

DETERMINATION OF ZINC SPECIES USING ULTRAFILTRATION AND DIFFERENT SOLID SORBENTS

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Abstract: *A method for the determination of operationally-defined metal species at natural concentration levels has been developed. The method is based on a combination of physical characterization by size fractionation using ultrafiltration and chemical characterization by retention studies on different solid sorbents. The aim of this study is to investigate the effect of pH on its performance. A set of three columns packed with different sorbents, namely, cation-exchange resin Chelex-100, anion-exchange resin Dowex 1-X8 and C-18 reversed phase was developed. The retention of metal species in each size fraction onto the sorbents at different pH conditions was investigated. Experiments were performed with metals in the presence of model ligands, namely, nitrilotriacetic acid (NTA), ethylenediamine tetraacetic acid (EDTA), humic acid (HA), 8-hydroxyquinoline-5-sulphonic acid (SOX) and 8-hydroxyquinoline (OX). The applicability of the method was investigated using synthetic river water samples spiked with species of zinc.*

Keywords: metal species, ultrafiltration, solid sorbents, speciation

Abstrak: *Suatu kaedah untuk menentukan spesies logam yang ditakrifkan secara operasi pada paras kepekatan semula jadi telah diperkembang berdasarkan suatu kombinasi yang terdiri daripada pencirian fizik melalui pemecahan saiz dengan penurasan ultra dan pencirian kimia melalui kajian retensi pada penjerap pepejal yang berlainan. Kajian ini bertujuan untuk meninjau kesan pH terhadap prestasinya. Suatu set daripada tiga turus yang diisi dengan penjerap yang berlainan, iaitu resin pertukaran kation Chelex 100, resin pertukaran anion Dowex 1-X8 dan fasa berbalik C-18 telah digunakan. Retensi spesies logam dalam setiap pecahan saiz pada penjerap pada keadaan pH yang berbeza dikaji. Eksperimen telah dilakukan dengan logam dalam kehadiran ligan model, iaitu asid nitriloasetik (NTA), asid etilenadiamina tetraasetik (EDTA), asid humik (HA), asid 8-hidroksikuinolin-5-sulfonik (SOX) dan 8-hidroksikuinolin (OX). Kebolehpakaian kaedah ini dikaji dengan menggunakan sampel air sungai sintetik yang ditambah dengan spesies zink.*

Kata kunci: spesies logam, penurasan ultra, penjerap pepejal, penspesiesan

1. INTRODUCTION

Trace metals such as Cu, Cd, Pb and Zn in natural waters are present in various physical and chemical forms such as free hydrated ions, organic or inorganic complexes and associated with colloidal or suspended particles. The determination of these metals is of increasing interest and importance because the impact of both their chemical reactivity and biological availability on any environmental systems are strongly dependent on the chemical species of metal. The studies of chemical speciation of trace metals are usually based on the discrimination for the operationally-defined classes of metal species having similar chemical properties and reactivities.

The discrimination procedure of metal species is based on the retention of metal forms with different chemical behaviors onto different solid sorbents, namely, chelating ion exchanger, anion exchanger and reversed-phase octadecyl silica. These sorbents have been extensively used for the uptake of metal species from aqueous samples and for their enrichment, under different mechanisms of ligands and of complex retention¹.

Liquid-solid extraction is commonly used for the determination of trace metal speciation in natural waters. The most widely used is the chelating ion exchanger Chelex-100 which discriminates between strongly and weakly bound or free metal species². Many schemes for metal speciation in natural waters based on the coupling of retention onto Chelex-100 and spectrometry and electrochemical technique have been developed and reported in several publications³⁻⁵. The excellent capacities of strongly basic anion exchange resins for preconcentration and separation of anionic metal complex species were employed by Ou-Yang and Jen⁶ to preconcentrate Cr(III) and Cr(VI) prior to speciation analysis.

The solid phase extraction (SPE) technique has been used increasingly in speciation analysis of metals in aqueous samples due to the advantage of high sensitivity of performing a simultaneous enrichment step and versatility⁷⁻¹⁰. Among the size fractionation methods for speciation studies of trace metals in natural waters, the ultrafiltration technique is commonly used to separate the dissolved species of metals by passage through molecular filters into various sizes in each molecular level⁵.

