REFERENCES

1. Kimbrough, D. E.; Cohen, Y. E.; Winer, A. M.; Creelman L. M. and Mabuni, C. M. A Critical Assessment of Chromium in the Environment. *Critical Reviews in Environmental Science and Technology*., **1999**, *29*, 1-46.
2. Kobla, H. V. and Volpe, S. L. Chromium, Exercise, and Body Composition. *Critical Reviews in Food Science and Nutrition*., **2000**, *40*, 291-308.
3. Maltez, H. F. and Carasek, E. Chromium speciation and preconcentration using zirconium(IV) and zirconium(IV) phosphate chemically immobilized onto silica gel surface using a flow system and F AAS. *Talanta*., **2005**, *65*, 537-542.
4. Florence, T. M. The speciation of trace elements in waters. *Talanta*., **1982**, *29*, 345-364.
5. Mondal, B. C.; Das, D. and Das, A. K. Synthesis and characterization of a new resin functionalized with 2-naphthol-3,6-disulfonic acid and its application for the speciation of chromium in natural water. *Talanta*., **2002**, *56*, 145-152.
6. Themelis, D. G.; Kika, F. S. and Economou, A. Flow injection direct spectrophotometric assay for the speciation of trace chromium(III) and chromium(VI) using chromotropic acid as chromogenic reagent. *Talanta*., **2006**, 69, 615-620.
7. Manzoori, J. L.; Sorouraddin, M. H. and Shemirani, F. Chromium speciation by a surfactant-coated alumina microcolumn using electrothermal atomic absorption spectrometry. *Talanta*., **1995**, *42*, 1151-1155.
8. Kot, A. and Namiesnik, J. The role of speciation in analytical chemistry. *TrAC - Trends in Analytical Chemistry*., **2000**, *19*, 69-79.
9. Templeton, D. M.; Ariese, F.; Cornelis, R.; Danielsson, L. G.; Muntau, H.; Van Leeuwen, H. and Lobinski, R. Guidelines for terms related to chemical speciation and fractionation of elements. Definitions, structural aspects, and methodological approaches. *Pure and Applied Chemistry*., **2000**, *72*, 1453-1470.

10. Szpunar, J. and Lobinski, R. Speciation in the environmental field - trends in Analytical Chemistry. *Fresenius' Journal of Analytical Chemistry.*, **1999**, *363*, 550-557.

11. Sanz-Medel, A. Toxic trace metal speciation: importance and tools for environmental and biological analysis. *Pure and Applied Chemistry.*, **1998**, *70*, 2281-2285.

12. Camel, V. Solid phase extraction of trace elements. *Spectrochimica Acta Part B: Atomic Spectroscopy.*, **2003**, *58*, 1177-1233.

13. Menegario, A. A.; Smichowski, P. and Polla, G. On-line preconcentration and speciation analysis of Cr(III) and Cr(VI) using baker's yeast cells immobilised on controlled pore glass. *Analytica Chimica Acta.*, **2005**, *546*, 244-250.

14. Wen, B.; Shan, X-Q. and Lian, J. Separation of Cr(III) and Cr(VI) in river and reservoir water with 8-hydroxyquinoline immobilized polyacrylonitrile fiber for determination by inductively coupled plasma mass spectrometry. *Talanta.*, **2002**, *56*, 681-687.

15. Bittner, M. and Broekaert, J. A. C. Speciation of chromium by solid-phase extraction coupled to reversed-phase liquid chromatography with UV detection. *Analytica Chimica Acta.*, **1998**, *364*, 31-40.

16. Filik, H. Preconcentration and speciation of chromium(III) in waters by using 5-palmitoyl-8-hydroxyquinoline immobilized on a nonpolar adsorbent. *Microchimica Acta.*, **2002**, *140*, 205-210.

17. Filik, H.; Dogutan, M. and Apak, R. Speciation analysis of chromium by separation on a 5-palmitoyl oxine-functionalized XAD-2 resin and spectrophotometric determination with diphenylcarbazide. *Analytical and Bioanalytical Chemistry.*, **2003**, *376*, 928-933.

18. Palmer, C, D. and Puls, R, W. Natual attenuation of hexavalent in groundwater and soil. *EPA Ground Water Issue, United States Environmental protection Agency.*, **1994**, 1-12.

19. Bodek, I.; Lyman, W. J,; Reehl, W. F. and Rosenblatt, D. H. *Environmental Inorganic Chemistry Properties, Provesses and Estimation Methods*. Bodek, I.., ed., New York: Pergamon Press, **1998**.

20. Cotton, F. A.; Wilkinson, G. and Gaus, P. L. *Basic Inorganic Chemistry*. *3rd*, **1976**.

21. Cieslak-Golonka, M. and Daszkiewicz, M. Coordination geometry of Cr(VI) species: structural and spectroscopic characteristics. *Coordination Chemistry Reviews*., **2005**, *249*, 2391-2407.

22. Saha, B.; Gill, R. J.; Bailey, D. G.; Kabay, N. and Arda, M. Sorption of Cr(VI) from aqueous solution by Amberlite XAD-7 resin impregnated with Aliquat 336. *Reactive and Functional Polymers*., **2004**, *60*, 223-244.

