REFERENCES

1. Kenneth, W.O., and Rodney, K.S. "Identification of Soil Lead Compounds from Automotive Sources." Environmental Science and Technology 9(3) (March 1975): 227-230.

2. Chow, T.I., et al. "Lead Pollution: Records in Southern California Coastal Sediments." Science 181 (August 1973) : 551-552.

3. Erlenkeuser, H.; Suess, E.; and Willkomm, H. "Industrialization Affects Heavy Metals and Carbon Isotope Concentrations in Recent Baltic Sea Sediments." Geochemica et Cosmochimica Acta 38 (1974): 823-842.

4. Menasveta, P., and Sawangwong, P. "Distribution of Heavy Metals in the Chao Phraya River Estuary." In Pollution Problem of Heavy Metal in the Environment in Thailand, pp. 107-145. The Institute of Environmental Research, Seminar Proceeding Number 2. Bangkok: Chulalongkorn University Press, 1978.

5. Sawangwong, P. "A study on the Distribution of Lead and Mercury in the Lower Section of the Chao Phraya River." Master's Thesis, Department of Marine Science, Graduate School, Chulalongkorn University, 1977.

6. Piyakarnchana, T., et al. "The Changing Amounts of Lead, Mercury and Cadmium in Sea Water and Marine Sediments from the Upper Portion of the Gulf of Thailand." In Pollution Problem of Heavy Metal in the Environment in Thailand, pp. 146-161. The Institute of Environmental Research, Seminar Proceeding Number 2. Bangkok : Chulalongkorn Press, 1978.

7. Asian Institute of Technology. Environmental Engineering Division and Water Resources Engineering Division. "Heavy Metals, DDT and PCBs in the Upper Gulf of Thailand." phase 1, Final Report for National Environmental Board of Thailand, 1979.

8. Donal, J.L.O. "Trace Metals in Soils, Plants and Animals." Advances in Agronomy 24 (1972): 267.

9. Eaton, J.G.; Mckim, J.M.,; and Halcombe, G.W. "Metal Toxicity to Embryos and Larvae of Seven Fresh water Fish Species. I). Cadmium." Bulletin of Environmental Contamination and Toxicology 19 (1979): 95-103.

10. Patrick, T.E. "Malformations and Inhibitory Tendencies Induced to *Brachydanio rerio* (Hamilton-Buchanan) Eggs and Larvae due to Exposures in Low Concentrations of Lead and Copper Ions." Bulletin of Environmental Contamination and Toxicology 21 (1979): 668-675.

11. Steeman-Nielson, E., and Wium-Anderson, S. "Copper Ions as Poison in the Sea and in Freshwater." Marine Biology 6 (1970): 93-97.

12. Sunda, W., and Guillard, R.R.L. "The Relationship Between Cupric Ion Activity and the Toxicity of Copper to Phytoplankton Activity." Journal of Marine Research 34 (1976): 511-529.

13. Anaerson, D.M., and Moral, F.M.M. "Copper Sensitivity of *Gonyaulax tamarensis*." Limnology and Oceanography 23 (1978): 283-289.

14. Andrew, R.W.; Biesinger, K.E.; and Glass, G.E. "Effects of Inorganic Complexing on the Toxicity of Copper to *Daphnia magna*." Water Research 11 (3) (1977): 309-315.

15. Pagenkopf, G.K.; Russo, R.C.; and Thurston, R.V. "Effect of Complexation on Toxicity of Copper to Fishes." Journal of the Fisheries Research Board of Canada 31 (1974) : 462-465.

16. Biesinger, K.E.; Andrew, R.W.; and Arthur, J.W. "Chronic Toxicity of NTA (Nitrilotriacetate) and Metal-NTA Complexes to *Daphnia magna*." Journal of the Fisheries Research Board of Canada 31 (1974): 486-490.

