CHAPTER V

CONCLUSION

A simple method of simultaneous preconcentration and speciation analysis of chromium was developed using the solid - phase extraction (SPE) technique. The chemically modified silica gel, containing amidoxime (Si-Amidoxime) and benzothiazolyl (Si-Benzothiazole), were used as sorbents. The sorption properties of Si-Amidoxime and Si-Benzothiazole were studied with batch and column system. The determination of chromium was carried on FAAS.

In batch system, the results showed that Si-Amidoxime adsorbed Cr(III) and Cr(VI) at 5.0-7.0 and 1.0-7.0 pH ranges, respectively. Whereas Si-Benzothiazole adsorbed Cr(III) and Cr(VI) at 4.0-7.0 and 1.0-7.0 pH ranges, respectively. The equilibrium time for the retention of Cr(III) onto Si-Benzothiazole and that of Cr(VI) onto Si-Amidoxime was observed at 60 min and 5 min, respectively. Adsorption behavior of Cr(III) and Cr(VI) obeyed Langmuir adsorption model. The maximum sorption capacity of Cr(III) on Si-Benzothiazole and Cr(VI) on Si-Amidoxime were 0.069 mmol g^{-1} and 0.071 mmol g^{-1}, respectively.

In column system, it was found that Cr(VI) and Cr(III) were completely retained on a mini-column containing 20 mg of Si-Amidoxime at a flow rate of 2.0 mL min^{-1} and 50 mg of Si-Benzothiazole at a flow rate of 0.5 mL min^{-1}, respectively. The sorption was quantitative up to 100 mL of sample solution and sorbed chromium was quantitative eluted by 5.0 mL of 10 % H_2O_2 in 0.1 M NaOH at a flow rate of 0.5 mL min^{-1}. The effect of interfering ions on chromium sorption was investigated. The results showed that the interfering cations (Na^+, K^+ and Ca^{2+}) did not affected for Cr(III) sorption onto Si-Benzothiazole. The interfering anions (Cl^- and NO_3^-) at 10 and 100 mg L^{-1} did not affected for Cr(VI) sorption onto Si-Amidoxime, but at higher concentration they

significantly decreased the sorption. For SO_4^{2-} interference, it significantly quenched Cr(VI) sorption onto Si-Amidoxime at all three concentrations. The preconcentration of Cr(III) and Cr(VI) was achieved, with preoconcentration factor of 20.

The chromium speciation method was achieved under the optimum conditions found from the preconcentration experiments using dual mini-column system, packed with 20 mg of Si-Amidoxime and 50 mg of Si-Benzothiazole, respectively.

The recoveries obtained for simultaneous preconcentration and speciation analysis of Cr(III) on Si-Benzothiazole and Cr(VI) on Si-Amidoxime from spiked synthetic sample were 83 and 99, respectively, showing the performance and the accuracy of method. The proposed procedure allowed the determination of Cr(III) and Cr(VI) with method detection limit of 2.4 and 2.1 μg L^{-1}, respectively. For application to real sample analysis such as drinking water, the results showed that the recoveries of Cr(III) and Cr(VI) were 86 and 95, respectively with the %RSD less than 5, showing the accuracy and good precision of method.

The simultaneous preconcentration and speciation procedure was simple and low cost. Due to its good characteristic, the proposed procedure was demonstrated to be promising for trace analysis. Table 5.1 shows a comparison between this method and other preconcentration and speciation procedures using functionalized sorbents and different determination techniques.

Table 5.1 Comparative data from some studies on Cr(III) and Cr(VI) speciation

Sorbents	Samples	Species	Pretreatment	Determination	%R	%RSD	MDL (μg L^{-1})	LOD (μg L^{-1})	Ref.
Modified silica gel (amidoxime and benzothiazolyl group)	Drinking water	Cr(III) Cr(VI)	PC	FAAS	84(III) 95(VI)	6(III) 4(VI)	2.4(III) 2.1(VI)	40	Present work
Amberlite XAD-16 resin	Tap water	Cr(VI) Cr total	PC, oxidation	FAAS	97	3	45	-	[43]
Hydrophilic polymer base anion exchange resin	Synthetic sample	Cr(III) Cr(VI)	PC, cpx	LC-ICP-MS	102-115	1.79(VI) 2.35(III)	-	88(VI) 81(III)	[83]
Chromatographic column Eurosphere RP C18	Drinking and deionized water	Cr(III) Cr(VI)	PC, cpx	HPLC-FAAS	-	-	-	0.5-1(VI) 1.6-5(III)	[84]
Anion exchanger	Waste water	Cr(III) Cr(VI)	PC	IC-ICPAES	-	-	-	270(VI) 250(III)	[85]
Modified C-18	Waste and drinking water	Cr(III) Cr(VI)	PC	HPLC-FAAS	-	1	-	20(VI) 30(III)	[86]
Agarose-based chelating adsorbent with imminodiacetic and agarose – based anion exchanger	River and waste water	Cr(III) Cr(VI)	PC	FAAS	100	0.4	7.7	-	[51]
Activated carbon		Cr(III) Cr total	PC, reduction	Online FI-ETAAS	-	4	0.003		[87]

PC = preconcentration, cpx = complexation, % R = % Recovery

Suggestions for Future Work

This present method was able to apply to the preconcentration and speciation of chromium in drinking water, but not in tap water. The effect of major cations and anions in tap water should be studied further.