

## DETERMINATION OF SOME METAL IONS IN AQUATIC ENVIRONMENTS BY ATOMIC ABSORPTION SPECTROMETRY AFTER CONCENTRATION WITH MODIFIED SILICA

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**Key words:** Separation and preconcentration, heavy metal ions, modified silica, natural waters.

### ABSTRACT

The complexes formed between N-propylsalicylaldehyde (IE11) and Cd (II), Cr (III), Cu (II), Mn (II, VII) and Pb (II) were identified and confirmed by IR, UV and pH-metric titration. The uptake behavior of porous silica modified with N-propylsalicylaldehyde (IE11) and these metal ions were studied. The Log  $k_d$  values were found to be within the range 2.19 – 5.16 depending on pH and time of stirring. IE11 was used in the separation and preconcentration of Cd (II), Cr (III, VI), Cu (II), Mn (II, VII) and Pb (II) from some natural water samples. The data were compared with those obtained by the solvent extraction method (APDC/MIBK). The proposed methodology allows to verify an improvement in the water quality of Nile River, probably attributed to high moderate floods in the last few years. The method was found to be accurate and precise and not subject to random error.

### INTRODUCTION

Within recent years, solvent extraction and coprecipitation have been increasingly replaced by sorbent (solid phase) extraction and ion exchange. The markedly lower quantity of reagents required is frequently quoted as an advantage, although this is strongly method-dependent. A further advantage is that the solid phase can be repeatedly used.

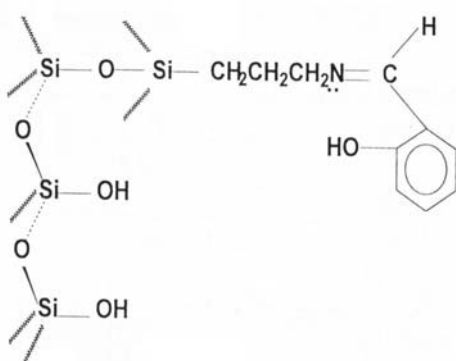
Sorption and ion exchange have been extensively studied for different analytical applications (Kenawy *et al.*, 1993 and 2000). Some natural and synthetic materials such as silica, carbon, cellulose and synthetic polymers have been used as it is or after modification by physical or chemical treatments. In the last two decades, the use of silica-based ion exchangers in preconcentration and separation of trace heavy metal ions from different media has been of particular interest. Advantages of silica as a base for chelating agents to be used as ion exchanger, over the organic polymers,

are its good mechanical and thermal stability and it is less susceptible to swelling, shrinking and microbial and radiation decay (Leyden and Luttrell, 1975).

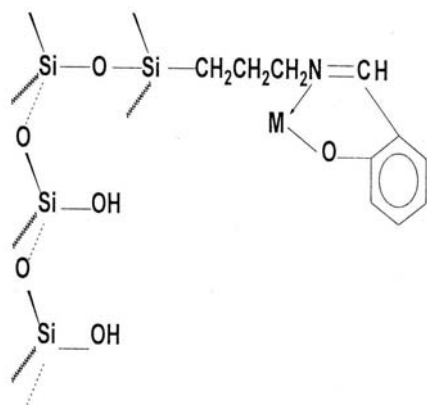
The using of chelating agents is promising route for the activation of the surface of the silica to raise its efficiency and selectivity of extraction. 3-aminopropyltriethoxysilane, propanethiol modified silica gel (Abou El-Sherbini *et al.*, 2003a), mono- and bis-salicylaldehyde and naphthaldehyde Schiff's bases based on silica gel Soliman *et al.*, 2001), hexathia-18-crown-6-tetraone based on octadecyl silica membrane disc Yamini *et al.*, 1997) and 8-hydroxyquinoline immobilized on fluorinated metal alkoxide glass (MAF-8HQ) Sohrin *et al.*, 1998) were used to separate trace amounts of heavy metal ions from their parent solutions. It was found that the efficiency of the separation depends on the concentration of the metal ion, the nature of the extractant and its surface area, temperature and the stability of the formed chelate.

## DETERMINATION OF SOME METAL IONS IN AQUATIC ENVIRONMENTS BY ATOMIC ABSORPTION SPECTROMETRY.

The synthesis and characterization of controlled pore silica modified with N-propylsalicylaldimine was reported (Abou El-Sherbini *et al.*, 2003a). B/Si ratio of 6.5/1 in borosilicate glass was effective in obtaining highly porous silica by acid leaching which led to high exchange capacity ( $C_{IE11} = 0.36$  mmole Cu/g, pH = 5.5) in the obtained ion exchanger (IE11, structure 1).



Structure (1)



Structure (2)

The complexation behavior of IE11 with  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Hg^{2+}$ ,  $Cr^{3+}$ ,  $Fe^{3+}$  and  $UO_2^{2+}$  was investigated and confirmed by electronic and infrared spectra and electrical properties (Abou El-Sherbini *et al.*, 2003b).