17. Branica, J.; Stainton, M.P.; and Hamilton, A.L. "Mobilization of Some Metals in Water and Animal Tissue by NTA, EDTA and TPP." Water Research 7 (1973): 1791-1804.

18. Dodge, E.E., and Theis, T.L. "Effect of Chemical Speciation on the Uptake of Copper by *Chironomus tentans*." Environmental Science and Technology 13 (October 1979): 1287-1288

19. Sunda, W.G.; Engel, D.W.; and Thuotle, R.M. "Effect of Chemical Speciation on Toxicity of Cadmium to Grass Shrimp *Palaemonetes pugio*: Importance of Free Cadmium Ion." Environmental Science and Technology 12 (April 1978) :409-413.

20. Garrels, R.M., and Thompson, M.E. "A Chemical Model for Sea Water at 25°C and One Atmosphere Total Pressure." American Journal of Science 260 (January 1962): 57-66.

21. Davies, C.W. "Structure of Electrolyte Solutions." In Incomplete Dissociation in Aqueous Salt Solution, pp. 26-29. Edited by Harmer, W.J. New York: John Wiley and Sons, 1959.

22. Garrels, R.M.; Thompson, M.E.; and Siever, R. "Stability of Some Carbonates at 25° and One Atmosphere Total Pressure." American Journal of Science 258 (1960): 402-418.

23. Harned, H.S., and Owen, B.B. The Physical Chemistry of Electrolytic Solutions. 3d ed. New York: Rheinhold, 1958.

24. Walker, A.C.; Bray, U.B.; and Johntson, J. "Equilibrium in Solutions of Alkali Carbonates." American Chemical Society Journal 49 (May 1927): 1235-1256.

25. Latimer, W.M. Oxidation Potentials. 2d ed. New Jersey: Prentice-Hall, 1956.

26. Goldberg, E.D. "Minor Elements in Sea Water." In Chemical Oceanography. vol 1., pp. 163-196. Edited by Riley, J.P., and Skirrow, G. London: Academic, 1965.

27. Zirino, A., and Yamamoto, S. "A pH-Dependent Model for the Chemical Speciation of Copper, Zinc, Cadmium, and Lead in Seawater." Limnology and Oceanography 17 (5) (September 1972) : 661-671.

28. Davies, C.W. Ion Association. London: Butterworth, 1962.

29. Davies, C.W. Electrochemistry. London: George Newnes, 1967.

30. Robinson, R.A., and Stokes, R.H. Electrolyte Solutions. 2d ed. London: Butterworths, 1959.

31. Nancollas, G.H. Interactions in Electrolyte Solutions. Amsterdam: Elsevier Publishing Company, 1966.

32. Sillen, L.G., and Martell, A.E. Stability Constants of Metal Ion Complexes. 2d ed. Chemical Society Special Publication 17. London: Burlington House, 1964.

33. Dyrssen, D. and Wedborg, M. "Equilibrium Calculation of the Speciation of Elements in Seawater." In The Sea, vol. 5, pp. 181-195, Edited by Goldberg, E.D. New York: Wiley-Interscience, 1974.

34. Sillen, L.G. and Martell, A.E. Stability Constants of Metal-Ion Complexes. Supplement No. 1, Chemical Society Special Publication 25. London: Burlington House, 1971.

35. Chau, Y.K., and Lum-Shue-Chan, K. "Determination of Labile and Bound Metals in Lake Water." Water Research 8 (1974): 383-388.

36. Florence, T.M., and Batley, G.E. "Trace Metals Species in Sea Water. I. Removal of Trace Metals from Sea Water by a Chelating Resin." Talanta 23 (1976): 179-186.

37. Princeton Applied Research Corporation. Model 315 Automated Electroanalysis Controller: Operating and Service Manual. New Jersey: Princeton Applied Research Corporation, 1974.

38. Copeland, T.R., and Skogerboe, R.K. "Anodic Stripping Voltammetry." Analytical Chemistry 46 (December 1974): 1257A-1268A.