The objective of this work is to develop a method for the determination of different forms of metal species and to study the effect of pH on its performance. The method is based on a combination of physical characterization by size fractionation using ultrafiltration and chemical characterization by retention studies on different solid sorbents. The retention of metal species with

different chemical behaviors onto a chelating cation exchange resin, Chelex-100, an anion exchange resin, Dowex 1-X8 and a reversed-phase C-18 sorbent was studied by the column method. A set of three columns was packed with the desired sorbents. The behavior of metal species as free hydrated ions and after conversion into negative or neutral complexes in each size fraction was investigated at different pH values. The ligands employed for the experiments were nitrilotriacetic acid (NTA), ethylenediamine tetraacetic acid (EDTA), humic acid (HA), 8-hydroxy-quinoline-5-sulphonic acid (SOX) and 8-hydroxyquinoline (OX). The applicability of the method was investigated by using synthetic river water samples spiked with the species of Zn. The results obtained are discussed in terms of the percentage distribution of the metal species and the effect of pH on the labilities of desired metal species.

2. MATERIALS AND METHODS

Sample preparation was carried out in a clean room laboratory with the ISSCO laminar flow Model BVT 124 fume cupboard.

2.1 Instrumentation

Metal determinations were performed by using two main techniques, namely, differential pulse anodic stripping voltammetry (DPASV) and electrothermal atomic absorption spectrometry (ETAAS). The DPASV was performed with Polarography analyzer Potentiostat PGSTAT 100 equipped with Metrohm 663 VA Stand using a hanging mercury drop electrode (HMDE), Ag/AgCl reference electrode with salt bridge and Pt counter electrode. A Perkin-Elmer Zeeman 800 atomic absorption spectrophotometer equipped with HGA-800 graphite furnace, a pyrolytic graphite platform and an AS800 autosampler was used. Size fractionation of the soluble metal was achieved by using ultrafiltration technique, which was performed with the Millipore Amicon disc membrane filters 76 mm i.d. in a Cole-Parmer stirred cell assembly under N₂ pressure. The Molecular Weight Cut-Off (MWCO) values of membrane filters were 100K, 30K, 10K, 5K and <1K. The pH was measured by a pH meter (Denver Instrument Model 15) with a combined glass-calomel electrode (Orion).

2.2 Reagents and Materials

The following analytical grade sorbents were used: 100–200 mesh Chelex-100 (Bio-Rad), 100-200 mesh Dowex 1-X8 (Supelco), 37–50 mesh size silica RP-C18 (Sigma). The ligands employed, namely Na-EDTA (BDH), NTA (Fluka), HA (Fluka), SOX (Fluka) and OX (Fluka), were all of analytical grade. Acids of suprapure grade, namely HNO₃ (System) and HCl (Merck), were used.

Other reagents used were all of analytical grade: NaOH (Fluka), NH₃ (R&M), CH₃OH (Merck), Ca(OH)₂ (R&M).

High purity water (HPW) produced from a Milli-Q system was used throughout. The synthetic river water (SRW) was prepared by dissolving Ca(OH)₂ and appropriate salts in HPW resulting in a pH of 6.5. The analytical concentrations of the principal cations and anions were as follows: Ca²⁺ 0.85, Mg²⁺ 0.20, Na⁺ 0.34, K⁺ 0.035, NH₄⁺ 0.017; total carbonate 1.7, SO₄²⁻ 0.2, Cl⁻ 0.38, NO₃⁻ 0.008 and total phosphate 0.0030 mM¹¹. The concentration of ligands used throughout was as follows: 1 × 10⁻⁴ M EDTA, 1.6 × 10⁻⁴ M NTA, 20 µg/L HA, 3 mM SOX and OX. Each of Na-EDTA and NTA was dissolved in HPW. A stock solution of HA was prepared by dissolving 0.100 g HA in 1 L of 0.1 M NaOH, then filtering through a 0.4 µm Nuclepore filter and the residue (~30%) was discarded. The OX was dissolved in 0.25 mL CH₃OH followed by the addition of 1.0 mL of 1 M HCl and the solution diluted to 200 mL with HPW. The SOX was dissolved in a few milliliters of 0.1 M NaOH and the solution brought to volume with HPW. The NH₄COOCH₃ buffer solution was prepared by mixing the proper amounts of NH₃ and CH₃COOH to a final concentration of 0.1 M for the desired pH used.