IR and UV spectra of IE11 and its complexes with Cd (II), Cr (III), Cu (II), Mn (II) and Pb (II) revealed that the bonding between these metal ions and the N-propylsalicylaldimine substrate is attributed to complexation through O and N. This is concluded from the disappearance of the IR bands at 1276 and 1492  $cm^{-1}$  in the spectra of the complexes assigned to  $\delta(O-H)_{in\ plane}$  and  $\delta(N-H)_{in\ plane}$ , respectively, in the free IE11 ligand (structure 2). Also, the UV absorption band detected in IE11 at 400 nm was blue shifted on complexation. The stoichiometry of the resulted solid complex preferred to be 1:1 (N-propylsalicylaldimine-M). This may be due to the steric hindrance of silica moiety and completed the coordination with two molecule of water (Abou-El-Sherbini *et al.*, 2003b)

The aim of the present paper is to study the uptake behavior of IE11 towards Cd (II), Cr (III, VI), Cu (II), Mn (II, VII) and Pb (II) to suggest the optimum conditions for the separation, preconcentration and elution of these metal ions from aquatic environments.

## MATERIALS AND METHODS

### Experimental - apparatus,

#### 1. Apparatus

##### 1.1. Atomic absorption spectrophotometer (AAS)

Analysis of Cd (II), Cr (III), Cu (II), Mn (II) and Pb (II) was performed by the Perkin Elmer 2380 flame atomic absorption spectrophotometer.

##### 1.2. Infrared spectra

Infrared reflectance spectra were recorded on a Bruker IFS 48 FTIR spectrometer using a gold ball as a reference. This measurement was kindly performed in the Physikalisch Technische Bundesanstalt Braunschweig, Germany.

##### 1.3. Electronic spectra

UV absorption spectrometric measurements were performed using UNICAM UV-Vis uvz spectrometer. The sample was introduced as slurry with nujol on a Whatmann filter paper strip using another

one wetted with nujol as a blank (Abou El-Sherbini *et al.*, 2003b).

#### 1.4. Adjustment of pH and pH-metric titration

The pH of each sample solution was adjusted to be within the range (3-11.5) using a Beckman (Fullerton, CA) digital pH meter with glass and saturated calomel electrodes calibrated on the operation state using standard buffer solutions at 25°C.

#### 2. Preparation of porous silica modified with *N*-propylsalicylaldimine (IE11) and its complexes with Cd (II), Cr (III), Cu (II), Mn (II) and Pb (II).

Porous silica (PS) was prepared by acid leaching of sieved borosilicate glass (<70 µm, B/Si = 6.5:1) obtained by sol-gel technique (Soliman, *et al.* 2001). The grafting with 3-aminopropyltrimethoxysilane (APMS) was achieved by refluxing 18 g PS with 36 mL APMS in xylene at 80°C for 24 h. 11 g of the yield was washed with ethyl alcohol and refluxed with 15 mL salicylaldehyde in 50 mL dimethyl sulfoxide (DMSO) at 90°C for 24 h. The obtained ion-exchange IE11 (yellow) was washed with EtOH and dried at 80°C (Abou El-Sherbini *et al.*, 2003a). For the preparation of complexes, 100 mg of the ion exchanger was added to 25 mL of 0.1 M of the metal chlorides solution (except for lead where nitrate was used instead) and pH value was adjusted to be below 5.5 (except for Cr where the pH was < 4) with 5% NaOH and 2% HCl (in case of Pb, HNO<sub>3</sub> was used instead). The sample was stirred for 24 h, then the M-IE11 complexes were filtered, washed with double distilled water and dried at 80°C.

#### 3. Batch procedure

The data are given as the simple mean of three replicates whereas those of application were repeated five times from which the statistical evaluation is performed.

A total of 20 mg of IE11 was suspended with constant stirring for 30 min in 25 mL of 10 µg/mL of Cd (II), Cr (III), Cu (II), Mn (II) or Pb (II) at the desired pH value in the range

3-11.5. The concentrations of the investigated ions in the filtrates were determined by AAS. The distribution coefficient ( $K_d$ ) is determined using the equation.

$$K_d = \frac{C_{i,ex}(\mu\text{g/g})}{C_{sol}(\mu\text{g/mL})} \text{ mL/g} \quad (1)$$

Where  $C_{i,ex}$  is the metal concentration in the ion exchanger (solid phase) and  $C_{sol}$  is the metal ion concentration in the solution phase.

The study of the separation of Cr<sup>3+</sup> and Mn<sup>2+</sup>, obtained by the reduction of CrO<sub>4</sub><sup>2-</sup> and MnO<sub>4</sub><sup>-</sup> respectively, was carried out. The reduction was performed by shaking with 0.5 mL H<sub>2</sub>O<sub>2</sub> (30% wt/vol) for 5 min after acidification with H<sub>2</sub>SO<sub>4</sub>. Excess H<sub>2</sub>O<sub>2</sub> was expelled by heating for 15 min at 90°C, then the separation process was performed as indicated above.

The optimum conditions (pH = 9.0 – 9.5, time of stirring = 30 min and weight of IE11 = 100 mg) were applied during the study of the interfering effects of different foreign ions on the efficiency of separation. The same conditions were also used in the study of the effect of concentration of the eluent acids (10 mL of HCl or HNO<sub>3</sub>) on the recovery.

