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1 **Separation of Dissolved Iron from the Aqueous System with Excess Ligand**

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23 **Abstract**

24   A new technique for the separation and preconcentration of dissolved Fe(III) from the ligand-

25 rich aqueous system is proposed. A solid phase extraction (SPE) system with an immobilized

26 macrocyclic material, commonly known as molecular recognition technology (MRT) gel and

27 available commercially, was used. Synthetic Fe(III) solution in aqueous matrices spiked with a

28 100-fold concentration of EDTA was used. Dissolved iron that was 'captured' by the MRT gel

29 was eluted using hydrochloric acid and subsequently determined by graphite furnace atomic

30 absorption spectrometry. The effect of different variables, such as pH, reagent concentration,

31 flow rate and interfering ions, on the recovery of analyte was investigated. Quantitative

32 maximum separation (~100%) of the dissolved Fe(III) from synthetic aqueous solutions at a

33 natural pH range was observed at a flow rate of 0.2 mL min^{-1}. The extraction efficiency of the

34 MRT gel is largely unaltered by the coexisting ions commonly found in natural water. When

35 compared with different SPE materials, the separation performance of MRT gel is also much

36 higher.

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1.0 Introduction

The accurate determination of iron in dissolved and particulate forms or size fractions is necessary for describing the iron chemistry within a given body of water (Bruland and Rue, 2001). The iron content in an aqueous system is important for environmental protection, hydrogeology and some chemical processes, such as photosynthesis and phytoplankton production in the open oceans (Riley and Chester, 1971; Martin and Fitzwater, 1988; Martin, 1990). Recent studies suggest that Fe(III) solubility in oceanic water is controlled by complexation with natural organic ligands (Kuma et al., 1996; Waite, 2001; Liu and Millero, 2002), and these complexation equilibria subsequently regulate the concentrations of dissolved iron in the oceanic system (Johnson et al., 1997; Kuma et al., 2003). Thus, the majority of dissolved iron in the oceans appears to be chelated (as FeL_i) with organic ligands (L_i) (Wu and Luther, 1995; Rue and Bruland, 1997; Boye et al., 2001).

Sensitive analytical methods, such as graphite furnace atomic absorption spectrometry (GF-AAS), have led the way in providing reliable profiles for iron in oceanic waters over the past three decades (Johnson et al., 1997; Bruland and Rue, 2001). However, precise determination of iron is very difficult due to the risk of sample contamination (Blain and Treguer, 1995; de Jong et al., 2008). Reports have shown that there are discrepancies between the estimated concentrations of dominant hydroxo-complex species of Fe(III), such as $Fe(OH)_2^+$, $Fe(OH)_3^0$ and $Fe(OH)_4^-$, and values (~ 0.1–10 nM) for the thermodynamic solubility of Fe(III) hydroxide in seawater (Byrne and Kester, 1976; Kuma et al., 1996; Liu and Millero, 2002). These low concentrations also make it difficult to measure iron in ocean waters (de Jong et al., 2008). For reliable analysis, method development is important to overcome limitations caused by the high salt matrix of oceanic water samples that could cause interferences during measurements. One of

69   the popular analysis methods is to separate and preconcentrate the desired metal ion(s) out of the

70   sample matrix for precise determination (Hosten and Welz, 1999). Various methods, such as co-

71   precipitation, liquid-liquid extraction, solid-liquid extraction, and ion exchange resins, have

72   been developed for the separation of trace metals from natural samples (Filik et al., 1997;

73   Pourreza and Mousavi, 2004; Ghaedi et al., 2005; Ghaedi et al., 2007; Ghaedi et al., 2008).

74   However, the solid phase extraction (SPE) approach has gained rapid acceptance since the 1980s

75   because it is one of the fastest, most economical and cleanest methods for separating and

76   concentrating trace metals from aqueous samples (Hosten and Welz, 1999; Firdaus et al., 2007).

77   In SPE, appropriate materials are immobilized onto support matrices to prepare solid phases

78   with a 'capturing capability' for separation and preconcentration (Masi and Olsina, 1993). Some

79   of the sorbent materials have the ability to interact with various metal ions while others are fairly

80   specific for a particular ion within complex matrices (Carbonell et al., 1992; Nickson et al.,

81   1995; Ghaedi et al., 2006; Ghaedi et al., 2008; Ghaedi et al., 2009). One group of SPE materials

82   includes those with macrocyclic ligands, such as crown ethers, immobilized on a silica or

83   polymer support; this type of SPE has been reportedly used for ion-selective separation and

84   preconcentration of metal ions, and the technique is commonly known as molecular recognition

85   technology (MRT) (Izatt et al., 1995; Hasegawa et al., 2010; Rahman et al., 2010). Reports on

86   the separation/preconcentration of dissolved iron using SPE from an aqueous system in which

87   Fe-organic ligand complexation is prevalent is still very limited (Wells and Bruland, 1998). The

88   extraction efficiency of SPE materials significantly decreases in aqueous systems containing

89   excess ligand because ligands often compete with SPE materials for metal ions. This limitation

90   can be minimized with the MRT-SPE systems, which can provide non-destructive separation of

91   metal ions from ligand-rich aqueous systems (Hasegawa et al., 2010).

