CHAPTER 2

EXPERIMENTAL

2.1 Instruments and Apparatus

1. Multi-channel peristaltic cartridge pump, QuikChem 4200, LACHAT INSTRUMENTS, USA
2. System Unit of Automated Ion Analyzer, QuikChem 4200, LACHAT INSTRUMENTS, USA
3. UVIS-200 detector, MODEL 200, LINEAR INSTRUMENTS, USA
4. Spectrophotometer, Shimadzu UV 265, Japan
5. Spectrophotometer, HITACHI U-2000, Japan
6. Chart recorder, PERKIN-ELMER, MODEL 056-1002, Hitachi Ltd., Tokyo, Japan
7. Injection valve, RHEODYNE, MODEL 7725, California, USA
8. Flow-through cell with screw fittings, Type No. 178.710-OS, Quartz, Light path 10 mm (ϕ 3 mm), Hellma, Germany
9. Phase separator, PTFE Membrane type, Home made
10. pH-meter, PHM61, Radiometer A/S Copenhagen, Denmark
11. Centrifuge, DYNAC, Becton, Dickinson and Company, Parsippany, NJ, USA

2.2 Chemicals

1. Sodium dodecylsulphate (SDS), $CH_3(CH_2)_{11}OSO_3Na$, puriss, Fluka, Switzerland
2. Methylene Blue (MB), $C_{16}H_{18}ClN_3S$, puriss, Fluka, Switzerland
3. Potassium dihydrogen phosphate, KH_2PO_4, GPR, BDH, England
4. Potassium sulphate, K_2SO_4, GPR, BDH, England
5. Sulfuric acid 95-97% (w/w), H_2SO_4, GR, MERCK, Germany
6. Chloroform, $CHCl_3$, GR, MERCK, Germany
7. di-Sodium tetraborate, $Na_2B_4O_7.10H_2O$, LAB, MERCK, Germany
8. Sodium hydroxide, NaOH, GPR, BDH, England
9. Hyoscine butylbromide (HB), $C_{21}H_{30}NO_4.Br$, A.R., SIGMA, Germany
10. Bromothymol blue (BB), $C_{27}H_{28}Br_2O_5S$, extra pure, MERCK, Germany

11. Boric acid, H_3BO_3, GPR, BDH, England
12. Yttrium oxide, Y_2O_3, puriss, Fluka, Switzerland
13. Hydrochloric acid fuming 37% (w/w), HCl, GR, MERCK, Germany
14. 2,7-Bis(2-arsonophenylazo)-1,8-dihydroxynaphthalenedi-sulfonic acid disodium salt (ArsenazoIII), $C_{22}H_{16}O_{14}N_4S_2Na_2As_2$, puriss, Fluka, Switzerland
15. Acetic acid glacial 100%, CH_3COOH, GR, MERCK, Germany
16. Sodium acetate trihydrate, $CH_3COONa.3H_2O$, LAB, MERCK, Germany
17. Potassium hydrogen phthalate (KHP), $COOH.C_6H_4.COOK$, GPR, BDH, England
18. Manganese(II) acetate tetrahydrate, $(CH_3COO)_2Mn.4H_2O$, extra pure, MERCK, Germany
19. Xylene, C_8H_{10}, GR, MERCK, Germany
20. Isopropanol, $(CH_3)_2CHOH$, A.R., LAB-SCAN, Ireland
21. Ammonium chloride, NH_4Cl, LAB, MERCK, Germany
22. Hydroxylamine hydrochloride, $NH_2OH.HCl$, A.R., AJAX, N.S.W., Australia
23. Formaldehyde solution 37% (w/w), HCHO, GR, MERCK, Germany
24. Cobalt(II) acetate tetrahydrate, $(CH_3COO)_2Co.4H_2O$, extra pure, MERCK, Germany
25. Citric acid, $C_6H_8O_7$, GPR, BDH, England
26. 4-(2-Pyridylazo)resorcinol (PAR), $C_{11}H_9N_3O_2$, puriss, Fluka, Switzerland
27. Ammonia solution, about 30% (w/w) NH_3, AnalaR, BDH, England
28. Urea, H_2NCONH_2, extra pure, MERCK, Germany
29. Sodium nitrate, $NaNO_3$, GPR, BDH, England
30. Sodium sulphide, Na_2S, GPR, BDH, England
31. Sodium chloride, NaCl, GPR, BDH, England
32. Sodium sulphate anhydrous, Na_2SO_4, GPR, BDH, England
33. Lactose, $C_{12}H_{22}O_{11}.H_2O$, AnalaR, BDH, England
34. Zirconyl chloride octahydrate, $ZrOCl_2.8H_2O$, puriss, Fluka, Switzerland
35. Cadmium sulfate hydrate, $CdSO_4.H_2O$, extra pure, MERCK, Germany
36. Zinc chloride, $ZnCl_2$, extra pure, MERCK, Germany
37. Lanthanum nitrate hexahydrate, $La(NO_3)_3.6H_2O$, GR, MERCK, Germany

