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"A CHELATION-SOLVENT EXTRACTION METHOD FOR ANALYSIS OF DISSOLVED MANGANESE IN MARINE SEDIMENT PORE WATERS BY FLAMELESS ATOMIC ABSORPTION SPECTROSCOPY"

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OPEN FILE
838
GEOLOGICAL SURVEY
OTTAWA

COMPLETED: SEPTEMBER 4, 1981.

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ABSTRACT

A chelation-solvent extraction method using 8-Hydroxyquinoline ("oxine") and methylisobutyl ketone (MIBK) was developed for analysis of dissolved Mn in pore waters by flameless atomic absorption spectroscopy. The extraction requires 2 ml of pore water sample, and the method can measure concentrations in the 0 to 50 ppb range. Samples with greater Mn concentrations are diluted.

Results obtained by the solvent extraction method agree to within 15% of those obtained by flame atomic absorption. Dilution of concentrations greater than 1 ppm to less than 50 ppb introduced increased analytical error and did not yield results superior to those given by flame atomic absorption.

The extraction method is recommended for samples containing Mn concentrations less than approximately 1 ppm because of its lower detection limit (approximately 6 ppb). Use of the flame atomic absorption method is recommended for samples containing more then 1 ppm Mn (detection limit 200 ppb).

I INTRODUCTION

The Environmental Marine Geology Subdivision laboratory at the Bedford Institute of Oceanography is presently concerned with evaluating possible deep-sea disposal sites for nuclear waste because other nations may dispose of nuclear waste in the deep oceans. Geochemical analysis of the sediment and associated pore waters is an important aspect of this project. Of primary consideration in the choice of a nuclear waste disposal site is the ability of the sediment to remove dissolved ions from the pore waters. Depending on Eh and pH conditions, anions or cations (including those of nuclear waste elements) can be oxidized or reduced from a soluble to an insoluble oxidation state which is precipitated and thus immobilized. Ideally, if the sediment is undisturbed by bioturbation or currents, the ions could then be retained until the radio-activity is below an accepted threshold level. However, elements in nuclear waste may not possess an insoluble oxidation state in the Eh and pH conditions of marine sediments. Fine-grained clay sites are therefore desired to enable removal by adsorption. An indication of the sediment's ability to remove an element from solution is given by the distribution coefficient (K_D), the ratio of the concentration of an element in the solid phase to that in solution. Consequently, a thick accumulation of sediment with high K_D is required for possible dump sites.

Pore water concentrations of Mn are a good indication of the redox conditions of the surrounding sediment; and, with particulate Mn data, the K_D can be calculated to determine manganese oxidation and reduction zones. Due to the inability of previous methods to analyse samples with concentrations below 200 ppb, a chelation-solvent extraction technique was developed to obtain pore water Mn concentration vs. depth profiles for core samples of deep-sea sediment.

IA Background

Interstitial waters react with surrounding sediments during diagenesis and thus possess ionic ratios different from those found in open ocean waters. Consequently, the composition of pore waters reflects the geochemistry of the surrounding sediment. Deep-sea sediments are enriched in Mn relative to continental rocks, with approximate concentrations of 6700 ppm and 950 ppm, respectively. (J.P. Riley and R. Chester, p. 65). To account for this difference, sources of Mn in addition to weathering have been suggested, such as volcanic and hydrothermal activity. Furthermore, the top layer of marine sediment is characteristically enriched in Mn. This enrichment is primarily due to upward diffusion of dissolved Mn^{2+} from deeper, more reducing layers in the sediment and subsequent precipitation of Mn^{4+} in the upper more oxidizing layers. Particulate manganese is also sedimented from the overlying water. Generally, at the sediment-water interface, settled particulate manganese is stable because oxic conditions are maintained by oxygen-rich bottom currents. Through bioturbation and/or subsequent sedimentation, Mn^{4+} is transported to more reducing environments in the sediment. The Mn^{4+} is then reduced to soluble Mn^{2+} which enters the pore waters and diffuses to the upper, oxidizing layer where it is reprecipitated. The dissolved Mn concentration in pore waters reflects this Mn^{4+} - Mn^{2+} cycle with typical profiles showing low dissolved Mn concentrations near the sediment-water interface and increasing concentrations with depth in the sediment.