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92 In this work, we propose a simple method using a MRT-SPE system for the separation of

93 dissolved iron from aqueous system of Fe-ligand complexes containing an excess amount of

94 ligand in solution. The SPE sorbent is a proprietary polymeric organic material comprised of ion-

95 selective sequestering agents based on molecular recognition and macrocyclic chemistry.

96 Synthetic, ligand-rich aqueous Fe-ligand matrices were used as the samples. Hydrochloric acid

97 was used as the eluent with subsequent determination of iron using GF-AAS.

98 **2.0 Experimental**

99 *2.1 Materials*

100 *2.1.1   Reagents*

101 Analytical grade commercial products were used as received. Stock solutions of Fe(III) and

102 Fe(II) were prepared by dissolving $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ (Wako Pure Chemical

103 Industries, Japan), respectively, in 1 M HCl. A Perkin-Elmer (Norwalk, CT, USA) Model ICP

104 Optima 3000 inductively coupled plasma emission spectrometer was used to standardize the iron

105 solutions.

106 Nitrilotriacetic acid (NTA), O,O'-bis(2-aminoethyl)ethyleneglycol-N,N,N',N'-tetraacetic

107 acid (GEDTA), ethylenediamine-N,N,N',N'-tetraacetic acid (EDTA) and diethylenetriamine-

108 N,N,N',N'',N''-pentaacetic acid (DTPA) were purchased from Dojindo Laboratories, Japan;

109 desferrioxamine B (DFB) was supplied by Sigma-Aldrich, St. Louis, MO. Each of these reagents

110 was dissolved in 0.1 M sodium hydroxide to prepare stock solutions of the chelating ligands.

111 Working standards of metal and ligand solutions in the μM to mM range were prepared by

112 dilution on a weight basis. The experimental pH range was 4 to 8, and solution pH was adjusted

113 using either 1 M HCl or 1 M NaOH. The pH was maintained using the following buffer

114 solutions: 0.1 M CH_3COONa/CH_3COOH (pH 4–5) and 0.1 M NaH_2PO_4/Na_2HPO_4 (pH 6–8).

115 Aqueous solutions of 10 mM chelating ligands in the appropriate buffer were spiked with 0.1

116 mM Fe(III) or Fe(II) in 1.0 M HCl, and allowed to stand for 20 min, and these solutions were

117 then added to the sample solutions. For Fe(II) sample solutions, 0.2% hydroxyl ammonium

118 chloride was added to prevent oxidation.

119 To study the effect of coexisting ions, NaCl, KCl, $CaCl_2$ and $MgCl_2$ were used as sources of

120 cations, and NaCl, $NaNO_3$, CH_3COONa, Na_3PO_4, Na_2SO_4, $NaClO_4$ were used as sources of

121 anions; all salts were purchased from Nacali Tesque, Japan. Working solutions at a concentration

122 of 10 mM were prepared in a H_2O matrix, and the pH was adjusted to 8.0. The final solutions

123 were allowed to equilibrate for 24 h before analysis. Considering the competitive behavior of

124 Ca^{2+} and Mg^{2+} ions in seawater in terms of ligand capturing, the metal-to-ligand ratio was

125 maintained at 1:100.

126 Deionized water obtained from a Barnstead 4 Housing E-Pure system was used to prepare all

127 solutions and is hereafter referred to as EPW.

128 *2.1.2 SPE materials*

129 Different SPE materials, as listed in Table 1, were used. MRT gel and AnaLig TE-01 were

130 purchased from GL Sciences, Japan. Other SPE materials were purchased from Bio-Rad

131 Laboratories (Chelex-100), GL Sciences (MetaSEP ME-1, ME-2 and ME-3) and Hitachi High-

132 Technologies Corporation (NOBIAS Chelate PA-1, PB-1, Ion SC-1 and SA-1).

133 **2.2 Cleaning**

134 Low-density polyethylene and laboratory equipment (Nalge, USA) were used to store the

135 solutions and to hold solutions during the experiments. Before use, bottles and laboratory

136   equipment were soaked in an alkaline detergent (Scat 20X-PF, Nacali Tesque, Japan) overnight

137   and rinsed with EPW; they were then soaked in 4 M HCl overnight and rinsed with EPW.

138   PerFluoroAlkoxy tubes and micropipette tips (Nichiryo, Japan) were cleaned according to the

139   procedure described by Sohrin et al. (1998).

140   **_2.3 Column separation procedure_**

141   _2.3.1   Column cleaning and conditioning_

142   SPE materials packed in 3-mL columns were used in this experiment. Column cleaning was

143   conducted with HNO_3 (8 mL) and EPW (6 mL). The appropriate buffer solution, consisting of 5

144   mL of 0.1 M CH_3COONa/CH_3COOH (pH 4–5) or 5 mL of 0.1 M NaH_2PO_4/Na_2HPO_4 (pH 6–8),

145   was allowed to flow through the column to ensure the desired pH conditions (4–8).