39. Meites, L. Polarographic Techniques 2d ed. New York: Interscience, 1965.

40. Lund, W. and Salberg, M. "Anodic Stripping Voltammetry with the Florence Mercury Film Electrode: Determination of Copper, Lead and Cadmium in Sea Water." Analytica Chimica Acta 76 (1975): 131-141.

41 Cotton, F.A. and Wilkinson, G. Advance Inorganic Chemistry. 2d ed. New York: Interscience, 1966.

42. Iwasaki, I. and et al. "Spectroscopic Determination of a Small Amount of Sulphate Ion." Nippon Kaguku Zasshi 79 (1958): 32-38.

43. Muir, G.L., and Johnson,,W.D. "Chemistry of the Bogan River New South Wales with Special Reference to the Sources Dissolved Material." Australian Journal of Marine and Freshwater Research 29 (4) (August 1978): 399-407.

44. Jagnes, D., and Årén, K. "A Rapid Semi-Automatic Method for the Determination of the Total Halide Concentration in Sea Water by Means of Potentiometric Titration." Analytica Chimica Acta 52 (1970): 491-502.

45. Lingane, J.J. "Potentiometric Precipitation Titrations." In Electroanalytical Chemistry. 2d ed. New York: Interscience, 1958.

46. Vogel, I. Textbook of Quantitative Inorganic Analysis. 4th ed. Bungay: Chaucer Press, 1978.

47. Gran, G. "Determination of the Equivalence Point in Potentiometric Titrations. Part II." Analyst 77 (November 1952): 661-671.

48. Dyrssen, D., and Sillen, L.G. "Alkalinity and Total Carbonate in Sea Water; A Plea for P-T-Independent Data." Tellus XIX 1 (1967): 113-120.

49. Hansson, I. "The Determination of Dissociation Constants of Carbonic Acid in Synthetic Sea Water in the Salinity Range of 20-40‰ and Temperature Range of 5-30°C. Acta Chimica Scandinavica 27 (3) (1973): 931-944.

50. Zirino, A., and Healy, M.L. "pH-Controlled Differential Voltammetry and Certain Trace Transition Elements in Natural Waters." Environmental Science and Technology 6 (March 1972): 243-249.

51. Skoog, D.A., and West, D.M. Fundamentals of Analytical Chemistry. 2d. ed. New York: Holt, Reinehart and Winston, 1969.

52. West, P.W.; Folse, P.; and Montgomesy, D. "Application of Flame Spectrophotometry to Water Analysis." Analytical Chemistry 22 (May)1950): 667-670.

53. Welcher, F.J. Standard Method of Chemical Analysis. 6th ed. New York: Huntigton, 1975.

54. Rubeska, I., and Moldan, B. Atomic Absorption Spectrophotometry. English Translation Edited by Woods, P.T., Great Britain: Pitman Press, 1971.

55. Batley, G.E., and Florence, T.M. "Determination of the Chemical Forms of Dissolved Cadmium, Lead and Copper in Sea Water." Marine Chemistry 4 (1976): 347-363.

56. Kanatharana, P., and Spritzer, M.S. Analytical Letter 6 (May 1973): 421.

57. Lund, W., and Onshus, D. "The Determination of Copper, Lead and Cadmium in Seawater by Differential Pulse Anodic Stripping Voltammetry." Analytica Chimica Acta 86 (1976): 109-122.

58. Duinker, I.C., and Kramer, J.M. "An Experimental Study on the Speciation of Dissolved Zinc, Cadmium, Lead and Copper in River Rhine and North Sea Water by Differential Pulsed Anodic Stripping Voltammetry." Marine Chemistry 5 (1977) : 207-228.

APPENDIX I

Gran's Plot for Determination of Equivalence Point in the Determination of Chloride Ion.