#### 4. Sampling

Surface water samples were collected on 20 November, 2003, from Nile River water from Mansoura, Faraskor, Damietta, Gerbi and Ras Elbar, Mediterranean sea from Ras Elbar and Damietta Port, El-Manzalah Lake, Suez canal, Suez Gulf and tap water from Mansoura city. All samples were filtered using a sintered glass G4 and suspended matter is determined. The pH, total dissolved salts (TDS), dissolved oxygen (DO) and total alkalinity (mg CaCO<sub>3</sub>/L) were determined according to the reported literature (Strickland and Parsons, 1968). The samples were then acidified with concentrated HNO<sub>3</sub> acid to pH ≅ 2 and preserved in polyethylene vessels.

The organic matter was digested prior to the separation process. 0.5 g of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and 5

mL of 98% (wt/vol)  $\text{H}_2\text{SO}_4$  were added to 1 L of the water sample and heated for 30 min at  $95^\circ\text{C}$ . After cooling to room temperature, 100 mg of IE11 was added to the sample and the pH value was adjusted to 9.0-9.5 and stirred for 30 min then filtered. 50 mg of the ion exchanger was added to the filtrate and the pH value was controlled. The sample was stirred again for 30 min and filtered. Both residues were gathered and the collected metal ions were released by 10 mL 2M  $\text{HNO}_3$ , to give a concentration factor of 100 fold.

The concentration of dissolved Cd (II), Cr (III), Cu (II), Mn (II) and Pb (II) were determined in water by solvent extraction using ammonium pyrolidine dithiocarbamate (APDC) and methyl isobutyl ketone (MIBK) as a standard method (APHA, 1989).

## RESULTS AND DISCUSSION

### 1. Uptake behavior of IE11

#### 1.1. Effect of pH

Fig. 1 represents the effect of pH on the uptake behavior of Cd (II), Cr (III), Cu (II), Mn (II) and Pb (II) on IE11. At low pH, the distribution coefficients were generally low for all the five analytes, which is attributed to the incomplete ionization of the ionogenic group of the ion exchanger. The distribution coefficient of the metal ions on IE11 increases with pH and reaches its maximum at  $\text{pH} \cong 9.0$  but decreases in case of  $\text{Cr}^{3+}$  and  $\text{Pb}^{2+}$  probably due to the formation of the anionic ions  $\text{CrO}_2^-$  and  $\text{PbO}_2^{2-}$  respectively. The  $\text{Log}K_d$  values at  $\text{pH} = 9.0-9.5$  were 4.68, 5.16, 4.83, 5.09, 4.70 for Cd (II), Cr (III), Cu (II), Mn (II) and Pb (II) respectively.

#### 1.2. Effect of time of stirring, concentration of eluent acids and some interfering species:

Fig. 2 represents the effect of time of stirring on the recovery of the investigated metal ions at  $\text{pH} = 9.0-9.5$  using IE11. The ion exchanger shows fast kinetics of equilibration where 30 min. of stirring was satisfactory to reach maximum values of

recovery. Fig. 2 shows that the recovery of metal ions under investigation take place in the range of 60 – 100% recovery after 1 min. This indicates that the reaction between solid-phase IE11 and metal ions is fast. While, the concentration of metal ion in aquatic environment is very low (Kenawy, *et al.* 2000).

Fig. 3a & b shows the effect of concentration of eluting acids on the recovery after separation at  $\text{pH} = 9.0-9.5$  and weight = 100 mg. HCl showed relatively better leaching efficiency of the metal ions from the ion exchanger than  $\text{HNO}_3$  except in case of  $\text{Cu}^{2+}$  where the recovery was lower with HCl. This may be attributed to the formation of anionic chloro-complex with  $\text{Cu}^{2+}$  which may be bonded to the protonated imine nitrogen of the substrate at  $\text{pH} < 4$  (Abou El-Sherbini *et al.*, 2003a). However, molar concentrations of HCl and  $\text{HNO}_3$  were sufficient to obtain maximum recovery but the latter is recommended for application due to the limitation of using HCl in case of  $\text{Pb}^{2+}$ . However, the eluting efficiency of CMPS-PAN resin (Kenawy *et al.*, 2000), is smaller than that of, IE11 accompanied with that strong chelation between the ion exchanger and the metal ions is not favored, due to irreversible binding (Leyden and Luttrell, 1975).

No effect on the recovery of the investigated metal ions was found from acetate, oxalate (200 mg/L), nitrate, sulfate, phosphate,  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  (1000 mg/L) ions. Citrate and EDTA (200 mg/L) showed strong interfering effect on the recovery of the investigated metal ions ( $R = 6.4 - 94.2\%$ ) due to the formation of complexes with the metal ions of higher stability than those with IE11. Consequently, the organic matter presents in the natural water samples (which may have the same effect) should firstly be digested prior to the application process.