146   _2.3.2   Treatment of samples_

147   Sample solution (5 mL) with ligand (10 mM) and spiked with Fe(III) or Fe(II) (0.1 mM),

148   which was pH adjusted with 0.1 M solution of pH 4–5 or 6–8 buffer, was passed through the

149   SPE column at the pre-set flow rate of 0.2 mL min^{-1}. The column effluent was collected. The

150   analyte concentration in the column effluent represents the unrestrained concentration of analyte

151   in the SPE system. The second and final step was the elution of analyte from the SPE system

152   using HCl (1 and 6 M). The analyte concentrations from the sample solution, in the effluent, and

153   in the eluent were measured with GF-AAS. The recovery efficiency was calculated as follows:

154
$$\text{Recovery}\,(\%) = \frac{\text{number of mol of Fe recovered in all fractions}}{\text{number of mol of Fe applied to the column}} 100 \qquad (1)$$

155   Three replicate measurements per sample were made in all instances. The peak height of the

156   reported signal was proportional to the concentration of the respective iron species and was used

157   for all measurements.

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2.4 Instruments

159   A Hitachi Model Z-8100 GF-AAS (Hitachi, Japan) operating at the 248.3 nm wavelength

160   with a slit width of 0.2 nm and 15.0 mA lamp current was used for analyzing iron concentrations.

161   A temperature program was performed with the following steps: drying at 100 ºC, ashing at 1000

162   ºC, atomization at 2700 ºC and cleaning at 3000 ºC with holding times of 60, 60, 10 and 4 s,

163   respectively. Argon was used as the inert gas at a flow rate of 200 mL min^{-1} except during the

164   atomization step (30 mL min^{-1}). After a calibration step, 20 μL of sample and 10 μL of matrix

165   modifier (NiSO$_4$) were introduced into the graphite furnace for three replicates of each

166   measurement. The pH of the sample solutions was measured with a Navi F-52 pH meter (Horiba

167   Instruments, Japan) and a combination electrode.

168   **3.0 Results and Discussion**

169   *3.1 Comparative study with different SPE materials*

170   The separation efficiencies of Fe(III) from aqueous solutions containing excess ligand with

171   AnaLig TE-01 and different commercially available SPE products were investigated in a non-

172   competitive environment (Fig. 1). Thermodynamic equilibrium calculations suggest that 99.9%

173   of the ambient, dissolved Fe(III) exists as Fe(III) chelates when the ligand concentrations are ~25

174   times higher in the aqueous system (Bruland and Rue, 2001).

175   Therefore, a maximal amount of Fe(III) is assumed to be present as the Fe-EDTA complex in

176   the EDTA-spiked sample solutions containing excess EDTA. As shown in Fig. 1, it is apparent

177   that AnaLig TE-01 ensures quantitative extraction of the total amount of Fe(III) from an aqueous

178   solution containing a 100-fold concentration of EDTA spiked with Fe(III). However, the

179   extraction efficiencies of other SPE products are limited to 10–50% for the same sample

180 solutions. Consequently, AnaLig TE-01 is a more suitable SPE-type system to separate the iron

181 dissolved as the metal-ligand complex in a ligand-rich aqueous environment.

3.2 Effect of pH

183 The retention of dissolved iron on the AnaLig TE-01 column containing immobilized

184 macrocyclic material was studied as a function of pH. The pH of the aqueous system with Fe(III)

185 and Fe(II) in excess EDTA was maintained in the range of 4–8 with pH 4–5 and 6–8 buffer

186 solutions at 0.1 M concentration. This study was restricted to the pH range 4–8 because EDTA is

187 not very water soluble at very low pH (Ueno et al., 1992), and the increasing solubility of silica

188 gel with pH (Vogelsberger et al., 1992) may dissolve the silica gel base support of AnaLig TE-01

189 column.

190 As shown in Fig. 2, quantitative retention of the Fe(III) and Fe(II) complexes from the

191 ligand-rich medium in the pH range 4–8 were at a maximum on the AnaLig TE-01 column. The

192 variation in the pH of the sample solution and the column effluent were insignificant. Therefore,

193 we can conclude that the MRT gel has significant affinity for dissolved iron in a ligand-rich

194 matrix or in iron-ligand complexes, and the iron-ligand complex is stable in the studied pH range.

195 In view of the fact that oceanic water is limited to the pH range of 7 to 9, the majority of the

196 dissolved iron (Fe(III)) is chelated with organic ligands of biological origin (Bruland and Rue,

197 2001), and further experiments were carried out at pH 8.0 ± 0.2.

3.3 Effect of sample loading flow-rate

199 The retention of analytes in the SPE system depends upon the flow rate of the metal-fortified

200 sample solution (Bag et al., 1998). The effect of sample loading flow rate on the recovery

201 percentage was examined under optimum conditions. The solution was passed through the SPE

202 column with the flow rates that were adjusted in the range of 0.2–4.0 mL min^{-1}. As shown in Fig.