Standard solutions of Zn were prepared by dilution from 1000 mg/L standard solutions (Merck). A working standard solution in SRW of 40 µg/L Zn was used throughout and prepared fresh as needed.

All plastic and glassware containers were cleaned by soaking for 48 hours in 10% HNO₃, then washed with HPW until no acid was retained. The stirred cell was cleaned between each experiment series by soaking for 24 hours in a 5% solution of Decon 90 surface active agent.

2.3 Column Preparation

Glass columns of 15 cm × 1.0 cm i.d. diameter with coarse sintered glass frits and teflon stopcocks were used. The column was joined to a 1 L polypropylene separatory funnel with teflon stopcock, which served as sample reservoir, with a 5.0 cm. polypropylene tubing. The flow rate was always maintained at 1 mL/min.

2.3.1 Preparation of NH₄-Chelex column

About 1.3 g of Chelex-100 resin in the Na-form was allowed to equilibrate in HPW for two days prior to use. The wet resin was then loaded into the glass column which was subsequently eluted with 10 mL of 2 M HNO₃ to

remove trace metal contaminants and washed with 20 mL of HPW. The column was eluted with 10 mL of 2 M NH_3 solution to convert the resin to the NH_4^+ form and then washed with 20 mL of HPW.

2.3.2 Preparation of Cl^- -Dowex column

Dowex 1-X8 resin of 3.0 g in weight was washed with HPW until the filtrate became clear. The wet resin was loaded as slurry into the column and activated by passing 30 mL of 1.0 M NaOH through the column followed by 10 mL of HPW to remove excess NaOH. The resin was converted to the Cl^- form by passing 30 mL of 1.0 M HCl through the column and washed with 10 mL of HPW to remove excess HCl.

2.3.3 Preparation of C-18 column

The silica RP-C18 (1.0 g) were initially cleaned by successive rinsing with 10 mL CH_3OH , 10 mL 1:1 $\text{H}_2\text{O} : \text{CH}_3\text{OH}$, 10 mL 0.6 M HCl and finally 20 mL HPW.

2.4 Procedure

2.4.1 Size fractionation by ultrafiltration

The fractionation procedure began with the membrane filter having the highest MWCO (100 K). The stirred cell and membrane was flushed with HPW. A buffered SRW of 100 mL was then introduced into the cell and the system pressurized with N_2 . The first 10% and the last 20% of ultrafiltrate were discarded. The ultrafiltrate from the above step, which consisted only the middle fraction, was sequentially fractionated using the next lower MWCO until the smallest MWCO (1K) was used. A flow diagram for size fractionation is shown in Figure 1.

2.4.2 Speciation procedure

All ultrafiltrates in each size fraction at different pH values were analyzed in triplicate. Loading and elution flow rates were 1.0 mL/min. The enrichment factor used during optimization was 2.5. The speciation schemes for the discrimination of the defined classes of metal species in the ultrafiltrate SRW are shown in Figures 2 to 4.

a) Chelex-100

A portion of ultrafiltrate in each size fraction was determined for "Very Labile" (VLB) fraction. The other portions in the same size fraction were loaded into the Chelex column for the studies on the degree of lability towards Chelex. "Moderately Labile" (MLB) fraction was determined from the eluant of Chelex column. "Slowly Labile" (SLB) and "Inert" (INT) fractions were determined from Chelex batch method. All fractions except the INT fraction were measured by ASV whereas the INT fraction was measured by ETAAS.

b) Dowex 1-X8

The ultrafiltrate in each size fraction was loaded into the Dowex column for the identification of the defined classes of metal species. Dowex Column Labile (DLB) as negatively charged metal complexes was determined from