23. Sule, P. A. and Ingle, J. J. D. Determination of the speciation of chromium with an automated two-column ion-exchange system. *Analytica Chimica Acta*., **1996**, *326*, 85-93.

24. Csoban, K. and Joo, P. Sorption of Cr(III) on silica and aluminium oxide: experiments and modelling. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*., **1999**, *151*, 97-112.

25. Saleh, F. Y.; Mbamalu, G. E.; Jaradat, Q. H. and Brungardt, C. E. Ion chromatography-photodiode array UV-Visible detection of Cr(III) hydrolytic polymerization products in pure and natural waters. *Analytical Chemistry*., **1996**, *68*, 740-745.

26. Csoban, K.; Parkanyi-Berka, M.; Joo, P. and Behra, P. Sorption experiments of Cr(III) onto silica. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*., **1998**, *141*, 347-364.

27. Wehrli, B.; Ibric, S. and Stumm, W. Adsorption kinetics of vanadyl (IV) and chromium (III) to aluminum oxide: Evidence for a two-step mechanism. *Colloids and Surfaces*., **1990**, *51*, 77-88.

28. Baes. and Mesmer. *John Wiley & Sons. Reprinted with permission*., **1976**.

29. bulletin, S. *Sigma-Aldrich Co.,* **1998**.

30. Kantipuly, C.; Katragadda, S.; Chow, A. and Gesser, H. D. Chelating polymers and related supports for separation and preconcentration of trace metals. *Talanta.*, **1990**, *37*, 491-517.

31. Sperling, M.; Yin, X. and Welz, B. Differential determination of chromium(VI) and total chromium in natural waters using flow injection on-line separation and preconcentration electrothermal atomic absorption spectrometry. *The Analyst.*, **1992**, *117*, 629.

32. *Standard test method for chromium in water*. Philadelphia, **1995**.

33. Kabasakalis, V. Fluorometric Cr(VI) and Cr(III) speciation with crystal violet. *Analytical Letters.*, **1993**, *26*, 2269.

34. Boussemart, M.; Van Den Berg, C. M. G. and Ghaddaf, M. The determination of the chromium speciation in sea water using catalytic cathodic stripping voltammetry. *Analytica Chimica Acta.*, **1992**, *262*, 103-115.

35. Cincinati, O. Chromium hexavalent (atomic absorption, chelation-extraction). *US EPA Methods for Chemical Analysis of Water and Wastes.*, **1983**.

36. Nakayama, E.; Kuwamoto, T.; Tokoro, H. and Fujinaga, T. Chemical speciation of chromium in sea water : Part 3. The determination of chromium species. *Analytica Chimica Acta.*, **1981**, *131*, 247-254.

37. Obiols, J. D. and Garcia-Berro, J. S. J. Speciation of chromium in waters by coprecipitation-AAS. *International Journal of Environmental & Analytical Chemistry.*, **1987**, *30*, 197.

38. Johnson, C, A. Rapid ion-exchange technique for the separation and preconcentration of chromium(VI) and chromium(III) in fresh waters. *Analytica Chimica Acta.*, **1990**, *238*, 273-278.

39. Hiraide, M. and Mizuike, A. Separation and determination of chromium(VI) anions and chromium(III) associated with negatively charged colloids in river water by sorption on DEAE-Sephadex A-25. *Fresenius' Journal of Analytical Chemistry.*, **1989**, *335*, 924-926.

40. Narin, I.; Soylak, M.; Kayakirilmaz, K.; Elci, L. and Dogan, M. Speciation of Cr(III) and Cr(VI) in tannery wastewater and sediment samples on Ambersorb 563 resin. *Analytical Letters.*, **2002**, *35*, 1437-1452.

41. Narin, I.; Surme, Y,; Soylak, M. and Dogan, M. Speciation of Cr(III) and Cr(VI) in environmental samples by solid phase extraction on Ambersorb 563 resin. *Journal of Hazardous Materials.*, **2006**, *136*, 579-584.

42. Dogutan, M.; Filik, H. and Tor, I. Preconcentration and speciation of chromium using a melamine based polymeric sequestering succinic acid resin: its application for Cr(VI) and Cr(III) determination in wastewater. *Talanta.*, **2003**, *59*, 1053-1060.

43. Tunceli, A. and Turker, A. R. Speciation of Cr(III) and Cr(VI) in water after preconcentration of its 1,5-diphenylcarbazone complex on amberlite XAD-16 resin and determination by FAAS. *Talanta.*, **2002**, *57*, 1199-1204.

44. Rao, T. P.; Karthikeyan, S.; Vijayalekshmy, B. and Iyer, C. S. P. Speciative determination of Cr(VI) and Cr(III) using flow-injection on-line preconcentration and flame atomic-absorption spectrometric detection. *Analytica Chimica Acta.*, **1998**, *369*, 69-77.

45. Yalcin, S and Apak, R. Chromium (III,VI) speciation analysis with preconcentration on a maleic-acid functionalized XAD sorbent. *Analytica Chimica Acta.*, **2004**, *505*, 25-35.