The equivalence point in a potentiometric titration was usually obtained from the plot of differentiate curves $\frac{\Delta pH}{\Delta V}$ or $\frac{\Delta E}{\Delta V}$ against volume of the titrant added. The peak on these curves corresponded to the point of maximum slope of the normal titration curve. Results obtained by this method may be in error if the titration curve was not symmetrical about the equivalence point. For the accurate determination, the Gran's plot which transformed the curve into straight lines is necessary (47).

For Complex-Formation Titration

When Vo cm^3 of a solution of a substance (A), with original concentration C_{Ao}, is titrated with a solution of a substance (B) of concentration C_{Bo}, a precipitate (A_xB_y) is formed according to the reaction.

$$xA + yB \rightleftharpoons A_xB_y$$

As long as A is present in excess

$$C_A = C_{A_o} \frac{V_o}{V_o + V} - \frac{x}{y} C_{B_o} \frac{V}{V_o + V}$$

$$= \frac{x}{y} \frac{C_{B_o}}{V_o + V} (Ve-V) \qquad \ldots\ldots\ldots\ldots \quad (1)$$

If the potential is given by

$$E = E_A^o + 2.30 \frac{RT}{n_A F} \log C_A \qquad \ldots\ldots\ldots\ldots \qquad (2)$$

E_A^o is a constant and can be written as

$$E_A^o = 2.30 \frac{RT}{n_A F} \log K_A^o \qquad \ldots\ldots\ldots\ldots \qquad (3)$$

which, together with equation (2) will give

$$E = 2.30 \frac{RT}{n_A F} \log (K_A^o C_A)$$

or

$$\log(K_A^o C_A) = \frac{E}{2.30 \frac{RT}{n_A F}} \simeq 17 n_A E$$

$$\therefore \quad C_A = \frac{1}{K^o A} 10^{17 n_A E} \qquad \ldots\ldots\ldots\ldots \qquad (4)$$

Equations (1) and (4) to gether give

$$\frac{1}{K^o A} 10^{17 n_A E} = \frac{x}{y} \frac{C_{B_o}}{V_o + V} (Ve-V)$$

which can be written more generally as

$$(V_o+V) \; 10^{17 n_A (E-k_1)} = k_2 (V_e-V) \qquad \ldots\ldots\ldots\ldots \qquad (5)$$

When B is present in excess

$$C_B = C_{Bo} \frac{V}{V_o + V} - \frac{y}{x} C_{Ao} \frac{V}{V_0 + V}$$

$$\therefore \quad C_B = \frac{C_{Bo}}{V_o + V} (V - Ve) \qquad \ldots\ldots\ldots\ldots \qquad (6)$$

The concentration of A is then related to the concentration of B by the equation

$$C_A^x \, C_B^y = K_{A_x B_y} \qquad \ldots\ldots\ldots\ldots \qquad (7)$$

where $K_{A_x B_y}$ is the solubility product of the precipitate $A_x B_y$

Equations (4), (6) and (7) give

$$\frac{1}{K^o{}_A} 10^{17 \, n_A E} = \frac{\left(K_{A_x B_y}\right)^{\frac{1}{x}}}{\left[\frac{C_{Bo}}{V_o + V} (V - Ve)\right]^{\frac{x}{y}}}$$

which can be transformed to

$$(V_o + V) \, 10^{\frac{x}{y} 17 \, n_A (k_3 - E)} = k_4 (V - Ve) \qquad \ldots\ldots\ldots\ldots \qquad (8)$$

Thus the equations (5) and (8) hold before and after the equivalence point, respectively. In this study the suitable equations are

$$F_1 = (V_o + V) \, 10^{\frac{E + 100}{59}} = k_2 (Ve - V)$$

and

$$F_2 = (V_o + V) \, 10^{\frac{-400 - E}{59}} = k_4 (V - Ve)$$

APPENDIX II

Gran's Plot for Determination of Equivalence Point in the Determination of Carbonate and Bicarbonate Ions.