203 3a, retention of Fe(III) on the MRT gel column was quantitative up to a flow rate of 0.25 mL

204 min^{-1}. A gradual decrease in retention with increasing flow rate was observed in the range of

205 0.3–1.0 mL min^{-1}, and retention decreased to about 60% at higher flow rates (2.0–4.0 mL min^{-1}).

206 This behavior indicates the constant retaining capability of the MRT gel at the initial loading

207 period. Because quantitative, maximum extraction of the analyte is desirable, we applied a flow

208 rate of 0.2 mL min^{-1} to further experiments to ensure selective pre-concentration of the sample

209 solution for analytical determination.

210 *3.4 Effect of eluent concentration*

211 A satisfactory eluent should effectively elute the extracted analytes using a small volume,

212 which is desired for a high enrichment factor of the analyte, but the eluent should not affect the

213 accurate determination of analytes (Chen et al., 2009). The effect of eluent concentration on the

214 elution of analyte from the MRT gel column was studied by first adding 2 mL of the Fe(III)-

215 spiked, aqueous EDTA solution at pH 8.0 onto the column, and the analyte extracted by the

216 MRT gel column was then eluted using 5 mL of eluent (0.1–6.0 M HCl). The recovery of the

217 analyte was determined with GF-AAS. The Fe(III) recovery percentage was found to increase as

218 the concentration of HCl increased up to a concentration of 0.5 M, at which point the recovery

219 level remained constant (Fig. 3b). This behavior indicates that a HCl concentration equal to 0.5

220 M is sufficient for quantitative elution of the bound ions in the TE-01 MRT gel column.

221 However, acid concentrations greater than or equal to 5.0 M were recommended as eluent for

222 TE-01 (IBC Advanced Technologies, 2007). Thus, a combination of 1 M HCl (4 mL) and 6 M

223 HCl (1 mL) was selected as eluent for subsequent experiments to ensure quantitative elution of

224 the analyte.

225 *3.5 Effect of metal-ligand stability constants*

226   Ligands form water-soluble metal complexes of high thermodynamic stability (Lim et al.,

227 2005). The high stability of the metal-ligand complexes may influence the extraction

228 performance of the SPE materials. Various investigators have suggested that dissolved iron

229 content in the open oceans exists primarily as Fe-ligand species (Bruland and Rue, 2001), and

230 two classes of Fe(III)-binding natural organic ligands were observed with the following

231 conditional stability constants K'_{ML}: 5×10^{12} M^{-1} (pK'_{ML} = 12.7) and 6×10^{11} M^{-1} (pK'_{ML} =

232 11.78) (Rue and Bruland, 1997).

233   The effect of the metal-ligand complexes' K'_{ML} values on the performance of the MRT-SPE

234 system was evaluated for the extraction of Fe(III) from the ligand-rich, Fe(III)-spiked aqueous

235 system. Solutions of ligands in 0.1 M HCl with varying iron complex stability constants (K_{ML}),

236 such as NTA, GEDTA, EDTA, DTPA and DFB (Table 2), were added to the iron-spiked

237 solution to prepare each sample solution. The Fe(III)-ligand complex stability at pH 8 was

238 considered during the selection of the chelating ligands. AnaLig TE-01 demonstrated better

239 separation efficiency than the other selected SPE materials (Chelex-100, InterSEP ME-1 and

240 NOBIAS Chelate PA-1) for the metal-ligand complexes of NTA, GEDTA and EDTA (Fig. 4). A

241 significant decrease in the AnaLig TE-01 separation performance was observed for metal-ligand

242 complexes with high K'_{ML} values, e.g., metal-DTPA and metal-DFB. In ocean waters, the pK'_{ML}

243 values for Fe(III)-binding organic ligand classes are limited to a pK of 12.7 (Rue and Bruland,

244 1997). However, quantitative separation performance for ligands with pK'_{ML} values of up to 22.8

245 was observed with the proposed MRT-SPE system. Therefore, the thermodynamic stability of

246 the commonly observed Fe(III)-ligand complexes in ocean waters has a negligible effect on the

247 iron separation performance of the AnaLig TE-01.

248 *3.6 Effect of coexisting ions*

249   The interference of other coexisting ions on the separation and preconcentration of dissolved

250 iron was examined under optimal conditions. Various cations, including Na^+, K^+, Ca^{2+} and Mg^{2+},

251 and anion species, including Cl^-, NO_3^-, CH_3COO^-, PO_4^{2-}, SO_4^{2-} and ClO_4^-, were added

252 individually to the ligand-rich Fe(III) sample solutions, which were then allowed to equilibrate

253 for 24 h. The studies were carried out in a non-competitive environment by applying 5 mL of the

254 ion-fortified sample at the optimized flow rate with subsequent collection using the appropriate

255 eluent. Variation in pH was negligible between the fortified samples and column effluents.