38. Uranyl nitrate, $UO_2(NO_3)_2.6H_2O$, GR, MERCK, Germany
39. Copper(II) sulfate, $CuSO_4$, GR, MERCK, Germany
40. Manganese(II) sulfate monohydrate, $MnSO_4.H_2O$, extra pure, MERCK, Germany
41. Titanium(III) chloride solution about 15% (w/v) (in about 10% HCl), $TiCl_3$, GR, MERCK, Germany
42. Magnesium chloride hexahydrate, $MgCl_2.6H_2O$, extra pure, MERCK, Germany
43. Thorium nitrate pentahydrate, $Th(NO_3)_4.5H_2O$, GR, MERCK, Germany
44. Barium nitrate, $Ba(NO_3)_2$, extra pure, MERCK, Germany
45. Calcium carbonate, $CaCO_3$, GR, MERCK, Germany
46. Ammonium ferric sulfate dodecahydrate, $NH_4Fe(SO_4)_2.12H_2O$, puriss, Fluka, Switzerland
47. Ammonium bromide, NH_4Br, puriss, Fluka, Switzerland

2.3 Preparation of Standard Solutions and Reagents

Use deionized water for all solutions.

1. Stock standard sodium dodecylsulphate (SDS), 1000 mg/l

Prepared by dissolving 0.1087 g of SDS in water and diluting to 100 ml. Further appropriate dilutions were daily prepared.

2. Stock methylene blue (MB) solution, 0.10% (w/v)

Prepared by dissolving 0.10 g of methylene blue in water and diluting to 100 ml. This stock MB solution was pre-extracted with three 25 ml aliquots of chloroform.

3. Working methylene blue (MB) reagent solution

Prepared by dissolving 8.50 g of KH_2PO_4 and 4.36 g of K_2SO_4 in water, 1.00 ml of conc. H_2SO_4 was added and diluted to 500 ml. 20 ml of pre-extracted stock MB 0.10% (w/v) solution (2) was added into this solution and mixed well.

4. Pre-equilibrated chloroform

700 ml of chloroform was pre-equilibrated with three 140 ml aliquots of water. To prevent bubble formation, pre-equilibrated chloroform was degased with air suction pump before use.

5. Alkaline borate solution

Prepared by dissolving 4.77 g of $Na_2B_4O_7.10H_2O$ and 1.00 g of NaOH in water and diluting to 500 ml.

6. H_2SO_4, 0.50 M

13.50 ml of conc. H_2SO_4 was added into water and diluted to 500 ml.

7. Stock methylene blue (MB) solution, 0.050% (w/v)

Prepared by dissolving 0.125 g of MB in water and diluting to 250 ml. This stock MB solution was pre-extracted with three 25 ml aliquots of chloroform.

8. Alkaline methylene blue (MB) solution

60 ml of pre-extracted stock MB 0.050% (w/v) solution (7) was added into 300 ml of alkaline borate solution (5) and diluted to 1000 ml with water.

9. Acid methylene blue (MB) solution

20 ml of pre-extracted stock MB 0.050% (w/v) solution (7) and 5 ml of 0.50 M H_2SO_4 (6) were added into 10 ml of alkaline borate solution (5) and diluted to 500 ml with water.