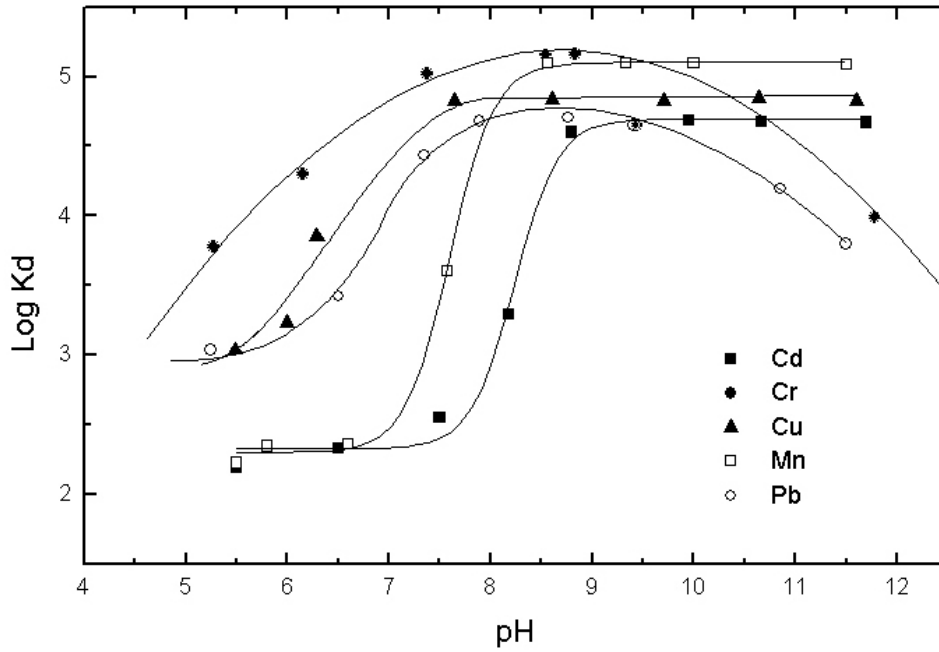
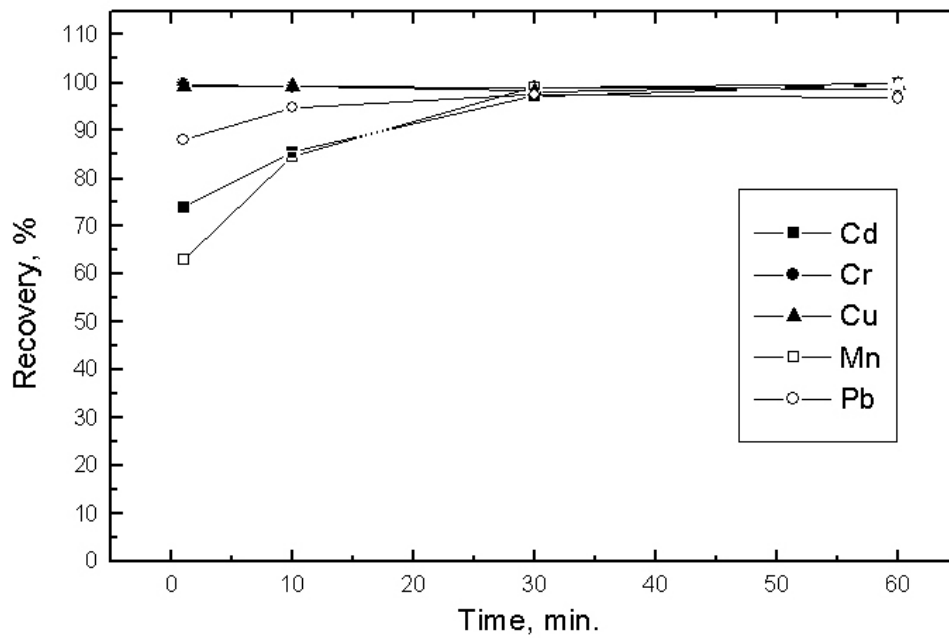


Fig. 1: Effect of pH on the distribution coefficient of Cr (III), Mn (II), Cu (II), Cd (II) and P(II) on IE11.



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Fig. 2: Effect of time of stirring on the recovery of Cr (III), Mn (II), Cu (II), Cd (II) and Pb (II) separated on 20 mg IE11 at pH = 9.0-9.5.