256 Quantitative recovery of Fe(III) was observed in the presence of the selected cations and anions

257 (Fig. 5). Therefore, it can be concluded that the developed method is reasonably free from

258 interference resulting from coexisting ions that are commonly found in open aqueous systems.

259 *3.7 Extraction capacity*

260   Extraction capacity is an important factor that must be evaluated because it determines how

261 much MRT gel is required for quantitative separation of Fe(III) from a solution. Batch method

262 experiments were used for a capacity study, and the experiments were conducted as follows: 0.5

263 g of the MRT gel was added to 20 mL of Fe-EDTA solution (Fe(III) – 0.1 mM, ligand: EDTA –

264 10 mM, matrix: H_2O, pH: 8.0), and the mixture was continuously shaken for one hour. Iron

265 concentrations in the filtrate were determined by GF-AAS. The extraction capacity for Fe(III)

266 under ligand-rich condition was 0.115 ± 0.002 mmol g^{-1} of AnaLig TE-01 (mean $\pm$ SD, $n = 3$).

267 This result was in good agreement with the certified value 0.1–0.3 mmol g^{-1} of AnaLig TE-01

268 (IBC Advanced Technologies, 2007) for the simultaneous complexation of Ag(I), Au(III), Cd(II),

269 Co(II), Cu(II), Fe(II), Hg(II), Ni(II), Pb(II), Pd(II) and Zn(II) from aqueous solutions to

270 concentrate the ions or remove interfering matrices.

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271 *3.8 Regeneration and reusability*

272   The regeneration ability and stability of the MRT gel were investigated because regeneration

273 is one of the key factors in evaluating the performance of an extraction material. The

274 experimental results indicated that AnaLig TE-01 is stable during operation of the column, and

275 this material could be regenerated for more than 100 loading and elution cycles without loss of

276 analytical performance. Systems with macrocycles attached onto solid supports (Bradshaw et al.,

277 1988; Izatt, 1997), which is used for the AnaLig TE-01, allow non-destructive separation of

278 metals from the matrix (ligand-rich aqueous solution) and also facilitate the repeated use of the

279 macrocycles because the material can be regenerated after each use. Thus, the initial high cost of

280 MRT gel synthesis is amortized over time.

281 *3.9 Analytical characteristics*

282   GF-AAS was used to measure the iron concentrations in the MRT gel treated, fortified

283 aqueous samples. Under optimum conditions, the linear range was found to be 0.01–0.11 μg mL^{-}

284 ^{1}. The method detection limits, as calculated from three times the standard deviation ($n = 15$) of

285 the blank, was 0.02 μg L^{-1}. Based on the relative standard deviation, the precision of the method

286 was calculated to be 1.4% from 10 replicate measurements at a concentration of 0.4 μM Fe(III).

287 *3.10   Recovery test with artificial seawater*

288   Artificial seawater was prepared according to Lyman and Fleming (1940) and used to

289 evaluate the ion-recovery performance of the MRT-SPE column in the presence of multiple

290 interfering ions. Artificial seawater samples spiked with 0.1 mM Fe(III) and 10 mM EDTA were

291 passed through the MRT-SPE system at pH 8. The recovery of Fe(III) was observed to be 96 $\pm$

292 3% ($n = 3$).

4.0 Conclusions

MRT gel, a column-packed, immobilized macrocyclic material, was used for the separation/preconcentration of dissolved iron from an aqueous system containing excess ligand, and GF-AAS was used to determine the concentrations of eluted iron. Quantitative collection of the dissolved iron was obtained under the following optimized conditions: pH range: 4–8; flow rate: 0.2 mL min^{-1}; eluent: 1 M and 6 M HCl.

Compared with previously tested SPE materials, MRT gel possesses several advantages. MRT gel is chemically stable with excellent separation properties and extraction capacity. It can be used repeatedly with little loss of performance. Separation of the dissolved iron is rapid, reproducible, and efficient. In addition, the presence of large concentrations of other coexisting ions had no affect on the separation process.

In natural oceanic systems, dissolved Fe(III) primarily exists as organically-bound Fe-ligand species, and the total organic ligand concentrations are ~25 times higher than total iron concentrations. In freshwater systems, Fe(III) often forms complexes with humic substances. Conventional SPE systems may not be applicable for the quantitative determination of dissolved iron in natural bodies of water due to competition with strong Fe(III)-binding organic ligands that limits their accuracy. This limitation is minimized with the proposed MRT-gel separation technique, and it is expected that the total dissolved iron content can be accurately measured with this technique in the presence of an excess of strong Fe(III)-binding organic ligands. Importantly, the quantitative separation performance of the proposed MRT-SPE system was achieved for metal-ligand complexes with a maximum pK'_{ML} of 22.8. Current work is underway to determine ultra-trace amounts of iron in an aqueous system containing excess organic ligands using the MRT gels; the goal of this work is to develop a technique for practical

316 separation/preconcentration and subsequent determination of dissolved iron in oceanic water

317 samples.