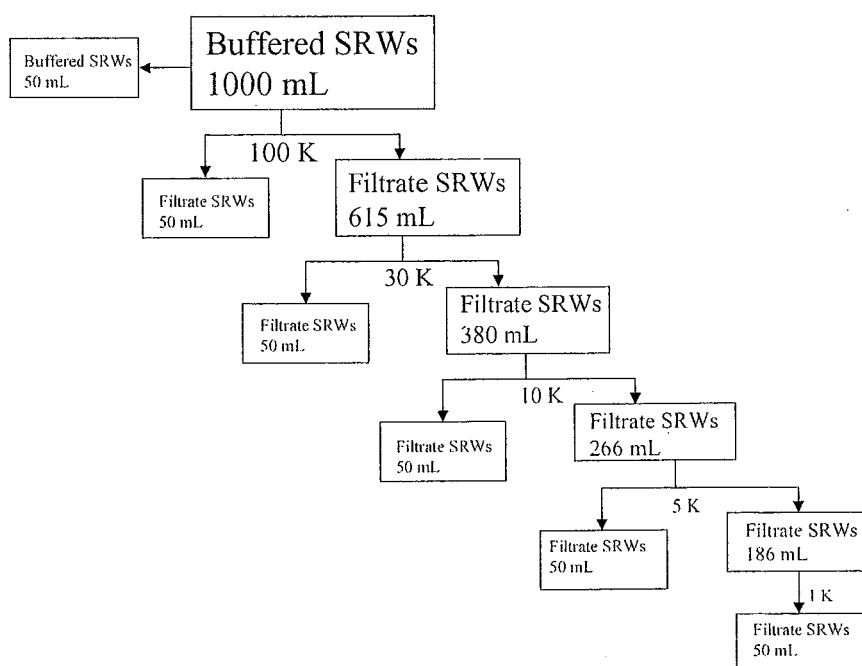


Figure 1: Flow diagram for sequential size fractionation by ultrafiltration

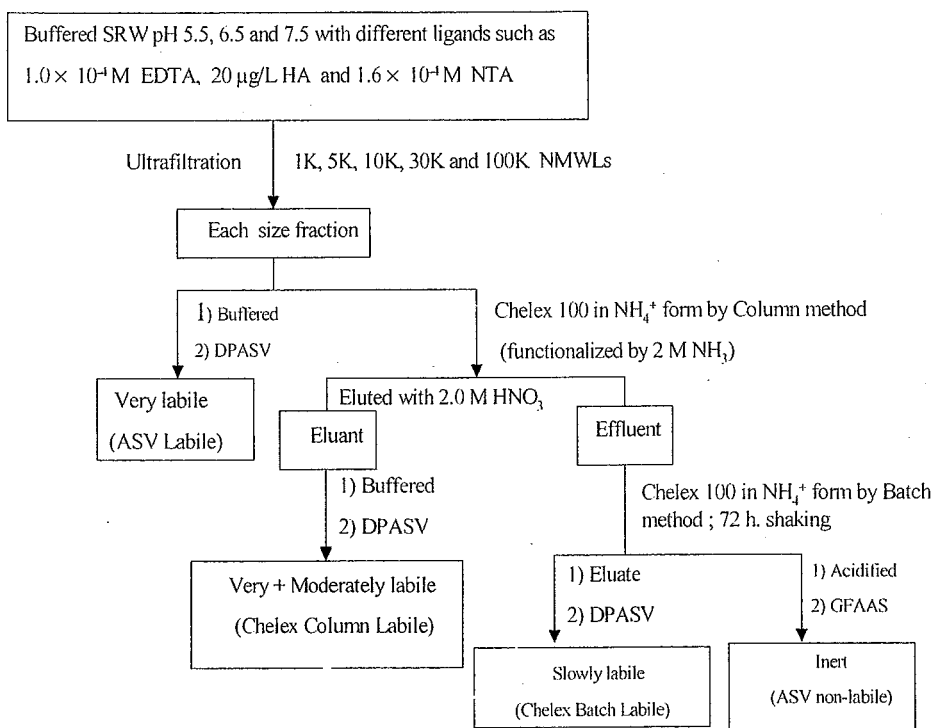


Figure 2: Speciation scheme for metal species in SRWs by using Chelex-100

the eluant of Dowex column by ETAAS. The ASV Labile as a free form of metal species was determined from the effluent of column by ASV. The non-ASV Labile or Dowex Less Labile (DLLB) as the neutral form of metal complexes was also determined from the column effluent by ETAAS.