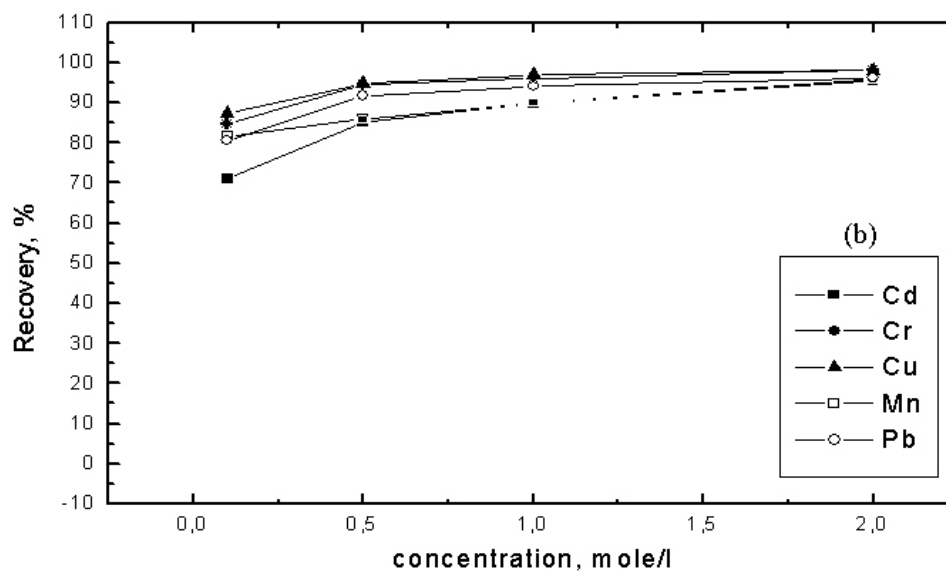
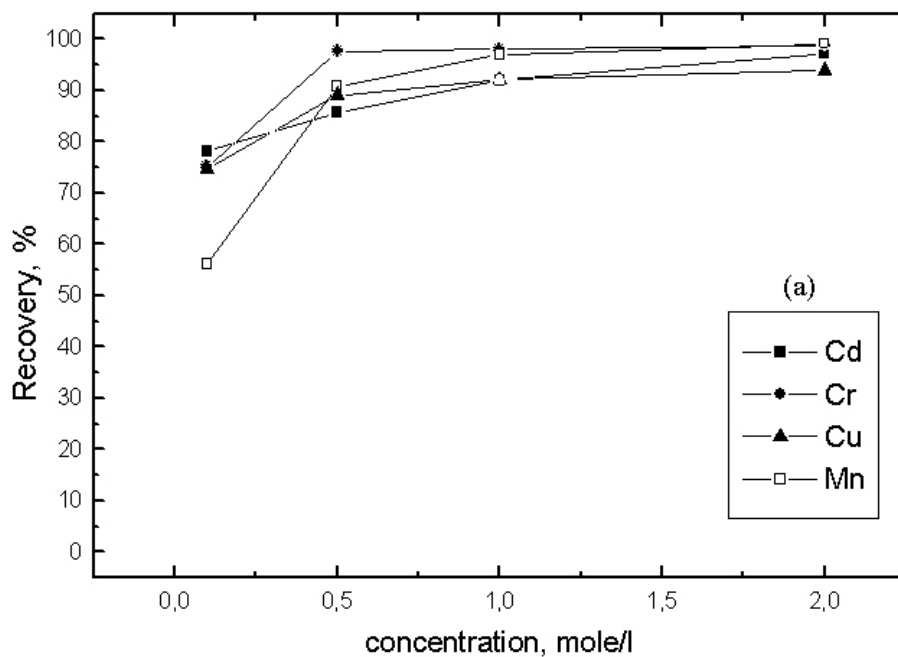


Fig. 3: Effect of HCl (a) HNO<sub>3</sub> (b) concentration on the recovery of Cr (III), Mn (II), Cu (II), Cd (II) and Pb (II) separated on 20 mg IE11 at pH = 9.0-9.5 and time of stirring = 30 min.

### 1.3. Separation of Cr (III) and Mn (II) obtained from chromate and permanganate

The separation of Cr (III) and Mn (II) obtained by reduction of their higher oxidation states from chromate (Cr (VI)) and permanganate (Mn (VII)), respectively, using  $H_2O_2$  in acidic medium led to a recovery of 94.5 and 98.5%, respectively. This is slightly lower than the values obtained without previous reduction (99.1 and 99.0 % respectively) indicating the effectiveness of the reduction process.

### 2. Nature of bonding between metal ions and IE11

The pH-metric titration of the free silica-based N-propylsalicylaldimine ion exchanger, and its complexes showed the presence of two inflections attributed to neutralization of the proton gained to the imine nitrogen (acidic range) and another from the phenolic group (basic range) (Abou El-Sherbini *et al.*, 2003a), Fig. 4. The second inflection in the free IE11 at pH = 9.7, was shifted to lower pH values and decrease in the sequences Cr (III) > Cu (II) > Pb (II) > Mn (II) > Cd (II), i.e. decreasing complex strength.

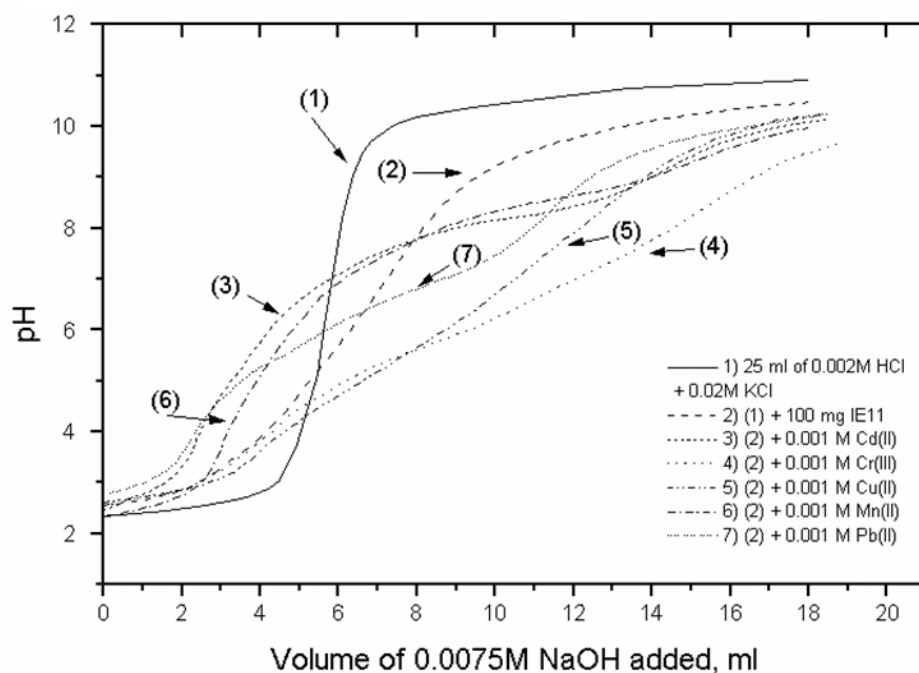


Fig. 4: The pH-metric titration curves of IE11, its complexes with Cr (III), Mn (II), Cu (II), Cd (II) and Pb (II).

