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APPENDIX I

TREATING SEAWATER BY MANGANESE DIOXIDE SUSPENSION

For treating seawater, as described by Dharmvanij(105), the method is as follows:

(a) Filter seawater by nucleopore membrane filter, mesh size 45 μm.

(b) Add concentrated H_2O_2 in ratio 1 drop : 1 L of seawater.

(c) Sterilized seawater by autoclave at 121 ^{o}C for 30 min, allow it to cool at room temperature and store in a precleaned bottle.

(d) Add 360 μl manganese dioxide suspension (0.052 M) into seawater while controlling pH of seawater at 8 by adding some ammonium hydroxide.

(e) Stirring seawater 4 -5 h. by magnetic stirrer.

(f) Filter seawater by 0.45 μ nucleopore membrane filter in order to separate seawater from manganese dioxide suspension. Store filtrate in precleaned bottle until use.

Note : - Magnetic bar should be cleaned by 10% nitric acid several times and wash throughly with Super Q water before use. After using, clean with 10% nitric acid several times and keep it in Super Q water until use.

- Nucleopore membrane filter should be cleaned by soaking in 10% nitric acid at least 1 h and rinse several times by Super Q water

then soak in Super Q water until use.

APPENDIX 2

PREPARATION OF MANGANESE DIOXIDE SUSPENSION

The manganese dioxide suspension used in the experiment is prepared by the reaction :

$$3\ Mn^{2+} + 2\ MnO_4 + 2\ H_2O \rightleftharpoons 5\ MnO_2 + 4\ H^+ \text{ (at neutral pH)}$$

1. Preparation Method. (Dharmvanij(105))

1.1 Reagents.

1.1.1 Ammonium Hydroxide Solution. Purify by placing two beakers of the same volume, one containing concentrated ammonium hydroxide solution (AR grade) and another containing Super Q water respectively, in a vacuum dessicator, reduce the pressure inside the dessicator by a vacuum pump. After leaving it for at least 24 h the purified ammonium hydroxide solution is obtained for the beaker originally containing Super Q water.

1.1.2 Primary Standard Oxalate Solution. Prepare 0.02 M primary standard oxalate solution by drying 1.5 g sodium oxalate (AR grade) at 105 - 110 ^{o}C for 2 h in an oven, allow it to cool in a covered vessel in a dessicator. Weigh out accurately 0.826 g of dried sodium oxalate and transfer it to a 250 ml-volumetric flask, add 0.1 M perchloric acid and make up the volume to 250 ml. Shaking until the sodium oxalate has completely dissolved and store in a precleaned polyethylene bottle.

1.1.3 Secondary Standard Permanganate Solution. Prepare 0.02 M secondary standard permanganate solution by weighing out 3.2 g of potassium permanganate (AR grade) and transfer it to a 1500 ml-beaker. Added 1 l of Super Q water and covered the beaker with a watch glass. Heate the solution to boiling and boil gently for 15-30 min. Allow it to cool to the room temperature. Filter the solution through a sintered glass No. 4. Collect the filtrate in a bottle of dark-brown colored glass and keeep it in the dark or in diffused light when not in use.

1.1.4 Solution A.(0.4 M Sodium hydroxide in 0.2 M Potassium Permanganate). : Prepare by dissolving 3.1606 g of potassium permanganate (AR grade) with 1.6 gm of sodium hydroxide (AR grade) in 100 ml of Super Q water. Store the solution in a precleaned bottle.

1.1.5 Manganese Solution. Prepare 0.2 M manganese solution by dissolving 3.958 g of manganese chloride ($MnCl_2.4H_2O$) in 100 ml of Super Q water.

1.1.6 Perchloric Acid. Prepare 0.1 M perchloric acid ($HClO_4$) by diluting 2.14 ml of concentrated perchloric acid (AR grade) to 250 ml with Super Q water.

1.1.7 Sodium Hydroxide Solution. Prepare 1 M sodium hydroxide solution by dissolving 10 g of sodium hydroxide (AR grade) and make volume to 250 ml with Super Q water.

2. Procedure.

(a) Add 75 ml of solution A to 50 ml of 0.2 M manganese chloride solution while stirring vigourously by a magnetic stirrer.

(b) During the formation of manganese dioxide, the pH drop. By immediately dropwise addition of 1 M sodium hydroxide solution, pH will be brought back to near 4 - 5.

(c) After the reaction is completed by noticing that pH is almost constant at neutral pH, the precipitated manganese dioxide is purified by repetitive centrifugation (ca. 3 times) about 15 min at 3,000 revolutions with 250 ml distilled water and store in a precleaned plastic bottle.