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319 **Acknowledgement**

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469 Table 1: Different SPE materials used in this study

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SPE material type	Commercial Name	Base Support	Functional group
MRT Gel	AnaLig TE-01	Silica gel	Crown ether
Ion-exchange resin	NOBIAS Ion SC-1	Hydrophilic methacrylate	Sulfonic acid
	NOBIAS Ion SA-1	Hydrophilic methacrylate	Quaternized amine
Chelate resin	Chelex-100	Styrene divinylbenzene	Iminodiacetic acid
	MetaSEP ME-1	Methacrylate polymer	Iminodiacetic acid
	MetaSEP ME-2	Methacrylate polymer	Iminodiacetic acid +a
	MetaSEP ME-3	Methacrylate polymer	Iminodiacetic acid +b
	NOBIAS Chelate PA-1	Hydrophilic methacrylate	Polyamino-polycarboxylic acid
	NOBIAS Chelate PB-1	Divinylbenzene/ methacrylate polymer	Polyamino-polycarboxylic acid

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482   Table 2: Acid dissociation constants (pK_a), stability constants (K_{ML}) and conditional stability
483   constants (K'_{ML}) of Fe(III)-ligand complexes at 25 °C

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Ligand	K_{ML}	pK_a	K'_{ML} (at pH 8)
NTA	15.9[a]	1.89, 2.49, 9.73	14.1
GEDTA	20.5[a]	2.00, 2.68, 8.85, 9.46	18.1
EDTA	25.0[a]	1.99, 2.67, 6.16, 10.26	22.8
DTPA	28.6[b]	2.14, 2.38, 4.26, 8.60, 10.53	25.4
DFB	31.9[c]	8.39, 9.03, 9.70	29.0

[a]Martell and Smith (1974), [b]Sillen and Martell (1964; 1993), [c]Morel and Hering (1993)
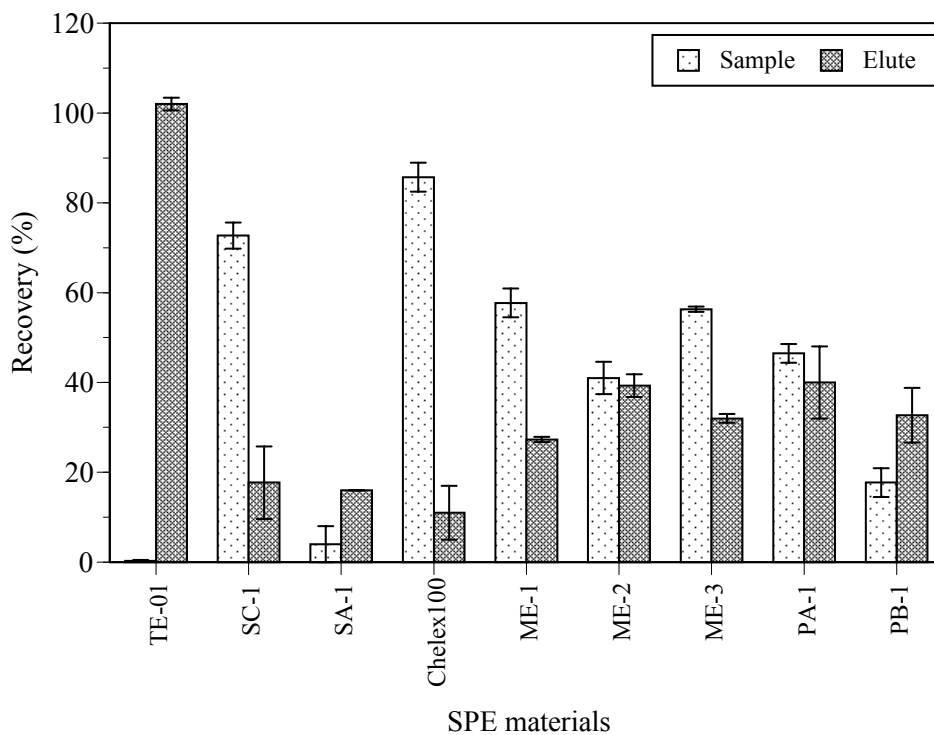
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506   Figure 1: Comparative performance of AnaLig TE-01 with different commercial SPE materials

507   for aqueous metal solution containing excess ligand (n = 3). Sample solution: Fe(III) – 0.1 mM,

508   ligand: EDTA – 10 mM, matrix: H_2O, pH: 8.0, sample volume: 5 mL, flow rate: 0.2 mL min^{-1},

509   eluent: 1 M HCl (4 mL) + 6 M HCl (1 mL). 'Sample' denotes the analyte concentration in the

510   column effluent collected after passing the sample solution through the MRT-SPE system;

511   'elute' denotes the analyte concentration in the collected eluent.