46. Tuzen, M. and Soylak, M. Chromium speciation in environmental samples by solid phase extraction on Chromosorb 108. *Journal of Hazardous Materials.*, **2006**, *129*, 266-273.

47. Battistoni, P.; Bompadre, S.; Fava, G. and Gobbi, G. Silica gel with adsorbed Adogen 464 as an analytical sampling tool for anions. *Talanta.*, **1983**, *30*, 15-19.

48. Sperling, M.; Xu, S. and Welz, B. Determination of chromium(III) and chromium(VI) in water using flow injection on-line preconcentration with selective adsorption on activated alumina and flame atomic absorption spectrometric detection. *Analytical Chemistry.*, **1992**, *64*, 3101-3108.

49. Kubrakova, I.; Kudinova, T.; Formanovsky, A.; Kuz' min, N.; Tsysin, G. and Zolotov, Y. Determination of chromium(III) and chromium(VI) in river water by electrothermal atomic absorption spectrometry after sorption preconcentration in a microwave field. *The Analyst.*, **1994**, *119*, 2477-2480.

50. Sun, H. W.; Kang, W. J.; Ha, J.; Liang, S. X. and Shen, S. G. Determination of Cr(III) and Cr(VI) in environmental waters by derivative flame atomic absorption spectrometry using flow injection on-line preconcentration with double-microcolumn adsorption. *Journal of the Iranian Chemical Society.*, **2004**, *1*, 40-46.

51. Hashemi, P.; Boroumand, J. and Fat'hi, M. R. A dual column system using agarose-based adsorbents for preconcentration and speciation of chromium in water. *Talanta.*, **2004**, *64*, 578-583.

52. Jal, P. K.; Patel, S. and Mishra, B. K. Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metal ions. *Talanta.*, **2003**, *62*, 1005-1029.

53. Lutfor, M. R.; Silong, S.; Yunus, W. M. Z. W.; Rahman, M. Z. A.; Ahmad, M. and Haron, J. Polymer bearing amidoxime groups for extraction of arsenic from aqueous media [on line]. (1997-2006). Available from: *http://WWW.eng-consult.com/BEN/Papers-lutfor#search=%22amidoxime%22* [cited 1 August 2006]

54. Lin, W.; Lu, Y. and Zeng, H. Extraction of gold from Au(III) ion containing solution by a reactive fiber. *Journal of Applied Polymer Science.*, **1993**, *49*, 1635-1638.

55. Kato, T.; Kago, T.; Kusakabe, K. and Morooka, S. Preparation of amidoxime fibers for recovery of uranium from sea water. *Journal of Chemical Engineering of Japan.*, **1990**, *23*, 744-750.

56. Morrison, G. H. and Freiser, H. *Solvent extraction in analytical chemistry.*, **1962**, 183.

57. Charles, R. G. and Freiser, H. Structure and behavior of organic analytical reagents IV chelates of 2-(o-hydroxyphenyl)-benzoxazole, 2-(o-hydroxyphenyl)-benzothiazole and 2-(o-hydroxyphenyl)-benzoyhiazoline. *Analytica Chimica Acta.*, **1954**, *11*, 1-11.

58. Angulo-Cornejo, J.; Lino-Pachecho, M.; Richter, R.; Hennig, L.; Hallmeier, K-H. and Beyer, L. Metals chelates of N-benzothiazol-2-yl, N-benzoxazol-2-yl-and N-(1-H benzimidazol-2-yl)-benzamide. *Inorganic Chemica Acta.*, **2000**, *305*, 38-45.

59. Ngeontae, W.; Sukpirom, N.; Aeungmaitrepirom, W. and Imyim, A. Preparation of gold nanoparticles by reduction of chloroaurate ions with amido-amidoxime functionalised silica. *Manuscript in preparation.*

60. Aeungmaitrepirom, W.; Ngeontae, W. and Tuntulani, T. Adsorption capabilities of novwl silica gel chemically modified with benzothiazolyl moiety. *Manuscript in preparation.*

61. Aeungmaitrepirom, W.; Hagege, A.; Astari, Z.; Vicens, J. and Leroy, M. J. Sovent extraction of selenate and chromate using a diaminocalix[4]arene. *Journal of Inclusion Phenomena and Macrocyclic Chemistry.*, **2001**, *40*, 225-229.

62. Georgiev, E. M.; Wolf, N. and Roundhill, D. M. Lower rim alkylammonium-substituted calix[4[arenes as "proton-switchable" extractants for chromate and dichromate anions. *Polyhedron.*, **1997**, *16*, 1581-1584.

63. Falana, O. M.; Koch, H. F.; Roundhill, D. M.; Lumetta, G. J. and Hay, B. P. Synthesis and extraction studies of 1,2- and 1,3- disubstituted butylcalix[4]arene amides with oxyions: geometric and conformational effects. *Chemical Commumications.*, **1998**, 503-504.

64. Marques, M. J.; Salvador, A.; Morales-Rubio, A. and de la Guardia, M. Chromium speciation in liquid matrices: a survey of the literature. *Fresenius' Journal of Analytical Chemistry.*, **2000**, *367*, 601-613.