### 3. Analytical application

#### 3.1. Water quality measurements

The pH of the water samples was in the alkaline side and ranged between 8.25 at Suez Gulf and 7.70 at Ras Elbar (brackish water). TDS determined for the water samples indicated that only samples collected from Nile River at Mansoura and Faraskor may be considered as fresh water (Abdallah, *et al.* 1999) while those from Nile River at Damietta Bridge, Gerbi and Ras Elbar, water at Damietta Port and El-Manzalah Lake are brackish water (Hamed and Said, 2000). Water samples from Ras Elbar, Port Said and Suez Gulf are saline (Hamed, 1996). It is noteworthy to mention that the relative low TDS in seawater taken from Damietta Port is

attributed to the fresh water effluent from a small canal. TSM of the Nile River and tap water was found to be low varying within the range from 0.075 to 0.159 g / L. DO varied from 3.54 mg O<sub>2</sub> / L at El-Manzalah to 6.94 mg O<sub>2</sub> / L at Ras Elbar. The minimum value of DO at El-Manzalah could probably be due to the effect of disposal of domestic wastewater (Meshal, 1967). Alkalinity of the surface water is varied from 138.0 to 176.5 mg CaCO<sub>3</sub> / L, at Ras Elbar sea and El-Manzalah Lake waters, respectively. The high alkalinity value at El-Manzalah is essentially due to the disposal of sewage with other domestic effluents in El-Manzalah Lake. The data of water quality measurements are presented in Table 1.

Table (1): Water quality measurements of the water samples collected from different locations at 20 Nov, 2003.

Parameter	pH	TDS (g/L)	TSM (g/L)	DO (mg O <sub>2</sub> / L)	Alkalinity (mg CaCO <sub>3</sub> / L)
Location					
Mansoura (river water)	7.9	0.506	0.075	4.10	145.0
Faraskor (river water)	8.08	0.988	0.101	6.60	147.5
Damietta Bridge (brackish water)	7.76	2.086	0.122	6.43	157.0
Gerbi (brackish water)	7.87	3.090	0.106	4.49	153.5
Ras-Elbar (brackish water)	7.70	6.994	0.159	6.94	156.0
Ras Elbar (seawater)	8.10	40.604	0.755	6.15	138.0
Damietta Port (brackish water)	8.13	20.400	0.299	6.83	148.5
Port Said (seawater)	8.16	43.120	0.245	5.92	138.0
Suez Gulf (seawater)	8.25	47.804	0.299	6.03	148.5
El-Manzalah (brackish water)	8.12	30.376	0.630	3.64	176.5
Mansoura city (tap water)	7.85	0.316	0.170	6.37	145.0



### 3.2. Water analysis

The ion exchange method was applied for the preconcentration and separation of Cd (II), Cr (III), Cu (II), Mn (II) and Pb (II) in the water samples whereas solvent extraction was used to evaluate the reliability of the ion exchange method, Table 2. Suez Gulf showed generally low concentrations of heavy metal ions and the lowest values for the investigated metal ions. These values are in agreement with those recorded in Suez Gulf with the APDC/MIBK system (Abou El-Sherbini and Hamed, 2000).

Generally, the concentrations of heavy metal ions increase in the region beginning from Damietta Bridge to the river effluent at Ras Elbar. The nearby locations showed higher concentrations of the investigated metal ions, may be attributed to the domestic and anthropogenic activities along the side of the river in this region. However, these results are within the permissible levels and in agreement with those reported (Kenawy *et al.*, 2000 and Fifield and Haines, 2000).

The decrease in the heavy metal concentration compared to the reported values within the last thirteen years (El-Defrawy *et al.*, 1992 and Kenawy *et al.*, 1993) could be due to the high to moderate floods of Nile River in 1998–2000 (Hafez *et al.*, 2001). This led to reclamation and improvement in the quality of water.