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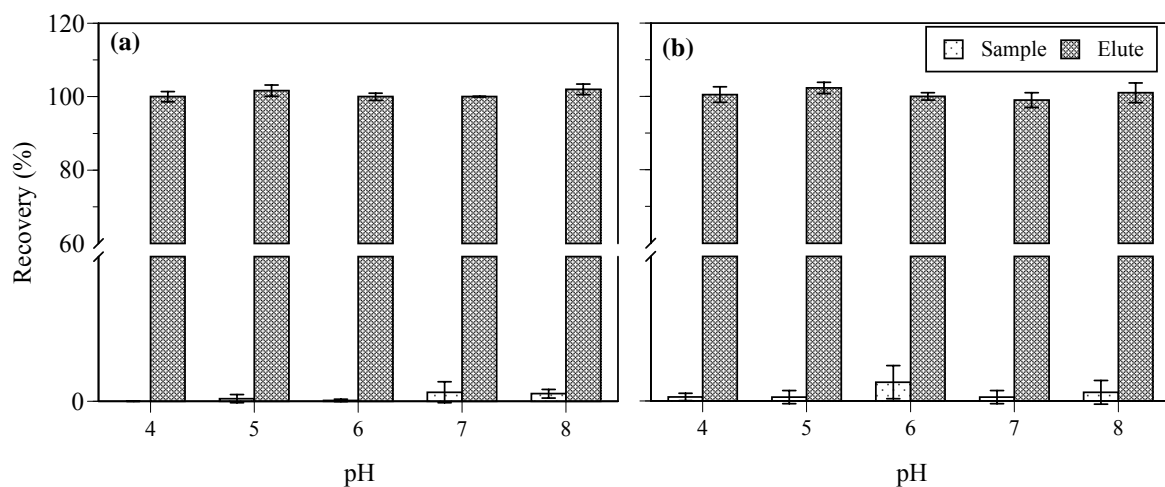
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519 Figure 2: Effect of pH on the recovery percentage ($n = 3$). Sample solution: (a) Fe(III) – 0.1 mM
520 and (b) Fe(II) – 0.1 mM, ligand: EDTA – 10 mM, matrix: H_2O, pH: 4.0–8.0, sample volume: 5
521 mL, flow rate: 0.2 mL min^{-1}, eluent: 1 M HCl (4 mL) + 6 M HCl (1 mL). 'Sample' denotes the
522 analyte concentration in the column effluent collected after passing the sample solution through
523 the MRT-SPE system; 'elute' denotes the analyte concentration in the collected eluent.
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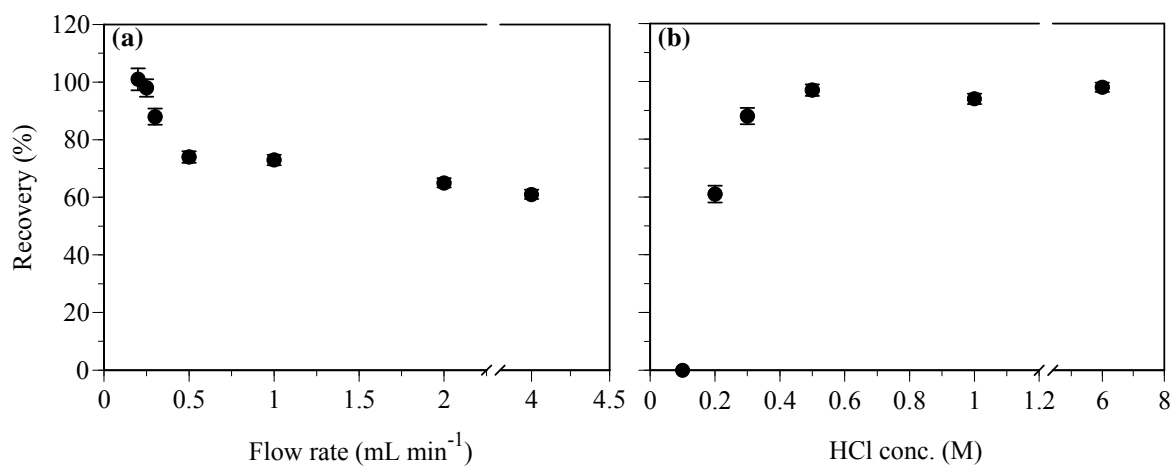
Figure 3: Effect of (a) sample loading flow rate and (b) eluent concentration on the recovery percentage of analyte (n = 3). Sample solution: Fe(III) – 0.1 mM, ligand: EDTA – 10 mM, matrix: H_2O, pH: 8.0, sample volume: 5 mL, flow rate: (a) 0.2–4.0 mL min^{-1} and (b) 0.2 mL min^{-1}, eluent: (a) 1 M HCl (4 mL) + 6 M HCl (1 mL) and (b) HCl (0.1–6.0 M) – 5 mL.