65. Hirata, S.; Umezaki, Y. and Ikeda, M. Determination of Chromium(III), Titanium, Vanadium, Iron(III), and Aliminum by inductively coupled plasma atomic emission spectrometry with an on-line preconcentrating ion-exchange column. *Analytical Chemistry.*, **1986**, *58*, 2602-2606.

66. Cespon-Romero, R. M.; Yebra-Biurrun, M. C. and Bermejo-Barrera, M. P. Preconcentration and speciation of chromium by determination of total chromium

and chromium(III) in natural waters by flame atomic absorption spectrometry with a chelating ion-exchange flow injection system. *Analytica Chimica Acta.*, **1996**, *327*, 37-45.

67. Abollino, O.; Sarzanini, C. and Mentasti, E. Trace metal preconcentation with sulphonated azo-dyes and ICP/AES determination. *Spectrochemica Acta Part B.*, **1993**, *49A*, 1411-1421.

68. Muhamumad, N.; Par, J.; Smith, M. D. and Wheatley, A. D. Adsorption of heavy metals in slow san filters. *24th WEDC Conference Sanitation and Water for All.* Islamabad Pakistan., **1998**, 346-349.

69. Suna Erses, A.; Fazal, M. A.; Onay, T. T. and Craig, W. H. Determination of solid waste sorption capacity for selected heavy metals in landfills. *Journal of Hazardous Materials.*, **2005**, *121*, 223-232.

70. Langmiur, I. The adsorption of gases on plane surface of glass, mica and platinum. *Journal of the American Chemical Society.*, **1918**, *40*, 1361-1403.

71. Villaescusa, I.; Fiol, N.; Martinez, M.; Miralles, N.; Poch, J. and Serarols, J. Removal of copper and nickel ions from aqueous solutions by grape stalks wastes. *Water Research.*, **2004**, *38*, 992-1002.

72. Filho, N. L. D.; Gushikem, Y.; Polito, W. L.; Moreira, J. and Ehirim, E. O. Sorption and preconcentration of metal ions in ethanol solution with a silica gel surface chemically modified with benzimidazole. *Talanta.*, **1995**, *42*, 1625-1630.

73. Santos, M. R. M. C. and Airoldi, C. Urea Derivatives Anchored on Silica Gel. *Journal of Colloid and Interface Science.*, **1996**, *183*, 416-423.

74. Chaiatchanarat, S. *Aminocalix[4]arene derivatives as extractant for chromate ion.* Master's Thesis, Department of chemistry, Faculty of Science, Chulalongkorn University., **2002**.

75. Akl, M. A. A-E.; Kenawy, I. M. and Lasheen, R. R. Silica gel modified with *N*-(3-Propyl)-*O*-phenylenediamine: functionalization, metal sorption equilibrium studies

and application to metal enrichment prior to determination by flame atomic absorption spectrometry. *Analytical Sciences*., **2005**, *21*, 923-930.

76. Abou-El-Sherbini, K. S.; Kenawy, I. M.; Hamed, M. A.; Issa, R. M. and Elmorsi, R. Separation and preconcentration in a batch mode of Cd(II), Cr(III, VI), Cu(II), Mn(II, VII) and pb(II) by solid-phase extraction by using of silica modified with N-propylsalicylaldimine. *Talanta*., **2002**, *58*, 289-300.

77. Threeprom, J.; Purachaka, S. and Potipan, L. Simultaneous determination of Cr(III)-EDTA and Cr(VI) by ion interaction chromatography using a C18 column. *Journal of Chromatography A*., **2005**, *1073*, 291-295.

78. Neubauer, K.; Reuter, W. and Perrone, P. Chromium speciation in water by HPLC/ICP-MS. *PerkinElmer Life and Analytical Sciences*., **2003**.

79. Andersen, J. E. T. Introduction of hydrogen peroxide as an oxidant in flow injection analysis: speciation of Cr(III) and Cr(VI). *Analytica Chimica Acta*., **1998**, *361*, 125-131.

80. Huber, L. *Validation and qualification in analytical laboratories*. Illinois: Interpharm., **1999**.

81. Scheerder, J.; Engbersen, J. F. J. and Reinhoudt, D. N. Synthetic receptors for anion complexation. *Recueil des Travaux Chimiques des Pay-Bas Journal of The Royal Netherlands Chemical Society*., **1996**, *115*, 307-320.

82. Schmidtchen, F. P. and Berger, M. Artificial organic host molecules for anions. *Chemical Review*., **1997**, *97*, 1609-1646.

83. Inoue, Y.; Sakai, T. and Kumagai, H. Simultaneous determination of chromium(III) and chromium(VI) by ion chromatography with inductively coupled plasma mass spectrometry. *Journal of Chromatography A*., **1995**, *706*, 127-136.

84. Groll, H.; Schaldach, G.; Berndt, H. and Niemax, K. Measurement of Cr(III)/Cr(VI) species by wavelength modulation diode laser flame atomic absorption spectrometry. *Spectrochimica Acta Part B: Atomic Spectroscopy*., **1995**, *50*, 1293-1298.

85. Prokisch, J.; Kovacs, B.; Gyodri, Z. and Loch, J. Interfacing ion chromatography with inductively coupled plasma atomic emission spectrometry for the determination of chromium(III) and chromium(VI). *Journal of Chromatography A.*, **1994**, *683*, 253-260.