In addition to the relationship between dissolved Mn concentrations in pore water and redox level of the sediment, the role of pore waters in

the formation of authigenic materials, such as manganese nodules, is of considerable interest. Elements such as Co, Cu, and Ni, have ratios to manganese in ferromanganese nodules which more closely resemble those found in pore waters than those in seawater. Indeed, the phenomenon of interstitial water being released into the overlying waters in zones of tectonic disturbance is considered to be one of the possible mechanisms involved in the formation of these heavy metal deposits.

IB Chelation-Solvent Extraction

Direct flame atomic absorption techniques cannot be used for the analysis of Mn in pore waters from sediments with high Eh due to inadequate detection limits (approximately 200 ppb). Greater sensitivity and lower detection limits can be achieved by using flameless atomic absorption. However, the presence of other salts in seawaters causes interferences which render the analysis of seawaters by direct injection into the graphite furnance impractical. This seawater matrix problem can be avoided by use of chelation-solvent extraction. 8-Hydroxyquinoline (8-quinolinol or "oxine") is a complexing ligand for Mn^{2+} that is readily extracted into methylisobutyl ketone (MIBK). MIBK is virtually insoluble in the aqueous phase (Brewer et al. (1969) report a 1.5% solubility of MIBK in seawater).

II EXPERIMENTAL

IIA Analytical Techniques

1 Apparatus

A Perkin-Elmer 503 atomic absorption spectrophotometer equipped with a Perkin-Elmer 500 HGA graphite furnance, a Perkin-Elmer 56 recorder,

a D_2-background corrector, and an AS-1 Autosampler set to deliver 20 µl was used for analysis. Instrumental settings used were those recommended by the manufacturer for maximum sensitivity with occasional adjustments of the recorder and the gas flow in the atomization step.

2 Reagents

2a Standard Solutions

A manganese atomic absorption reference standard (1,000 ppm Mn) was used. Standards of 0, 10, 20, 30, 40, and 50 ppb were prepared from 0, 0.2, 0.4, 0.6, 0.8, and 1.0 ml respectively of a 100 ppb Mn solution (diluted from stock solution with Super-Q water and acidified to pH approximately 1.7) made up to 2.0 ml with previously extracted seawater.

2b Chelate and Organic Solvent.

A $2x10^{-3}$M solution of 8-Hydroxyquinoline in MIBK was used as the chelating ligand. Methylisobutyl ketone (MIBK) was used both as a solvent for the chelate and as the organic phase for extraction.

3 Cleaning Procedures

Polyethylene cups were used for the autosampler and 7 ml PFA (perfluoralkoxy) teflon vials were used in the extractions. Both were soaked overnight in a dilute HCL solution, rinsed with Super-Q water, and stored in plastic bags. Between analysis, the labware was rinsed in dilute acid and Super-Q water. Disposable Fisher pipette tips were used directly from the rack.

4 Procedure for Oxine-MIBK Extraction

Pore water samples previously analyzed by flame atomic absorption were diluted to fall within the range of 0 - 50 ppb, acidified to pH 1.7 - 2.0 by addition of 30 µl of 1N HCL (prepared from Ultrex HCL diluted with Super-Q water) and left overnight. The pore waters were acidified to dissociate hydrolysed Mn which does not chelate with oxine. The following day, 2.0 ml of a $2x10^{-3}$M oxine solution were added to 2.0 ml of the sample. Then 40 µl of 1.48 M ammonium hydroxide, prepared from Ultrex NH_4OH, were added to raise the pH of the water to 8 ±0.2 and the samples were shaken for 20 minutes. After separation, 1 ml of the organic phase was removed by pipette and analyzed by flameless atomic absorption.

Due to incomplete extraction of samples with concentrations greater than 50 ppb, pore waters from Mn reducing zones had to be diluted accordingly. This dilution introduced errors from the Mn present in Super-Q water. Although the Mn concentration was seemingly insignificant in Super-Q blanks, a 300 fold dilution, for example, would magnify a mere 2 ppb to 600 ppb. Also, variations in this increase would occur with changes in the Mn^{2+} concentrations of the Super-Q. Precision tests carried out on diluted samples, however, showed less than 7% standard deviation.

Excess oxine was used in extraction to ensure complete chelation. As a result of this high oxine concentration, magnesium oxinate formed at pH 9.2, the usual pH for Mn-oxine chelation (Yeats, unpublished). Lowering the pH to approximately 8 dissolved the precipitate while providing the same extraction efficiency.