c) Silica C-18 sorbent

The procedure for the identification of defined classes of metal species by silica C-18 sorbent was similar to Dowex 1-X8 studies. The C-18 Labile (C-18 LB) as the neutral metal complexes was determined from the eluant of C-18 column by ETAAS. The ASV Labile as the free form of metal species was determined from the effluent of column by ASV. The negatively charged metal Complexes as the non-ASV Labile or C-18 Less Labile (C-18 LLB) was determined from effluent of column by ETAAS.

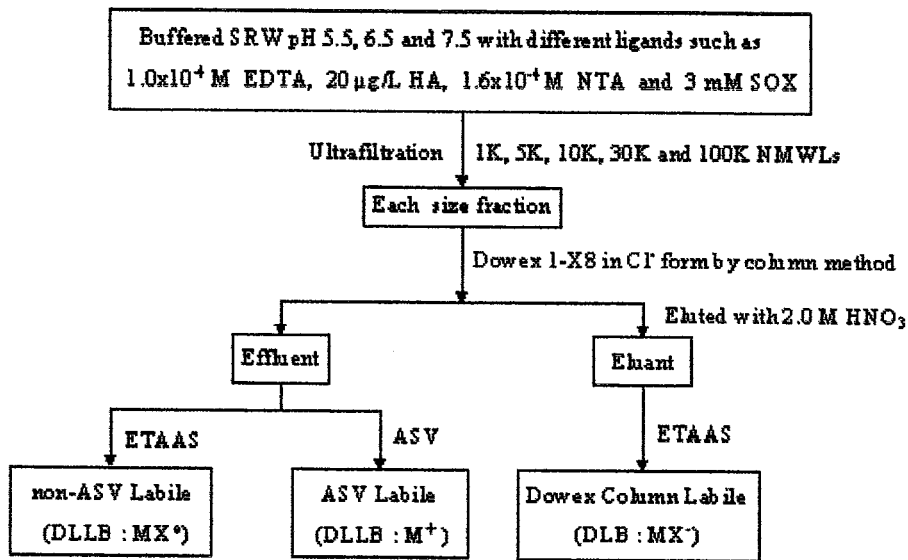


Figure 3: Speciation scheme for metal species in SRWs by using Dowex 1-X8

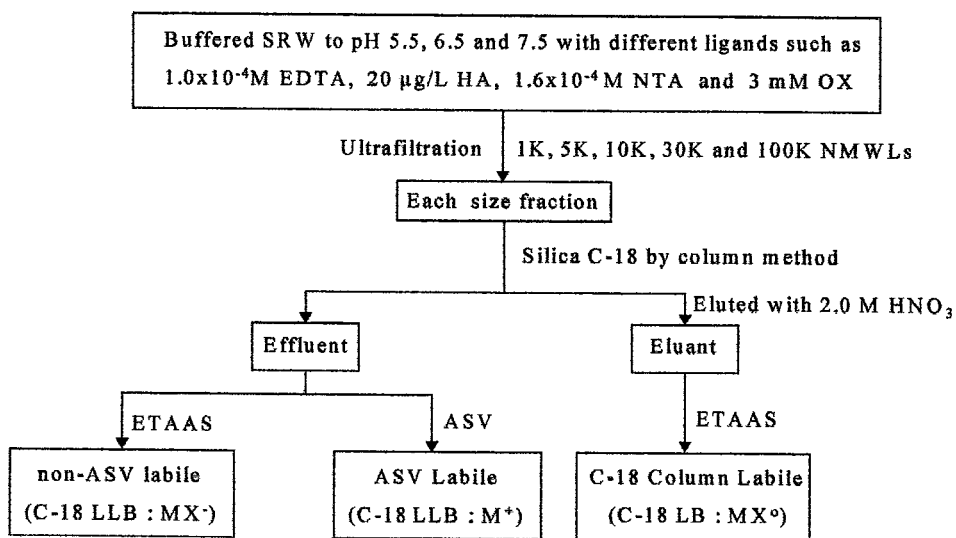


Figure 4: Speciation scheme for metal species in SRWs by using silica C-18

3. RESULTS AND DISCUSSION

3.1 Classification of Degree of Lability Based on Sorbent Used

The Zn species are categorized according to their interaction with different kinds of sorbents, i.e. positively-charged Zn complexes with Chelex-100, negatively-charged Zn complexes with Dowex 1-X8 and neutral organic Zn complexes with reversed phase C-18. The operationally-defined Zn species based on their labilities towards various kinds of sorbents are illustrated in Table 1.

The species retained by Chelex-100 are hydrated metal and relatively weak ML complexes. The speciation of Zn in SRW by Chelex-100 was studied according to the procedure proposed by Figura and McDuffie⁴ which classified the degree of lability of positively-charged Zn complexes into four types, namely “Very Labile”, “Moderately Labile”, “Slowly Labile” and “Inert”, as shown in Table 1.

Dowex 1-X8 is a strongly basic anion-exchanger which is able to retain anion species in both the acid and alkaline water samples. The anion-exchange speciation procedure is based on the charge interaction law, that is, the higher the charge on the ion, the greater is the interaction between the ion and the bed¹². As mentioned above, the degree of lability of negatively-charged ML complexes was categorized into three types, namely, “Dowex Labile”, “ASV Labile” and “Dowex Less Labile” or “non-ASV Labile” as shown in Table 1.