If Vo cm^3 of dibasic acid (H_2A) with original concentration C_{H_2A} is titrated with strong acid concentration Cx

Thus ,

$$H_2A \underset{}{\overset{k'_a}{\rightleftharpoons}} HA^- + H^+ \qquad \ldots\ldots\ldots \qquad (1)$$

$$HA^- \underset{}{\overset{k''_a}{\rightleftharpoons}} H^+ + A^{2-} \qquad \ldots\ldots\ldots \qquad (2)$$

and from equation (1) will give

$$a_{H+} = k_a \frac{C_{H_2A}}{CHA^-} \qquad \ldots\ldots\ldots \qquad (3)$$

After the addition of V cm^3 of acid

$$C_{HA^-} = \frac{C_x V}{V_o + V} \qquad \ldots\ldots\ldots \qquad (4)$$

and

$$C_{H_2A} = C_{HA^-} \frac{V_o}{V_o + V} - \frac{C_x V}{V_o + V} \qquad \ldots\ldots\ldots \qquad (5)$$

At the first equivalence point

$$C_{HA^-} V_o = C_x V_{e_1} \qquad \ldots\ldots\ldots \qquad (6)$$

where V_{e_1} is the volume of acid added when the first equivalence point is reached.

Substituting in equation (5) will get

$$C_{H_2A} = C_x \frac{\left(V_{e_1} - V\right)}{V_o + V} \quad \ldots\ldots\ldots \quad (7)$$

From equation (3), (4) and (7)

$$a_{H^+} = k_a' \frac{\left(V_{e_1} - V\right)}{V}$$

but $a_{H^+} = f_H + C_{H^+} = 10^{-pH}$

therefore $10^{-pH} = k_a' \frac{\left(V_{e_1} - V\right)}{V}$

$$V \; 10^{k_1 - pH} = k_2 \left(V_{e_1} - V\right) \quad \ldots\ldots\ldots \quad (8)$$

After the first equivalence point has been passed

$$a_{H^+} = k_a'' \frac{C_{HA^-}}{C_{A^{2-}}} \quad \ldots\ldots\ldots \quad (9)$$

and $C_{A^{2-}} = \frac{C_x}{V_o + V} (V - V_{e_1})$ .... (10)

where $C_{HA^-} = C_{A^{2-}} \frac{2 V_o}{V_o + V} - C_x \frac{V}{V_o + V}$ .... (11)

At the second equivalence point

$$2 \, C_{A^{2-}} V_o = C_x V_{e_2} \quad \ldots\ldots\ldots \quad (12)$$

Substituting in equation (11) will get

$$C_{HA^-} = C_x \frac{V_{e_2} - V}{V_o + V} \qquad \text{.........} \qquad (13)$$

From (9), (10) and (13)

$$a_{H^+} = k_a'' \frac{\left(V_{e_2} - V\right)}{V - V_{e_1}}$$

which gives

$$10^{-pH} = k_a'' \frac{\left(V_{e_2} - V\right)}{V - V_{e_1}} \qquad \text{.........} \qquad (14)$$

In determination the first equivalence point this equation should be used in the form

$$(V_{e_2} - V)\ 10^{pH - k_3} = k_4 (V - V_{e_1}) \qquad \text{.........} \qquad (15)$$

and for the second equivalence point the equation is rewritten to give

$$(V - V_{e_1})\ 10^{k_5 - pH} = k_6 (V_{e_2} - V) \qquad \text{.........} \qquad (16)$$

After the second equivalence point has been passed,

$$C_{H^+} = C_x \frac{V}{V_o + V} - C_{A^{2-}} \frac{2\ V_0}{V_0 + V}$$

$$= C_x \frac{\left(V - V_{e_2}\right)}{V_o + V}$$

$$a_{H^+} = 10^{-pH} = f_{H^+} C_x \frac{\left(V - V_{e_2}\right)}{V_o + V}$$

$$(V_o + V)\ 10^{k-pH} = k_8\ (V - V_{e_2}) \qquad \ldots\ldots\ldots \quad (17)$$

Thus, equation (8) and (15) will give the first equivalence point and equation (16) and (17) give the second equivalence point. In this study, the suitable equations are

$$F_1 = (V_o + V)\ 10^{7-pH} = k_2\ (V_{e_2} - V)$$

$$F_2 = (V_{e_2} - V)\ 10^{pH-3} = k_4\ (V - V_{e_1}).$$

APPENDIX III

A typical calculation for percentage of metal species

Percentage of cadmium species in surface water sample collected on 12/10/79 was calculated as shown below and other metals species were calculated similarily (Results were shown in Tables 3.15 and 3.16).