5 Recovery and Precision Tests

Several recovery and precision tests were carried out to determine the success of the extraction method. Analysis of three replicate acidified seawater samples and five such samples spiked at 30 ppb gave a recovery of 105.8% and a precision of 7.6% (2σ). In addition, non-extracted calibration standards were prepared in Super-Q water. Spiked seawater sample concentrations calculated with the Super-Q calibration ($y= 0.29x + 0.89$) correlated well ($r= 0.99999$) with those calculated with the MIBK calibration curve ($y= 0.28x + 0.97$) as shown in Figure 1. A second recovery test was done on four replicate seawater samples and ten samples spiked at 40 ppb giving a 91.5% recovery and a precision of 15% (2σ). Results of the two tests are shown in Tables I and II.

To indicate the precision of dilution, nine samples were prepared by one-hundred fold dilutions of a 4 ppm Mn^{2+} seawater solution. Analysis gave results shown in Table III with 98.7% recovery and a precision of 13.7% (2σ).

To determine the effect of different dilutions, five samples were prepared by separate dilutions of a 10 ppm solution. A 100-fold and 200-fold dilution were done directly on the 10 ppm sample. In addition, dilutions of 150, 100 and 50 fold were done on a 2.5 ppm sample which was prepared by a four fold dilution of the 10 ppm stock solution. The analysis results (Table IV) gave a mean value of 13.5 ppm and a precision of 10.1% (2σ).

The detection limit for the chelation-extraction method was calculated from the recovery and precision tests to be approximately 6 ppb (3σ).

IIB Sites and Collection

This analytical method was used to measure dissolved Mn in pore waters from the Northeast Pacific Ocean. Two gravity cores (GC05 and GC13), one piston core (PC 19), and one box core (BC44) were obtained for geochemical analysis on the 1981 Wecoma cruise (cruise number 81-03) from a 100 km square section of Cape Mendocino Basin, approximately 200 nautical miles off Northern California. (Cranston et al, unpublished). Core sections were squeezed at 4 ±2°C and under a N_2 pressure of approximately 240 kPa to extract the pore water (Stoffyn-Egli, unpublished).

III RESULTS

The Wecoma 81 pore water Mn concentration data from both the extraction method and flame method (Fitzgerald, unpublished) are given in Table V. The two methods correlate well (see Figure II, r = .95776 and N = 125) with the extraction results an average of 15.5% higher than those from the flame. Such agreement shows comparable precision in the two methods and indicates the validity of the values obtained by the extraction method below the 200 ppb detection limit of the flame technique. The lack of a seawater standard makes the accuracy of the method difficult to assess.

Pore water Mn concentration vs depth profiles for the cores show similar trends for both sets of data. Profiles for GC05 are shown in Figure III.

IV DISCUSSION

To locate Mn reduction zones in the Wecoma 81 cores, Mn distribution coefficients (K_D) were calculated from the pore water Mn concentrations and hydroxylamine leachable Mn (HA Mn) data (Fitzgerald,

unpublished). A correction for the water content of the wet sediment (LeBlanc, unpublished) was included as follows:

$$K_D = \frac{\text{HA Mn } (\mu g/g)}{\text{Mn } (\mu g/l)} \times 1000 \text{ g/l } \left(\frac{100-\%H_2O}{\%H_2O}\right)$$

where K_D = distribution coefficient

HA Mn = hydroxylamine leachable Mn measured in μg/g of dry sediment

Mn = dissolved Mn in pore water measured in μg/l.

% H_2O = % water content measured as $\frac{\text{Mass water (g)}}{\text{Mass wet sediment (g)}}$ x 100%.

Plots of log K_D vs depth for each core are given in Figures IV, V, VI and VIII along with the colour log (based on Munsell soil colours) and depth profiles of dissolved Mn, pE, pH (Cranston et al., unpublished), and HA Mn to show Mn oxidizing and reducing zones. High K_D values occur in dark brown manganese oxidizing sediments which are generally found in the top layers of the cores. In these oxidizing sediments, Mn is present as particulate MnO_2. Low K_D values are usually found below the top 20 cm of sediment in manganese reducing conditions with Mn^{2+} dissolved in the pore waters. Anomalies in the profiles can be attributed to localized oxidation of organic matter which causes a reduction of MnO_2 in sediments depleted of O_2 and NO_3^-. (J.W. Murray, et al., p, 968).