10. Stock standard hyoscine butylbromide (HB), 1000 mg/l

Prepared by dissolving 0.1000 g of hyoscine butylbromide (HB) in water and diluting to 100 ml. Further appropriate dilutions were freshly made.

11. Borate buffer solution (pH 10.0)

Prepared by dissolving 7.30 g of boric acid and 4.00 g of NaOH in water and diluting to 1000 ml.

12. Stock bromothylmol blue (BB) solution, 0.048% (w/v)

Prepared by dissolving 0.240 g of bromothymol blue (BB) in borate buffer solution (pH 10.0) (11) and diluting to 500 ml with this buffer solution. This stock BB solution was pre-extracted with three 50 ml aliquots of chloroform. Further appropriate dilutions were diluted with borate buffer solution (pH 10.0).

13. Stock standard yttrium, 1000 mg/l

Prepared by dissolving 0.1270 g of Y_2O_3 in hot hydrochloric acid solution (1:1; 5 ml) and diluting with water to 100 ml. Working standard solutions were freshly prepared by appropriate dilution.

14. Stock arsenazoIII solution, 0.10% (w/v)

Prepared by dissolving 0.10 g of arsenazoIII in water and adjusted to a volume of 100 ml. Further dilutions were made for appropriate concentrations.

15. Acetate buffer solution (pH 4.0)

Prepared by adding 42.4 ml of 1.0 M acetic acid into 100 ml of water, dissolving 1.04 g of $CH_3COONa.3H_2O$ in this solution and diluting with water to 500 ml.

16. KHP/HCl buffer solution (pH 4.0)

Prepared by mixing 250 ml of 0.10 M KHP and 0.50 ml of 0.10 M HCl, and diluting with water to 500 ml.

17. Mixed solvent (70:22:8 by volume of glacial acetic acid: xylene: deionized water)

Prepared by mixing 140 ml of glacial acetic acid, 44 ml of xylene and 16 ml of deionized water.

18. Isopropanol solution, 50% (v/v)

500 ml of isopropanol was mixed with 500 ml of deionized water.

19. Stock standard manganese, 2500 mg/l

Prepared by dissolving 1.1150 g of $(CH_3COO)_2Mn.4H_2O$ in 8 ml of deionized water, adding 50 ml of glacial acetic acid and 22 ml of xylene and diluting with glacial acetic acid to 100 ml. The stock standard solutions (100, 300, 600, 900 mg/l) were prepared by appropriate diluting with mixed solvent. Working standard solutions (1.0, 3.0, 6.0, 9.0 mg/l) were freshly prepared by diluting 1.00 ml of each stock standard solution (100, 300, 600, 900 mg/l) to 100 ml with 50% (v/v) isopropanol solution.

20. NH_4Cl/NH_4OH buffer solution (pH 10.0), 9.70 M

Prepared by dissolving 7.0 g of NH_4Cl in 40 ml of water and 60 ml of conc. NH_4OH was added and mixed well. Further appropriate dilutions were freshly made.

21. Hydroxylamine hydrochloride solution, 20% (w/v)

Prepared by dissolving 20.0 g of hydroxylamine hydrochloride in water and diluting to 100 ml.

22. Formaldoxime solution, 2.05 M

10 ml of 37% (w/w) formaldehyde was added into 50 ml of 20% (w/v) hydroxylamine hydrochloride solution and mixed well. Further appropriate dilutions were freshly made.

23. Stock standard cobalt, 2500 mg/l

Prepared by dissolving 1.0563 g of $(CH_3COO)_2Co.4H_2O$ in 8 ml of deionized water, adding 50 ml of glacial acetic acid and 22 ml of xylene and diluting with glacial acetic acid to 100 ml. The stock standard solutions (100, 300, 600, 900 mg/l) were prepared by appropriate diluting with mixed solvent. Working standard solutions (1.0, 3.0, 6.0, 9.0 mg/l) were freshly prepared by diluting 1.00 ml of each stock standard solution (100, 300, 600, 900 mg/l) to 100 ml with 50% (v/v) isopropanol solution.