### 4. Comparison between the accuracy and precession of the present method with the reference solvent extraction APDC/MIBK method

The reliability of the ion exchange method was statistically examined for the analysis of Cd (II) and Pb (II), Tables 3 and 4 respectively, compared with the standard method of solvent extraction, based on the null hypothesis of  $|t|_2$  for  $P=0.05$  and  $n=10$  (Miller and Miller, 1986). It was found that  $|t|_2=0.00-2.3$  for all the five metal ions which are less than the tabulated values ( $|t|_2=2.31$ ) (Miller and Miller, 1986) with the exception of Cu (II) at Faraskor, Ras Elbar (brackish water) and El-Manzalah and Mn (II) at Damietta Port. No significant difference was found between the data obtained by the ion exchange and the solvent extraction methods. The precession and the random errors of the two sets of data (Tables 3 and 4) were deduced using the two-tailed F-test (Miller and Miller, 1986). It is clear that all the experimental  $F_{4,4}$  values are between 1.00 and 2.54, less than the tabulated value of  $F_{4,4}$  for  $P=0.05$  and  $n=10$  (9.6) (Fifield and Haines, 2000). So, no significant difference between the two standard deviations at  $P=0.05$  for both methods and the results obtained by both methods are not subjected to random errors (i.e. precise)

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Table 2: Multi-elements analysis of natural water samples using AAS for determination of some heavy metal ions in  $\mu\text{g/L}$  ( $\cong$  ppb) after preconcentration with solvent extraction (SE) (APDC/MIBK), and ion exchange separation by IE11. Ion exchange conditions: pH = 9.0-9.5, weight of IE11 = 150 mg, stirring time = 30 min at 25°C,  $\bar{x} \pm \frac{s}{\sqrt{n}}$  for n = 5, where  $\bar{X}$  is the average, t is the student factor and equals 2.57 for P = 0.05 and s is the standard deviation. The samples were collected at 20 Nov, 2003.

Element Location	Cd (II)		Cr			Cu (II)		Mn (II)		Pb (II)	
	SE	IE11	SE	IE11	(VI) IE11	SE	IE11	SE	IE11	SE	IE11
Mansoura (river water)	0.07±0.01 0.02 [8], 0.2-2.3[6]	0.08±0.01 0.51±0.03 1.0 [8], 0.19-25.8[12]	0.50±0.03 0.19-25.8[12]	0.50±0.03 0.19-25.8[12]	3.83±0.34 0.75-7.29 [12]	2.05±0.04 5.0[8], 3-30[6]	2.07±0.03 3-30[6]	2.50±0.07 7.0[8], 8.0-95.9[12]	2.57±0.07 8.0-95.9[12]	3.86±0.10 3.0[8], 1.5-41.0[6]	3.95±0.09 1.5-41.0[6]
Faraskor (river water)	0.61±0.05 0.02[8], 0.2-2.3[6]	0.59±0.07 1.0[8], 0.19-25.8[12]	0.47±0.05 0.19-25.8[12]	0.47±0.05 0.19-25.8[12]	2.90±0.19 0.75-7.29 [12]	2.00±0.06 5.0[8], 3-30[6]	1.90±0.04 3-30[6]	1.26±0.05 7.0[8], 8.0-95.9[12]	1.27±0.06 8.0-95.9[12]	2.90±0.09 3.0[8], 1.5-41.0[6]	2.92±0.08 1.5-41.0[6]
Damietta Bridge (brackish water)	0.65±0.06	0.66±0.07 1.58±0.05	1.56±0.05	1.56±0.05	1.81±0.12 0.75-7.29 [12]	3.22±0.52	3.37±0.34	11.32±0.46	11.41±0.59	4.15±0.08	4.18±0.08
Gerbi (brackish water)	1.44±0.03	1.46±0.04	2.60±0.07	2.62±0.07	3.28±0.28 0.75-7.29 [12]	3.00±0.07	3.05±0.07	3.11±0.55	3.21±0.46	6.20±0.40	6.22±0.39
Ras-Eilbar (brackish water)	0.62±0.05	0.63±0.05	2.02±0.05	1.99±0.05	4.01±0.42	1.58±0.05	1.65±0.04	9.20±0.33	9.27±0.31	3.28±0.17	3.30±0.15
Ras Eilbar (seawater)	3.41±0.14 0.1[5], 3.2-4.3[6]	3.45±0.17 0.05[8], 0.02-0.18 [12]	2.74±0.06 0.48 [17] 0.15-0.3 [14]	2.77±0.06 0.48 [17] 0.15-0.3 [14]	2.32±0.17 0.48 [17] 0.15-0.3 [14]	4.28±0.48	4.10±0.45	4.50±0.35	4.54±0.31	10.29±0.52	10.38±0.57 0.03[8], 4.5-18[6]

Cont.

Table (2) Cont.