Box core BC44 consisted of oxidizing sediment with higher K_D values than the other cores. A manganese oxidizing zone was prominent in the first 12 cm with most MnO_2 below 4 cm. Little particulate or dissolved Mn is present from 0-4 cm, indicating essentially no diffusion of dissolved Mn to the top layer of sediment.

The upper 32 cm of the gravity core GC05 was also a Mn oxidation zone. An abrupt colour change to dark grey at 32 cm coincided with a significant decrease in leachable Mn and an increase in dissolved Mn, indicating a MnO_2 reduction zone. A Mn oxidation zone occurred in the anomolous dark brown core section from 112-121 cm found immediately below a strong reducing zone for Fe. (Stoffyn, unpublished).

In the second gravity core, GC13, a Mn oxidation zone was again present in the top dark brown section of the core (above 26 cm). Dissolved Mn first occurred with a colour change to olive at 60 cm, and the sediment remained MnO_2 reducing to a depth of 140 cm. At 140 cm, a small dark brown zone coincided with manganese enrichment in the sediment and low dissolved Mn. The sediment returned to an olive grey manganese reducing zone until 259 cm with a constant increase of dissolved Mn in the pore waters. Leachable MnO_2 concentrations increased at 260 cm with the sharp colour change to dark yellow brown at 259 cm. A second small oxidizing zone was present in the grey brown sediment at 274 cm. At 284 cm a drop in pE occurred with a sharp increase in pH and dissolved Mn and a decrease in particulate MnO_2 and log K_D.

Geochemical analysis for the piston core, PC19, was only carried out on the lower half, from 680 to 1,660 cm, in primarily MnO_2 reducing sediment. A sharp Mn oxidizing zone present in dark brown sediment found from 1,599-1,642 cm coincides with a three order of magnitude increase of the K_D.

V CONCLUSIONS AND RECOMMENDATIONS

The oxine-MIBK extraction technique developed for the analysis of

dissolved Mn in pore waters provides a precision of approximately 7 - 15% (2σ) and has a detection limit of approximately 6 ppb. Therefore, the extraction method can be used to analyze samples from Mn oxidizing zones whereas flame atomic absorption cannot be used for concentrations below 200 ppb. The method also requires only 0.1 - 2.0 ml of sample, depending on the dilution factor. For diluted pore water samples, analytical error was increased slightly with the addition of Super-Q water. However, the trends of the Mn profiles were not affected significantly.

Because dilution is not necessary for analysis by the flame technique, this method has a greater precision than the extraction method in the analysis of samples with high Mn concentrations. Furthermore, little sample handling is required with flame analysis thus lowering the chance of contamination and decreasing analysis time. Therefore, to employ the advantage of both methods, the extraction method is recommended for analysis of samples with concentrations near and below the detection limit of the flame technique.

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TABLE I - Test #1

Seawater Samples (ppb)	Seawater +30 ppb MIBK Calibration (ppb)	Spike Super-Q Calibration (ppb)
DL*	29.89	29.42
DL	31.50	31.00
DL	32.82	32.28
	32.75	32.21
	31.68	31.16
	$\overline{X}$=31.73 ±1.19	

Recovery = 105.8%

TABLE II - Test #2

Seawater Samples (ppb)	Seawater + 40 ppb Spike (ppb)
DL	33.91
DL	36.36
DL	32.52
DL	40.33
	37.97
	35.41
	36.09
	36.20
	40.24
	36.86
	$\overline{X}$=36.59 ±2.74

Recovery = 91.5%

* DL: below dection limit

TABLE III - Dilution Test #1

Seawater Samples (ppb)	Seawater + 40 ppb Spike (ppb)
DL	41.79
DL	35.59
DL	42.10
DL	40.52
	39.04
	39.90
	41.90
	38.97
	35.50
	$\bar{X}$=39.48 ±2.71

Recovery = 98.7%

TABLE IV - Dilution Test #2

Stock Solution	Dilution Factor	Concentration (ppb)
10 ppm	300	13,599.7
	200	12,908.8
2.5 ppm	150	13,418.6
	100	14,647.4
	50	12,784.0
		X=13,471.7 ±740.1