C-18 is a bonded-phase on silica which is able to adsorb hydrophobic species and/or partially hydrophilic with a hydrophobic core of ML complexes. The speciation procedure of neutral organic metal complexes by silica C-18 is based on ionic interaction between ML complexes and the functional group of sorbent. The degree of lability of neutral organic metal complexes was classified into three types, namely, “C-18 Labile”, “ASV Labile” and “C-18 Less Labile” or “non-ASV Labile” as illustrated in Table 1.

Table 1: Operationally-defined metal species based on lability towards various sorbents

Sorbent	Metal classification	Lability	Measurement technique	Time scale
Chelex-100	Positively-charged metal complexes	Very labile (VLB)	Direct ASV	2 ms
		*Moderately labile (MLB)	Chelex column uptake + ASV	7 s
		Slowly labile (SLB)	Chelex batch uptake + ASV	72 h
		Inert (INT)	Direct ETAAS	-
Dowex 1-X8	Negatively-charged metal complexes	Dowex labile (DLB)	Dowex column uptake + ETAAS	7 s
		Total Dowex less labile (TDLLB)	Direct ASV	9 s
		-ASV labile	Direct ETAAS	9 s
		-Dowex less labile (DLLB)		
C-18	Neutral hydrophobic organic complexes	C-18 labile (C-18 LB)	Silica C-18 column uptake + ETAAS	7 s
		Total C-18 less labile (TC-18 LLB)	Direct ASV	9 s
		-ASV labile	Direct ETAAS	9 s
		-C-18 less labile (C-18 LLB)		

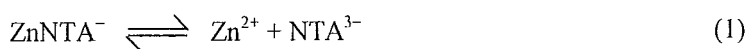
*Calculated by subtracting VLB from the Chelex-labile species

3.2 Determination of Zn Species in Synthetic River Water

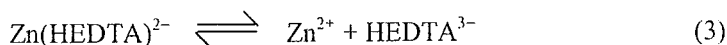
The proposed procedure was employed to determine the speciation of Zn in SRW. The percentage recoveries of Zn from each sorbent were evaluated from the ratio of total amount found in the eluates and in the starting concentration in the model solution used. The retention of Zn complexes onto different solid sorbents was investigated at pH 5.5, 6.5 and 7.5 which represents the pH range of natural waters. The results obtained are shown in Tables 2 to 4.