86. Posta, J.; Berndt, H.; Lou, S-K. and Schaldach, G. High-performance flow frame atomic absorption spectrometry for automated on-line separation and determination of chromium(III)/cheomium(VI) and preconcentation of chromium(VI). *Analytical Chemistry.*, **1993**, *65*, 2590-2595.

87. Gil, R, A.; Cerutti, S.; Gasquez, J. A.; Olsina, R. A. and Martinez, L.D. Preconcentration and speciation of chromium in drinking water samples by coupling of on-line sorption on activated carbon to ETAAS determination. *Talanta.*, **2006**, *68*, 1065-1070.

APPENDICES

APPENDICES

A. Calculation of the concentration of Cr(VI) species [22]

The mathematical derivations for calculating the concentrations of various chromium species within the range of our experimental conditions are shown below. Chromium exists in five main forms in aqueous solution. The reactions between these species and the reaction equilibrium constants (*K*) are shown in equations A.1 – A.4.

$$H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^- \quad K_1 = 1.21 \quad (A.1)$$

$$HCrO_4^- \rightleftharpoons H^+ + CrO_4^{2-} \quad K_2 = 3.0\times10^{-7} \quad (A.2)$$

$$2\,HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O \quad K_3 = 35.5 \quad (A.3)$$

$$HCr_2O_7^- \rightleftharpoons H^+ + Cr_2O_7^{2-} \quad K_4 = 0.85 \quad (A.4)$$

Chromium (VI) can exist in two other forms but the concentrations were considered too low to be significant. The reactions to produce these forms are shown in equations A.5 and A.6.

$$Cr_2O_7^{2-} + H^+ + HCrO_4^- \rightleftharpoons Cr_3O_{10}^{2-} + H_2O \quad (A.5)$$

$$Cr_3O_{10}^{2-} + H^+ + HCrO_4^- \rightleftharpoons Cr_4O_{13}^{2-} + H_2O \quad (A.6)$$

Disregarding to chromium in the form of $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$, the total number of chromium atoms (Cr) in a closed system is given by equation A.7.

$$[Cr] = [H_2CrO_4] + [HCrO_4^-] + [CrO_4^{2-}] + \frac{1}{2}[Cr_2O_7^{2-}] + \frac{1}{2}[HCr_2O_7^-] \quad (A.7)$$

The equilibrium constants (K) are the ratio of the forward and reverse reaction rate constants. All reactions were considered to be first order with respect to each species with the exception of water as all reactions take place in the aqueous phase. Equations A.8–A.11 define K_1–K_4 respectively.

$$K_1 = \frac{[H^+][HCrO_4^-]}{[H_2CrO_4]}, \tag{A.8}$$

$$K_2 = \frac{[H^+][CrO_4^{2-}]}{[HCrO_4^-]}, \tag{A.9}$$

$$K_3 = \frac{[Cr_2O_7^{2-}]}{[HCrO_4^-]^2}, \tag{A.10}$$

$$K_4 = \frac{[H^+][Cr_2O_7^{2-}]}{[HCr_2O_7^-]}. \tag{A.11}$$

In order to calculate the amount of any species in the system, equations A.8–A.11 must be rearranged and substituted into A.7.

1. Calculation of concentration of $[H_2CrO_4]$

From equation A.8:

$$[HCrO_4^-] = \frac{K_1[H_2CrO_4]}{[H^+]} \tag{A.12}$$

From equations A.8 and A.9:

$$[CrO_4^{2-}] = \frac{K_1K_2[H_2CrO_4]}{[H^+]^2} \tag{A.13}$$

From equations A.8 and A.10:

$$[Cr_2O_7^{2-}] = \frac{K_1^2 K_3 [H_2CrO_4]^2}{[H^+]^2} \qquad \text{(A.14)}$$

From equations A.8, A.10 and A.11:

$$[HCr_2O_7^-] = \frac{K_1^2 K_3 [H_2CrO_4]^2}{K_4 [H^+]} \qquad \text{(A.15)}$$

Substituting equations A.12–A.15 into A.7 gives the total amount of Cr(VI) atoms as a function of $[H_2CrO_4]$ and $[H^+]$.

$$[Cr] = [H_2CrO_4] + \frac{K_1[H_2CrO_4]}{[H^+]} + \frac{K_1K_2[H_2CrO_4]}{[H^+]^2} + \frac{K_1^2K_3[H_2CrO_4]^2}{2[H^+]^2} + \frac{K_1^2K_3[H_2CrO_4]^2}{2K_4[H^+]}$$

(A.16)

Equation A.16 is a quadratic equation. Grouping the terms gives equation A.17:

$$\left[\frac{K_1^2K_3}{2[H^+]^2} + \frac{K_1^2K_3}{2K_4[H^+]}\right][H_2CrO_4]^2 + \left[\frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2} + 1\right][H_2CrO_4] - [Cr] = 0 \qquad \text{(A.17)}$$