Note : - For the gratest desorption of contaminated heavy metals, the centrifugation should be carried out on the suspension at a pH around 5.

- The final manganese dioxide suspension should form a finely distributed suspension which can be pipetted reproducibly upon careful shaking of the container.

3. Determination the Concentration of Manganese Dioxide Suspension.

The concentration of MnO_2 is determined by treatment with an excess of an acidified solution of a reducing agent, sodium oxalate solution. The excess of reducing agent is determined by titration with secondary standard potassium permanganate solution. This technique is called Back Titration.

$$MnO_2 + C_2O_4 + 4H^+ \rightleftharpoons Mn^{2+} + 2CO_2 + 2H_2O + C_2O_4(\text{Excess})$$

$$2MnO_4 + 5H_2C_2O_4(\text{Excess}) + 6H^+ \rightleftharpoons 2Mn^{2+} + 10CO_2 + 8H_2O$$

3.1 Procedure.

(a) Add 20 ml of 0.02 M primary standard sodium oxalate solution to 5 ml of manganese dioxide suspension (ratio 4:1).

(b) Add secondary standard potassium permanganate solution(0.02 M) from a burette to a solution in beaker, while stirring slowly by magnetic stirrer.

(c) Heat the solution to 55 - 60°C and complete the titration by adding permaganate solution until a faint pink colour persists for 30 sec.

(d) Add the last 0.5 - 1 ml dropwise, with particular care to allow each drop to become decolourised before the next is introduced.

(e) Repeat the determination with two other similar quantities of oxalate solution and manganese dioxide suspension. Duplicate determinations should agree within 0.1 - 0.2 percent.

3.3 Result.

Results from the experiments are as follows:

Volume of MnO_2 = 5 ml

Volume of $Na_2C_2O_4$(0.02 M) = 20 ml

Temperature of solution = 58 °C

Volume of $KMnO_4$(0.02 M) = 14.32 , 14.33 , 14.35 ml

Concentration of MnO_2-suspension are 0.052 , 0.052 , 0.050 M

Average concentration of manganese dioxide suspension is 0.052 M .

4. Standardisation of Secondary Standard Permanganate Solution.

4.1 Procedure.

(a) Transfer 10 ml of 0.02 M primary standard sodium oxalate solution in a 50 ml beaker and place it in a controlled-temperature water bath and control water temperature at $58^{o}C$.

(b) Add permanganate solution from burette while stirring slowly .

(c) Complete the titration by adding permanganate solution until a faint pink colour persists for 30 sec.

(d) Add the last 0.5 - 1 ml dropwise, with particular care to allow each drop to become decolourised before the next is introduced.

(e) Repeat the determination with two other similar quantities of sodium oxalate.

4.2 Results. Results from the experiments are as follows

Volume of sodium oxalate solution = 10 ml

Volume of permanganate solution = 7.46 ,7.51 , 7.49 ml

From the calculation, concentration of permanganate solution are 0.0268 , 0.0266 and 0.0267 M .

Average concentration of secondary standard potassium permanganate solution is 0.027 M .

APPENDIX 3

CLEANING PROCEDURE

1. For New Labware.

1.1 Plastic Ware.(Patterson and Settle (106))

(a) Initially rinse in acetone and wash with detergent.

(b) Rinse with Super Q water several times.

(c) Soak for at least one day in hot 3 M (GFS) HCl (or for one week in 6 M HCl at room temperature).

(d) Rinse with Super Q water several times.

(e) Soak in 0.5 - 1 M (GFS) and/or purified HNO_3 for at least 3 days and rinse with Super Q water.

(f) Discard the nitric acid and refill with Super Q water and store in the plastic bag.

(g) In addition, plastic ware in which sample will be stored or processed is further rinsed with Super Q water and soak in 0.5 - 1 M purified HNO_3 and store in the plastic bag for at least a week.

2. During the Analysis.

(a) Rinse with Su3per Q water several times.

(b) Rinse several times with 10 % HNO_3.

(c) Do the same as step (a).

(d) Dry in the laminar-flow clean air bench.