24. Citrate buffer solution (pH 6.0), 0.30 M

Prepared by dissolving 62.6 g of citric acid and 31.6 g of NaOH in water and diluting to 1000 ml. Further appropriate dilutions were freshly made.

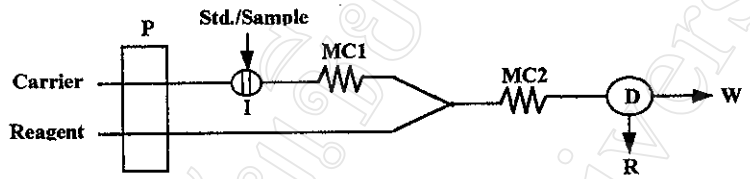
25. Stock 4-(2-pyridylazo)resorcinol (PAR) solution, 0.030% (w/v)

Prepared by dissolving 0.030 g of PAR in 1.0 ml of conc. NH_4OH and diluting to 100 ml with water. Further appropriate dilutions with citrate buffer solution (pH 6.0) (24) were freshly made.

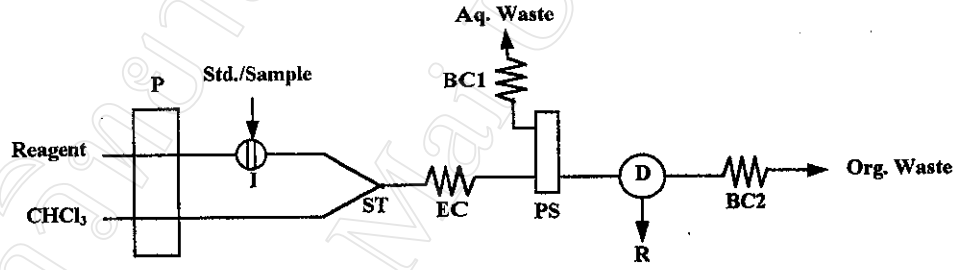
2.4 FIA Systems

The FIA systems used, as depicted in Figure 2.1 are as follows:
(a) double line system,
(b) single solvent extraction system and
(c) double solvent extraction system.

(a) double line system



(b) single solvent extraction system



(c) double solvent extraction system

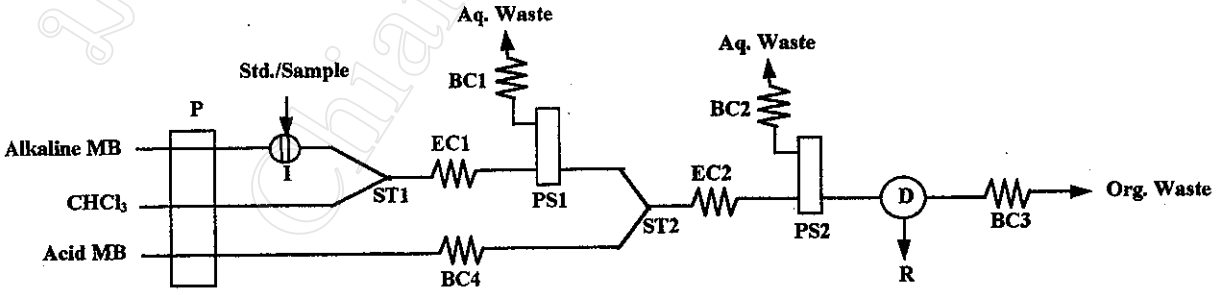


Figure 2.1 FIA systems used
P = peristaltic pump; I = injection valve; ST = segmentor;
EC = extraction coils; BC = back pressure coils;
MC = mixing coils; PS = PTFE membrane phase separator;
D = spectrophotometer; R = chart recorder; W = waste

The FIA systems were for analytes as specified in Table 2.1.

Table 2.1 The FIA systems used in this work

FIA system	For the determination of	See section
(a) Double line system	Yttrium	3.3
	Cobalt	3.4.2
	Manganese	3.4.3
(b) Single solvent extraction system	Anionic surfactants	3.1.1
	Hyoscine butylbromide	3.2
(c) Double solvent extraction system	Anionic surfactants	3.1.2