	1.00 $\pm$ 0.05 (0.64–16.8)	0.05	1.21 $\pm$ 0.03	0.02
Sn	0.72 $\pm$ 0.02 (3.0)	0.03	0.95 $\pm$ 0.04	0.04
V	1.35 $\pm$ 0.04 (0.05–9.11)	0.03	1.78 $\pm$ 0.03	0.02

Figures in parentheses indicate the reference levels.

metal contents for Cd, Cr, Cu, Fe, Hg, Ni, Pb and V in seawater are in good accordance^{20–26} with those found elsewhere, as shown in Table 4. The standard deviation (SD) and relative standard deviation (S_r) were found to be 0.01–0.05 $\mu\text{g dm}^{-3}$ and 2.8–13% respectively (Table 4).

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