Element Location	Cd (II)		Cr			Cu (II)		Mn (II)		Pb (II)	
	SE	IE11	(II)		(VI)	SE	IE11	SE	IE11	SE	IE11
			SE	IE11	IE11						
Damietta Port (brackish water)	1.19±0.06	1.20±0.06	0.29±0.02	0.28±0.02	3.98±0.41	1.60±0.05	1.61±0.06	2.15±0.28	2.17±0.26	3.01±0.16	3.04±0.15
	0.1[8], 3.2-4.3[6]		0.05[8], 0.02-0.18[12]		0.48 [14] 0.15-0.3 [17]	2.0[8], 0.71-5.3[6]		0.2[8], 1.1-1.8[12]		0.03[8], 4.5-18[6]	
Port Said (seawater)	0.69±0.05	0.70±0.05	1.50±0.05	1.47±0.05	2.24±0.17	2.32±0.07	2.31±0.07	2.56±0.15	2.57±0.19	0.33±0.02	0.34±0.02
	0.1[8], 3.2-4.3[6]		0.05[8], 0.02-0.18[12]		0.48 [14] 0.15-0.3 [17]	2.0[8], 0.71-5.3[6]		0.2[8], 1.1-1.8[12]		0.03[8], 4.5-18[6]	
Suez Gulf (seawater)	0.25±0.01	0.26±0.01	0.06±0.01	0.07±0.01	2.53±0.19	0.20±0.01	0.19±0.01	0.26±0.05	0.27±0.05	0.73±0.06	0.74±0.05
	0.1[8], 3.2-4.3[6]		0.05[8], 0.02-0.18[12]		0.48 [14] 0.15-0.3 [17]	2.0[8], 0.71-5.3[6]		0.2[8], 1.1-1.8[12]		0.03[8], 4.5-18[6]	
El-Manzalah (brackish water)	0.58±0.01	0.58±0.01	1.30±0.05	1.29±0.05	2.15±0.18	2.05±0.04	2.12±0.03	1.81±0.10	1.80±0.11	2.79±0.08	2.84±0.09
	0.58±0.05	0.62±0.07	0.42±0.03	0.41±0.03	2.62±0.24	1.01±0.04	1.04±0.03	1.03±0.06	1.04±0.07	1.50±0.08	1.53±0.08
Mansoura city (tap water)	0.02[8], 0.2-10[6]		1.0[8], 0.15-50[12]		50 [7]	3.0[8], 3.3-5.0[6]		10.0[8], 3.2-19.5[12]		1.0[8], 2.7-17.3[6]	

Mn (VII) was not detected in all samples., NB[No.]= number of reference alphabetically

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Table (3) : Statistical evaluation for Cd (II) analysis in natural water samples after preconcentration by solvent extraction (method (1)) and ion exchanger (method (2)), n = 5.

Sample (location)	Method (1)		Method (2)		$s_p$	$ t _2$	Two-tailed F-test
	$\bar{X}_1$ ng/mL	$s_1$	$\bar{X}_2$ ng/mL	$s_2$			
Tap water (Mansoura city)	0.58	0.050	0.62	0.060	0.06	1.15	1.44
Seawater (Ras-ElBar)	3.41	0.120	3.45	0.150	0.14	0.47	1.56
River water (Faraskour)	0.61	0.050	0.59	0.060	0.06	0.57	1.44
River water (Mansoura)	0.07	0.010	0.08	0.010	0.01	1.58	1.00
River water (Gerbi)	1.44	0.027	1.46	0.031	0.03	1.09	1.32

Table (4). Statistical evaluation for Pb (II) analysis in natural water samples after preconcentration by solvent extraction (method 1) and ion exchanger (method 2), n = 5.

Sample (location)	Method (1)		Method (2)		$s_p$	$ t _2$	Two-tailed F-test
	$\bar{X}_1$ ng/mL	$s_1$	$\bar{X}_2$ ng/mL	$s_2$			
Tap water (Mansoura city)	1.50	0.069	1.53	0.072	0.071	0.70	1.09
Seawater (Ras-ElBar)	10.29	0.450	10.38	0.500	0.48	0.30	1.23
River water (Faraskour)	2.90	0.080	2.92	0.070	0.075	0.42	1.21
River water (Mansoura)	3.86	0.089	3.95	0.081	0.085	1.67	1.21
River water (Damietta)	4.15	0.071	4.18	0.068	0.07	0.70	1.09

## CONCLUSION

The optimum conditions of separation of Cd (II), Cr (III), Cu (II), Mn (II) and Pb (II) using N-propylsalicylaldimine based on porous silica were found to be pH = 9.0-9.5, time of stirring =  $\geq 30$  min. A concentration of 2M HNO<sub>3</sub> as an eluent was sufficient to obtain maximum recovery, 95.5, 98.1, 98.1, 95.7, 96.2% for Cd (II), Cr (III), Cu (II), Mn (II) and Pb (II). In case of HCl, the recovery values were 97.2, 98.7, 93.9 and 99.0% for Cd (II), Cr (III), Cu (II), and Mn (II), respectively.

Citrate and EDTA showed interference to the separation of different metal ions, therefore, it was necessary to digest organic matter in natural samples before application.

The separation of Cr (III) and Mn (II) obtained by reduction of their higher oxidation state forms, e.g., chromate and permanganate, using H<sub>2</sub>O<sub>2</sub> in acidic medium, giving a recovery of 94.5 and 98.5%, respectively.

The ion exchange method was applied for preconcentration and separation of Cd (II), Cr (III, VI), Cu (II), Mn (II, VII) and Pb (II) in the water samples in comparison with the standard solvent extraction method. The concentration of heavy metal ions increased obviously in the region beginning from Damietta Bridge to the river effluent at Ras Elbar, probably due to the domestic and anthropogenic activities along the side of the river in this region. However, although the results lie within the permissible level, an obvious decrease in the heavy metals concentration was observed compared with those reported at the early 1990's. This was explained in view of the high floods in the last few years leading to reclamation and improvement of the water quality of Nile River.

The reliability of the ion exchange method was statistically examined compared with the standard method of solvent extraction. Testing of the experimental means and the standard deviations for the two

methods using the null hypothesis of  $|t|_2$  and the two-tailed F-test respectively, for P=0.05 and n=10, indicated that the ion exchange method is accurate and precise.

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