3.2.1 Chelex-100

The experiment was performed by adding different ligands, namely NTA, EDTA and HA, to complex with Zn at three investigated pHs and the results are shown in Table 2. In the absence of ligands, Zn species present was classified as the VLB species in the <1K size fraction at all the pH values. This indicates that almost 100% of Zn species were present as aqua ions. In the presence of NTA, the Zn species existed as $ZnNTA^-$. More than 85% of Zn was found as the MLB species indicating that the dissociation of $ZnNTA^-$ as represented by the equation:



occurred sooner than the time of contact with the resin phase. Thus, there was sufficient time for almost complete dissociation of the complex before the uptake of Zn by the resin. Nonetheless, there was some pH effect on the dissociation of the complexes as the MLB fraction decreased at higher pH. In contrast, there was no observed Zn uptake from the EDTA system by the Chelex column and that the speciation pattern in terms of the SLB and INT species was pH dependent. This observation can be explained by employing the following mechanism of dissociation of the $Zn(EDTA)^{2-}$ complex proposed by Figura and McDuffie¹³:



The protonation step (Reaction 2) is pH dependent and was reported to be the rate-determining step¹³. The protonation of the Zn complex followed by dissociation was obviously too slow for the uptake of Zn on the Chelex column for the pH range studied. It was observed that the percentage of the SLB species identified under the Chelex batch method decreased at increasing pHs. This is in agreement with the proposed mechanism.

In the case of the HA system, Table 2 shows that the percentage of Zn identified as MLB species increased from 52% at pH 5.5 to 97% at pH 7.5. Figura and McDuffie¹³ showed that there was no formation of nonlabile Zn-HA complexes at pH 7.8. This implies that the MLB species found were most probably the Zn which remained uncomplexed to HA. At lower pH, the formation of some Zn-HA complexes did occur and they appeared as the INT species with the molecular size up to 10,000 MW cut-off.

Table 2: Uptake (%) of zinc with different ligands on Chelex-100

pH	Size fraction	SRW							
		NTA $1.6 \times 10^{-4}M$			EDTA $1.0 \times 10^{-4}M$		HA 20 $\mu g/L$		
		VLB	MLB	SLB	SLB	INT	MLB	SLB	INT
5.5	<1K	100	98	2	57	43	52	-	8
	1K-5K	-	-	-	-	-	-	-	28
	5K-10K	-	-	-	-	-	-	-	12
6.5	<1K	99	90	10	20	80	78	2	2
	1K-5K	1	-	-	-	-	-	-	10
	5K-10K	-	-	-	-	-	-	-	8
7.5	<1K	99	85	15	15	85	97	1	-
	1K-5K	1	-	-	-	-	-	2	-

3.2.2 Dowex 1-X8

Table 3 shows the percent retention of Zn with different ligands, namely NTA, EDTA, HA and SOX, at pH 5.5, 6.5 and 7.5. In the NTA system, the dissociation of $ZnNTA^-$ as shown in Eq. (1) was sufficiently rapid for the majority of the Zn species not to be retained by the resin. Evidence that the dissociation of the complex resulted in free or aquo metal ions can be seen in the ASV fraction in the Dowex column effluent. The pH dependence was in agreement with what was observed in the Chelex-100 resin. In comparison, the uptake of Zn as the DLB fraction in the presence of EDTA was quantitative at all studied pH conditions. The stability constant of $Zn(EDTA)^{2-}$ complex is 18.3. This indicates that EDTA forms very stable complexes with Zn so that the presence of negative charges on the molecule allows their retention onto Dowex resin.

The results for the HA system show that the majority of the Zn species was identified as the ASV-labile fraction. This is in agreement with the

observation made earlier that most of the Zn remained uncomplexed to HA and more so at relatively higher pH. Both anionic and neutral complexes were found in this study as the DLB and non-ASV fractions, respectively. This phenomenon can presumably be explained by the presence of the predominant functional groups (carboxylic, phenolic) and hydrophobic component in the HA molecule. The binding strength will be strongly pH dependent because of the protonation of functional groups¹².