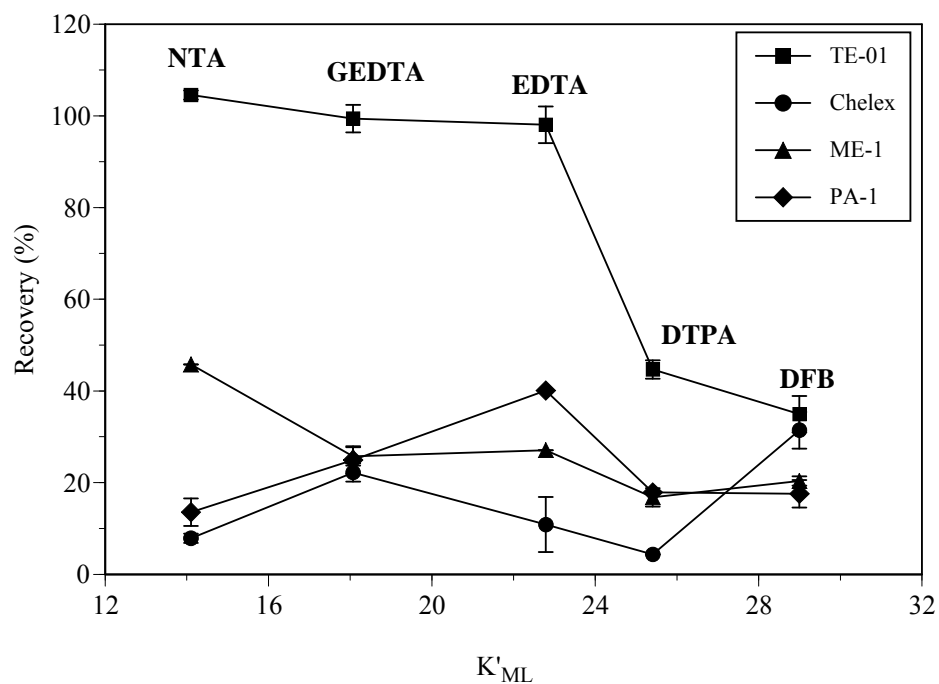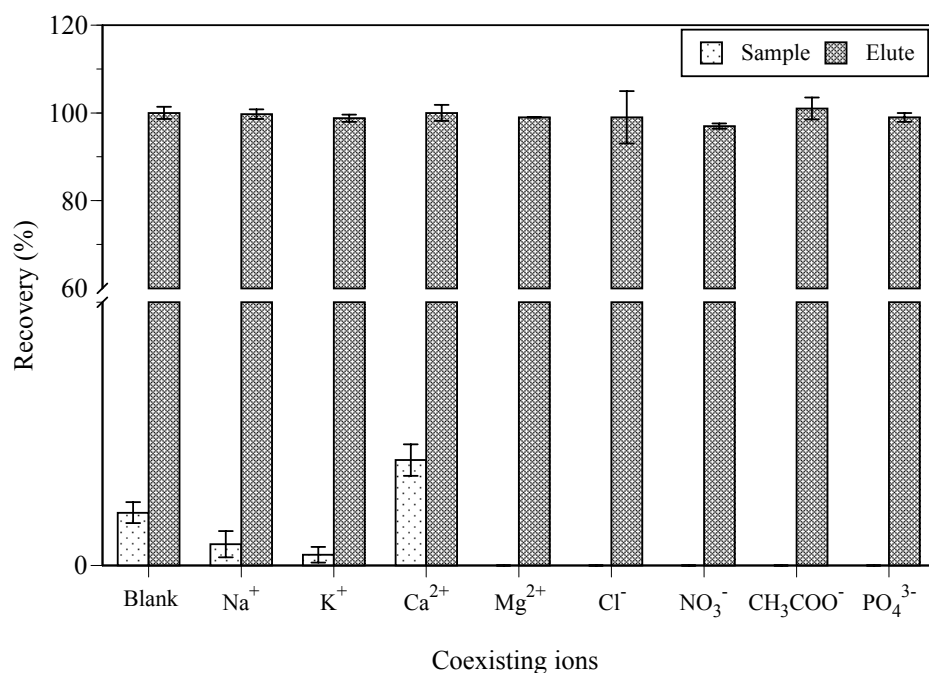
Figure 4: Effect of metal-ligand stability constants on the performance of SPE materials ($n = 3$). Sample solution: Fe(III) − 0.1 mM, ligand: NTA, GEDTA, EDTA, DTPA, DFB − 10 mM, matrix: H_2O, pH: 8.0, sample volume: 5 mL, flow rate: 0.2 mL min^{-1}, eluent: 1 M HCl (4 mL) + 6 M HCl (1 mL).

Figure 5: Effect of coexisting ions on the performance of AnaLig TE-01 (n = 3). Sample solution: Fe(III) – 0.1 mM, ligand: EDTA – 10 mM, ion concentration – 10 mM, matrix: H_2O, pH: 8.0, sample volume: 5 mL, flow rate: 0.2 mL min^{-1}, eluent: 1 M HCl (4 mL) + 6 M HCl (1 mL). 'Sample' denotes the analyte concentration in the column effluent collected after passing the sample solution through the MRT-SPE system; 'elute' denotes the analyte concentration in the collected eluent.