Rearranging for H_2CrO_4 gives:

$$[H_2CrO_4] = \frac{-\left[\frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2} + 1\right] + \sqrt{\left[\frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2} + 1\right]^2 + 4\left[\frac{K_1^2K_3}{2[H^+]^2} + \frac{K_1^2K_3}{2K_4[H^+]}\right][Cr]}}{2\left[\frac{K_1^2K_3}{2[H^+]^2} + \frac{K_1^2K_3}{2K_4[H^+]}\right]}$$

(A.18)

2. Calculation of concentration of $[HCrO_4^-]$

From equation A.8:

$$[H_2CrO_4] = \frac{[H^+][HCrO_4^-]}{K_1} \qquad \text{(A.19)}$$

From equation A.9:

$$[CrO_4^{2-}] = \frac{K_2[HCrO_4^-]}{[H^+]} \qquad \text{(A.20)}$$

From equation A.10:

$$[Cr_2O_7^{2-}] = K_3[HCrO_4^-]^2 \qquad \text{(A.21)}$$

From equation A.10 and A.11:

$$[HCr_2O_7^-] = \frac{K_3[H^+][HCrO_4^-]^2}{K_4} \qquad \text{(A.22)}$$

Substituting A.19–A.22 into A.7 gives total chromium as a function of $[HCrO_4^-]$ and $[H^+]$.

$$[Cr] = \frac{[H^+][HCrO_4^-]}{K_1} + [HCrO_4^-] + \frac{K_2[HCrO_4^-]}{[H^+]} + \frac{K_3[HCrO_4^-]^2}{2} + \frac{K_3[H^+][HCrO_4^-]^2}{2K_4}$$

(A.23)

Equation A.23 is a quadratic equation. Grouping the terms gives equation A.24:

$$\left[\frac{K_3}{2} + \frac{K_3[H^+]}{2K_4}\right][HCrO_4^-]^2 + \left[\frac{[H^+]}{K_1} + \frac{K_2}{[H^+]} + 1\right][HCrO_4^-] - [Cr] = 0 \qquad \text{(A.24)}$$

Rearranging for $[HCrO_4^-]$ gives:

$$[HCrO_4^-] = \frac{-\left[\frac{[H^+]}{K_1} + \frac{K_2}{[H^+]} + 1\right] + \sqrt{\left[\frac{[H^+]}{K_1} + \frac{K_2}{[H^+]} + 1\right]^2 + 4\left[\frac{K_3}{2} + \frac{K_3[H^+]}{2K_4}\right][Cr]}}{2\left[\frac{K_3}{2} + \frac{K_3[H^+]}{2K_4}\right]} \quad (A.25)$$

3. Calculation of concentration of $[CrO_4^{2-}]$

From equations A.8 and A.9:

$$[H_2CrO_4] = \frac{[H^+]^2[CrO_4^{2-}]}{K_1K_2} \quad (A.26)$$

From equation A.9:

$$[HCrO_4^-] = \frac{[H^+][CrO_4^{2-}]}{K_2} \quad (A.27)$$

From equations A.9 and A.10:

$$[Cr_2O_7^{2-}] = \frac{K_3[H^+]^2[CrO_4^{2-}]^2}{K_2^2} \quad (A.28)$$

From equations A.9, A.10 and A.11:

$$[HCr_2O_7^-] = \frac{K_3[H^+]^3[CrO_4^{2-}]^2}{K_4K_2^2} \quad (A.29)$$

Substituting A.26–A.29 into A.7 gives:

$$[Cr] = \frac{[H^+]^2[CrO_4^{2-}]}{K_1K_2} + \frac{[H^+][CrO_4^{2-}]}{K_2} + [CrO_4^{2-}] + \frac{K_3[H^+]^2[CrO_4^{2-}]^2}{2K_2^2} + \frac{K_3[H^+]^3[CrO_4^{2-}]^2}{2K_4K_2^2}$$

(A.30)

Equation A.30 is a quadratic equation. Grouping the terms gives equation A.31:

$$\left[\frac{K_3[H^+]^2}{2K_2^2}+\frac{K_3[H^+]^3}{2K_4K_2^2}\right][CrO_4^{2-}]^2+\left[\frac{[H^+]^2}{K_1K_2}+\frac{[H^+]}{K_2}+1\right][CrO_4^{2-}]-[Cr]=0 \qquad (A.31)$$

Rearranging for $[CrO_4^{2-}]$ gives:

$$[CrO_4^{2-}]=\frac{-\left[\frac{[H^+]^2}{K_1K_2}+\frac{[H^+]}{K_2}+1\right]+\sqrt{\left[\frac{[H^+]^2}{K_1K_2}+\frac{[H^+]}{K_2}+1\right]^2+4\left[\frac{K_3[H^+]^2}{2K_2^2}+\frac{K_3[H^+]^3}{2K_4K_2^2}\right][Cr]}}{2\left[\frac{K_3[H^+]^2}{2K_2^2}+\frac{K_3[H^+]^3}{2K_4K_2^2}\right]}$$

(A.32)