The uptake of SOX complexes onto Dowex resin was studied to simulate the behaviour of organic aromatic anion species. The Zn complexes was quantitatively present as $Zn(SOX)_2^{2-}$ in all studied conditions, whereas 1:1 and 1:2 (Zn:SOX) complexes exist for Zn at pH 4.0 (from theoretical calculation). The results obtained show that the retention of Zn at the size fraction of <1K increased from 60% at pH 5.5 to 93% at the higher pH. It was observed in this study that precipitation occurred after elution due to the formation of barely soluble neutral form of ligand. The precipitate redissolved after 8 hours probably due to the slow protonation of nitrogen and consequent formation of more soluble charged species.

Table 3: Uptake (%) of zinc with different ligands on Dowex 1-X8

pH	Size fraction	SRW									
		NTA $1.6 \times 10^{-4}M$			EDTA $1.0 \times 10^{-4}M$			HA 20 $\mu g/L$		SOX 3 mM	
		DLB	ASV	Non-ASV	DLB	DLB	ASV	Non-ASV	DLB	Non-ASV	
5.5	<1K	8	90	2	95	5	50	20	60	10	
	1K–5K	-	-	-	5	10	-	-	30	-	
	5K–10K	-	-	-	-	15	-	-	-	-	
6.5	<1K	12	85	3	94	4	61	10	87	2	
	1K–5K	-	-	-	6	8	-	17	11	-	
	5K–10K	-	-	-	-	-	-	-	-	-	
7.5	<1K	18	79	3	92	2	81	3	93	-	
	1K–5K	-	-	-	8	-	-	14	7	-	

3.2.3 Silica C-18

The ligands selected to form a neutral complex of Zn species in SRW were HA and OX. The results of the uptake of Zn in the HA and OX systems, respectively, on Silica C-18 at pH 5.5, 6.5 and 7.5 are shown in Table 4. It can be seen that most of the Zn species found in the presence of HA was identified as

the ASV labile species with the molecular size of <1K whereas some was identified as the C-18 LB species with the molecular size up to 10,000 MWCO and no non-ASV labile species was found. Silica C-18 is not specific for neutral compounds as it is also able to adsorb hydrophobic species or partially hydrophilic ones with hydrophobic core. Thus, the C-18 LB fraction consisted not only the neutral organic complexes but also anionic Zn-HA complexes. The ASV labile fraction found was basically Zn^{2+} unbound to HA.

For OX, Zn was both partially retained and unbound at pH 5.5 as seen in the almost equal distribution of the C-18 LB and ASV fractions. The complete retention of Zn occurred at pH 6.5 and higher pH values. In the presence of 3 mM OX, the Zn complexes sorbed was most likely the $Zn(OX)_2$. The 1:1 complexes namely $Zn(OX)^+$, which exists at lower pH, could also be sorbed because of its hydrophobic nature².

Table 4: Uptake (%) of zinc with different ligands on Silica C-18

pH	Size fraction	SRW				
		HA 20 μ g/L		OX 3 mM		
		C-18 LB	ASV	C-18 LB	ASV	Non-ASV
5.5	<1K	27	52	45	51	4
		8	-	-	-	-
		13	-	-	-	-
6.5	<1K	12	65	96	-	-
	1K-5K	23		4	-	-
7.5	<1K	16	84	92	4	-
	1K-5K			4	-	-

4. CONCLUSIONS

This technique allows for the speciation study of zinc based on a combination of physical characterization by size fractionation using ultrafiltration and chemical characterization by retention studies on different solid sorbents. Its applicability to synthetic river water sample spiked with zinc in the presence of different ligands at different pH values was demonstrated. This technique also provides some insight into the physical and chemical nature of the metal forms. The study with model compounds shows that the pH range from 5.5 to 7.5 plays

an important role in influencing the speciation patterns of the zinc species in the presence of various types of ligands on different sorbents.

5. ACKNOWLEDGEMENT

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