The chemical speciation for cadmium is

$$[Cd^{2+}] + [CdCl^{+}] + [CdCl_2] + [CdCl_3^{-}] + [CdSO_4] + [CdCO_3] + [CdHCO_3^{+}] +$$

$$[CdOH^{+}] + [Cd(OH)_2] + [Cd(OH)_3^{-}] + [Cd(CH)_4^{2-}] + [CdOHCl] = 100$$

Let $[Cd^{2+}] = x$; and other cadmium species were calculated from equation shown below.

$$a_{ML} = \beta_{ML} \; a_M \; a_L$$

therefore $$[ML] = \beta_{ML} [M] [L] \frac{\gamma_M \gamma_L}{\gamma_{ML}}$$

Then $$[CdCl^{+}] = \beta_{CdCl^{+}} [Cd^{2+}] [Cl^{-}] \frac{\gamma_{Cd^{2+}} \gamma_{Cl^{-}}}{\gamma_{CdCl^{-}}}$$

$$= 10^{1.46} \times 0.2724 \; \frac{0.217 \times 0.654}{0.706}$$

$$= 1.5792 \; x$$

$$[CdCl_2] = \beta_{CdCl_2}[Cd^{2+}][Cl^-]^2 \frac{\gamma_{Cd^{2+}} \gamma^2_{Cl^-}}{\gamma_{CdCl_2}}$$

$$= 10^{1.83} x \,(0.2724)^2 \frac{0.217 \times (0.654)^2}{0.956}$$

$$= 0.4870\ x$$

As the same calculation will give

$[CdCl_3^-]$	$= 0.1586\ x$	$[CdSO_4]$	$= 0.0702\ x$
$[CdCO_3]$	$= 0.0423\ x$	$[CdHCO_3^+]$	$= 0.0069\ x$
$[CdOH^+]$	$= 0.0106\ x$	$[Cd(OH)_2]$	$= 0.0273\ x$
$[Cd(OH)_3^-]$	$= 0$	$[Cd(OH)_4^{2-}]$	$= 0$
$[CdOHCl]$	$= 0.8847\ x$		

$$x + 1.5792\ x + 0.4870\ x + 0.1586\ x + 0.0070\ x + 0.0423\ x$$
$$+ 0.0069\ x + 0.0106\ x + 0.0273\ x + 0.8847\ x = 100$$
$$4.2670\ x = 100$$
$$x = 23.43$$

Hence, Cd

$\lvert CdCl^+ \rvert$	= 37.01 %	$[CdCl_2]$	= 11.41 %
$\lvert CdCl_3 \rvert$	= 3.72 %	$[CdSO_4]$	= 1.64 %
$\lvert CdCO_3 \rvert$	= 0.99 %	$[CdHCO_3^+]$	= 0.16 %
$\lvert CdOH^+ \rvert$	= 0.25 %	$[Cd(OH)_2]$	= 0.64 %
$\lvert CdOHCl \rvert$	= 20.73 %	$[Cd^{2+}]$	= 23.43 %

VITA

Miss Wilaiwan Thumtrakul was born on March 1, 1955. She was awarded a B.Sc. degree in Chemistry from Chiengmai University in 1977. She was supported by the University Development Commission Scholarship during the study towards the Master's degree of Science. After her graduation, she will be an instructor at the Department of Marine Science, Chulalongkorn University.