4. Calculation of concentration of $[Cr_2O_7^{2-}]$

From equations A.8 and A.10:

$$[H_2CrO_4]=\frac{[H^+][Cr_2O_7^{2-}]^{0.5}}{K_1K_3^{0.5}} \qquad (A.33)$$

From equation A.10:

$$[HCrO_4^-]=\frac{[Cr_2O_7^{2-}]^{0.5}}{K_3^{0.5}} \qquad (A.34)$$

From equations A.9 and A.10:

$$[CrO_4^{2-}]=\frac{K_2[Cr_2O_7^{2-}]^{0.5}}{K_3^{0.5}[H^+]} \qquad (A.35)$$

From equation A.11:

$$[HCr_2O_7^-]=\frac{[H^+][Cr_2O_7^{2-}]}{K_4} \qquad (A.36)$$

Substituting equations A.33–A.36 into A.7 gives:

$$[Cr]=\frac{[H^+][Cr_2O_7^{2-}]^{0.5}}{K_1K_3^{0.5}}+\frac{[Cr_2O_7^{2-}]^{0.5}}{K_3^{0.5}}+\frac{K_2[Cr_2O_7^{2-}]^{0.5}}{K_3^{0.5}[H^+]}+\frac{[Cr_2O_7^{2-}]}{2}+\frac{[H^+][Cr_2O_7^{2-}]}{2K_4}$$

(A.37)

Equation A.37 is a quadratic equation. Grouping the terms gives equation A.38:

$$\left[\frac{1}{2}+\frac{[H^+]}{2K_4}\right][Cr_2O_7^{2-}]+\left[\frac{[H^+]}{K_1K_3^{0.5}}+\frac{1}{K_3^{0.5}}+\frac{K_2}{K_3^{0.5}[H^+]}\right][Cr_2O_7^{2-}]^{0.5}-[Cr]=0 \qquad \text{(A.38)}$$

Rearranging for $[Cr_2O_7^{2-}]$ gives:

$$[Cr_2O_7^{2-}]=\left[\frac{-\left[\frac{[H^+]}{K_1K_3^{0.5}}+\frac{1}{K_3^{0.5}}+\frac{K_2}{K_3^{0.5}[H^+]}\right]+\sqrt{\left[\frac{[H^+]}{K_1K_3^{0.5}}+\frac{1}{K_3^{0.5}}+\frac{K_2}{K_3^{0.5}[H^+]}\right]^2+4\left[\frac{1}{2}+\frac{[H^+]}{2K_4}\right][Cr]}}{2\left[\frac{1}{2}+\frac{[H^+]}{2K_4}\right]}\right]^2$$

(A.39)

5. Calculation of concentration of $[HCr_2O_7^-]$

From equations A.8, A.10 and A.11:

$$[H_2CrO_4]=\frac{K_4^{0.5}[H^+]^{0.5}[HCr_2O_7^-]^{0.5}}{K_1K_3^{0.5}} \qquad \text{(A.40)}$$

From equations A.10 and A.11:

$$[HCrO_4^-]=\frac{K_4^{0.5}[HCrO_7^-]^{0.5}}{K_3^{0.5}[H^+]^{0.5}} \qquad \text{(A.41)}$$

From equations A.9 and A.10:

$$[CrO_4^{2-}]=\frac{K_2K_4^{0.5}[HCr_2O_7^-]^{0.5}}{K_2[H^+]^{1.5}} \qquad \text{(A.42)}$$

From equation A.11:

$$[Cr_2O_7^{2-}] = \frac{K_4[HCr_2O_7^-]}{[H^+]} \qquad (A.43)$$

Substituting equations A.40–A.43 into A.7 gives:

$$[Cr] = \frac{K_4^{0.5}[H^+]^{0.5}[HCr_2O_7^-]^{0.5}}{K_1K_3^{0.5}} + \frac{K_4^{0.5}[HCr_2O_7^-]^{0.5}}{K_3^{0.5}[H^+]^{0.5}} + \frac{K_2K_4^{0.5}[HCr_2O_7^-]^{0.5}}{K_2[H^+]^{1.5}} + \frac{K_4[HCr_2O_7^-]}{2[H^+]} + \frac{[HCr_2O_7^-]}{2} \qquad (A.44)$$

Equation A.44 is a quadratic equation. Grouping the terms gives equation A.45:

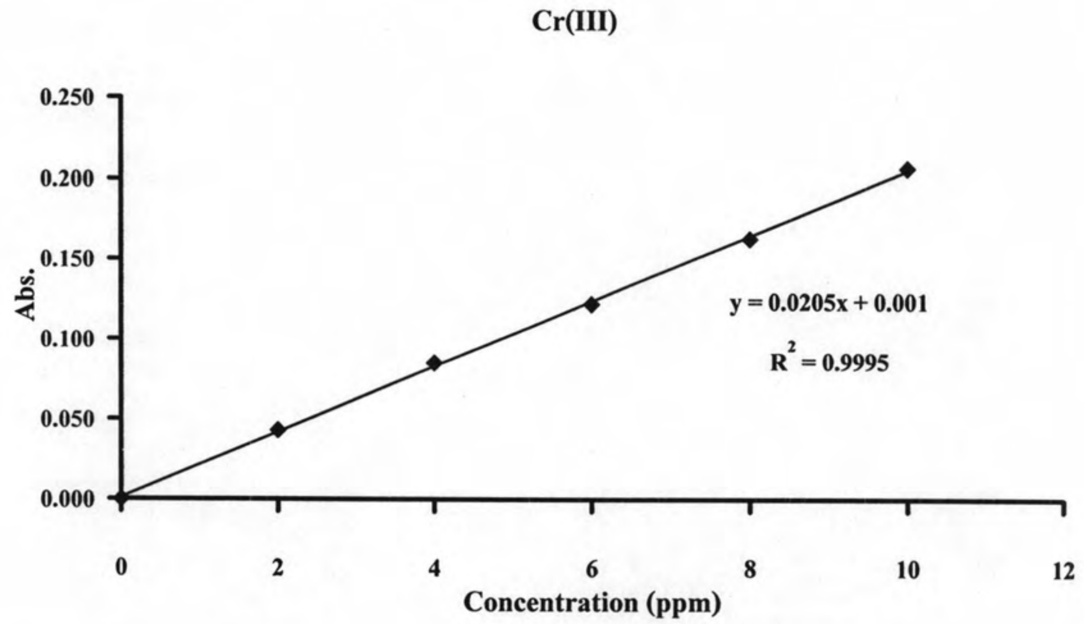
$$\left[\frac{K_4}{2[H^+]} + \frac{1}{2}\right][HCr_2O_7^-] + \left[\frac{K_4^{0.5}[H^+]^{0.5}}{K_1K_3^{0.5}} + \frac{K_4^{0.5}}{K_3^{0.5}[H^+]^{0.5}} + \frac{K_2K_4^{0.5}}{K_2[H^+]^{1.5}}\right][HCr_2O_7^-]^{0.5} - [Cr] = 0 \qquad (A.45)$$

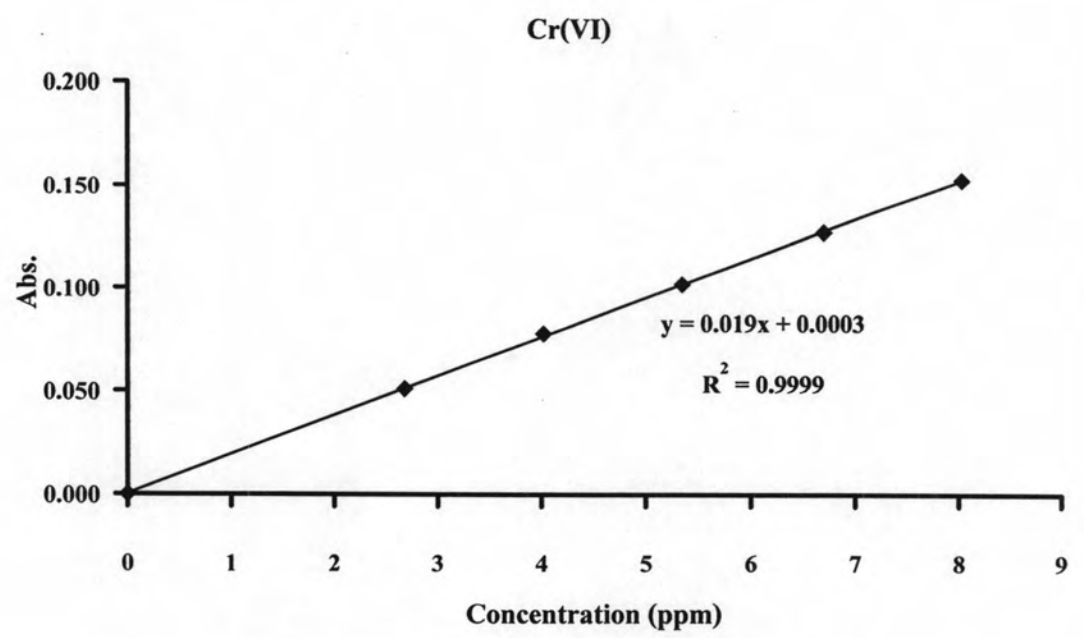
Rearranging for $[HCr_2O_7^-]$ gives:

$$[HCr_2O_7^-] = \left[\frac{-\left[\frac{K_4^{0.5}[H^+]^{0.5}}{K_1K_3^{0.5}} + \frac{K_4^{0.5}}{K_3^{0.5}[H^+]^{0.5}} + \frac{K_2K_4^{0.5}}{K_2[H^+]^{1.5}}\right]^2 + \sqrt{\left[\frac{K_4^{0.5}[H^+]^{0.5}}{K_1K_3^{0.5}} + \frac{K_4^{0.5}}{K_3^{0.5}[H^+]^{0.5}} + \frac{K_2K_4^{0.5}}{K_2[H^+]^{1.5}}\right] + 4\left[\frac{K_4}{2[H^+]} + \frac{1}{2}\right][Cr]}}{2\left[\frac{K_4}{2[H^+]} + \frac{1}{2}\right]}\right. \qquad (A.46)$$

After calculating the concentrations of various chromium species within the range of our experimental conditions (at a specific total concentration of Cr(VI) and at different pHs of the equilibrium solution) using the above mentioned equations, the speciation diagram has been produced.

B. Calibration curve of Cr(III) and Cr(VI) with FAAS





VITA

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