APPENDIX 4

CERTIFIED REFERENCE MATERIALS

1. Seawater Reference Material for Trace Metals (NASS-1).

	Micrograms/Litre
Arsenic (a,h)*	1.65 ± 0.19
Cadmium (a,c,i,m,s)	0.029 ± 0.004
Chromium (g,m)	0.184 ± 0.016
Cobalt (i,m)	0.004 ± 0.001
Copper (a,c,i,m,s)	0.099 ± 0.010
Iron (i,m,s)	0.192 ± 0.036
Lead (a,i,m)	0.039 ± 0.006
Manganese (i,s)	0.022 ± 0.007
Molybdenum (d,m)	11.5 ± 1.9
Nickel (e,i,m,s)	0.257 ± 0.027
Zinc (a,i,m,s)	0.159 ± 0.028

* a - Anodic stripping voltammetry

c - Coprecipitation separation/GFAAS determination

d - Direct determination by GFAAS

e - Chelation/hanging drop mercury electrode determination

g - Isotope dilution gas chromatography/mass spectrometry

h - Hydride generation atomic absorption spectrometry

i - Immobilized ligand separation/GFAAS determination

m - Isotope dilution solid source mass spectrometry

s - Chelation-solvent extraction separation/GFAAS determination

2. Nearshore Seawater Reference Material for Trace Metals (CASS-1).

	Microgram/Litre
Arsenic (a,g,h)*	1.04 ± 0.07
Cadmium (a,i,m,p,q,s)	0.026 ± 0.005
Chromium (c,m,q)	0.118 ± 0.021
Cobalt (i,m,s)	0.023 ± 0.004
Copper (a,i,m,p,q,s)	0.291 ± 0.027
Iron (i,m,s)	0.873 ± 0.076
Lead (a,i,m,p,q,s)	0.251 ± 0.027
Manganese (d,i,s)	2.27 ± 0.17
Nickel (a,i,m,p,q,s)	0.290 ± 0.031
Zinc (a,i,m,p,q,s)	0.980 ± 0.099

* a - Anodic stripping voltammetry

c - Isotope dilution gas chromatography mass spectrometry

d - Direct determination by GFAAS

g - Gas chromatography

h - Hydride generation atomic absorption spectrometry

i - Immobilized ligand separation/GFAAS determintion

m - Isotope dilution spark source mass spectrometry

p - Inductively coupled plasma mass spectrometry

q - Isotope dilution inductively coupled plasma mass spectrometry

s - Chelation-solvent extraction separation/GFAAS determination

3. Riverine Water Reference Material for Trace Metals (SLRS-1).

	Milligrams/Litre	
Sodium (f,n,p)*	10.4	± 0.6
Magnesium (f,o,q)	5.99	± 0.28
Potassium (f,n,p)	1.30	± 0.20
Calcium (f,n,o,p)	25.1	± 0.9

	Microgram/Litre	
Aluminum (d,n,p)	23.5	± 1.2
Vanadium (n,p)	0.66	± 0.09
Chromium (d,m,p,q)	0.36	± 0.04
Manganese (d,n,p,s)	1.77	± 0.23
Iron (d,m,p)	31.5	± 2.1
Cobalt (i,p,s)	0.043	± 0.010
Nickel (a,d,i,j,s)	1.07	± 0.06
Copper (a,d,j,q,s)	3.58	± 0.30
Zinc (d,i,j,p,q,s)	1.34	± 0.20
Arsenic (a,p,u,v,w)	0.55	± 0.08
Strontium (f,m,n,o)	136	± 3
Molybdenum (d,q)	0.78	± 0.04
Cadmium (i,j)	0.015	± 0.002
Antimony (h,p)	0.63	± 0.05
Barium (d,n,o,p)	22.2	± 1.7
Lead (i,j,p)	0.106	± 0.011
Uranium (j,q)	0.28	± 0.03

* a - Anodic stripping voltammetry

d - Direct determination by GFAAS

f - Direct determination by FAAS

h - Hydirde generation AAS

i - Immobilised ligand separation/GFAAS determination

j - Immobilised ligand separation/isotope dilution ICP-MS determination

m - Isotope dilution solid source mass spectrometry

n - Instrumental neutron activation analysis

o - Inductively coupled plasma atomic emission spectrometry

p - Inductively coupled plasma mass spectrometry

q - Isotope dilution inductively coupled plasma mass spectrometry

s - Chelation-solvent extraction separation/GFAAS determination

u - UV photolysis/hydride generation AAS

v - Acid decomposition/hydride generation AAS

w - Acid decomposition/gas chromatography

BIBLIOGRAPHY

Mr. Watana Sukasem graduated from the Department of Marine Science, Chulalongkorn University in 1978. At the present time he took the position at the Water Quality Standard Section, Environmental Quality Standard Division, the Office of National Environment Board as an environmetalist.