TABLE V - Results

Core #	Sample #	Depth (cm)	Dissolved Mn (ppb) Extraction	Flame
GC05	2901	0-10	18	200
	2902	10-15	485	247
	2903	15-20	1894	1280
	2904	20-25	2348	1910
	2905	25-30	3290	4050
	2906	30-35	3509	3030
	2907	35-40	5494	5000
	2908	40-45	5068	4960
	2909	45-50	7189	5780
	2910	50-60	7164	5580
	2911	60-70	7533	5650
	2912	70-78	7560	5760
	2913	80-90	8550	6610
	2914	90-100	8569	6630
	2915	100-112	8278	6520
	2916	112-121	4869	4220
	2917	121-130	8160	5850
	2918	130-140	7276	5400
GC13	2931	252-256	8082	8860
	2932	256-260	12257	8170
	2933	260-264	1525	1240
	2934	264-268	1511	625
	2935	268-272	4806	4630
	2936	272-276	2456	3500
	2937	276-280	5814	4790
	2938	280-284	11240	8220
	2939	284-288	16546	12900
	2940	288-292	15695	12600
	2941	292-296	13882	12700
	2942	296-300	12746	12100
	2943	140-144	82	200
	2944	156-160	3572	2280
	2945	168-171	3833	3280

TABLE V (Continued)

Core #	Sample #	Depth (cm)	Dissolved Mn (ppb) Extraction	Flame
GC13	2946	180-184	4314	4190
	2947	194-198	6780	5110
	2948	206-210	7476	5560
	2949	60-64	3100	734
	2950	70-74	1281	1650
	2951	80-84	3425	2190
	2952	90-94	3564	3010
	2953	100-104	4480	3470
	2954	116-120	4430	3490
	2955	0-3	6	200
	2956	3-6	6	200
	2957	6-9	6	200
	2958	9-12	6	200
	2959	12-15	6	200
	2960	15-18	9	200
	2961	18-21	8	200
	2962	21-24	6	200
	2963	24-27	6	200
	2964	27-30	6	200
	2965	30-33	6	200
	2966	33-36	20	200
PC19	2967	1578-1583	16511	13200
	2968	1583-1588	14249	12400
	2969	1588-1593	16933	13600
	2970	1593-1598	15456	13000
	2971	1599-1604	2316	1570
	2972	1604-1609	4970	4220
	2973	1609-1614	7036	5190
	2974	1614-1619	8743	6260
	2975	1626-1634	7122	8060
	2976	1634-1642	14003	8890
	2977	1642-1650	13616	9570
	2978	1654-1660	13214	10900
	2979	1297-1302	8743	6480
	2980	1302-1307	8555	6330
	2981	1307-1312	8625	6410
	2982	1312-1317	9236	6690
	2983	1317-1322	8401	6240
	2984	1322-1327	8678	6530
	2985	1327-1332	8621	6550
	2986	1332-1337	7839	5400
	2987	1337-1342	5628	4880
	2988	1342-1347	8417	6090
	2989	1347-1352	8600	5914
	2990	1352-1357	8697	6430
	2991	1140-1145	9920	7120
	2992	1145-1150	10724	7380
	2993	1150-1155	11336	7350

TABLE V (Continued)

Core #	Sample #	Depth (cm)	Dissolved Mn (ppb) Extraction	Flame
PC19	2994	1155-1160	10667	7290
	2995	1160-1165	11089	7470
	2996	1165-1170	7395	7290
	2997	1170-1175	7205	7100
	2998	1175-1180	5282	4350
	2999	1180-1185	7279	7350
	3000	1185-1190	8015	7630
	3001	1190-1195	7700	7280
	3002	1195-1200	8599	7690
	3003	975-980	8566	7880
	3004	980-985	9344	8450
	3005	985-990	12214	9920
	3006	990-995	10155	9280
	3007	995-1000	9752	8930
	3008	1000-1005	8844	8050
	3009	1005-1010	8603	8430
	3010	1010-1015	8270	7790
	3011	1015-1020	8784	8460
	3012	1020-1025	7686	7390
	3013	1025-1030	9298	9000
	3014	1030-1035	8094	7430
	3015	824-829	9812	8870
	3017	834-839	9891	9020
	3018	839-844	9432	8110
	3019	844-849	8913	8610
	3020	849-856	9131	8230
	3021	856-861	9089	8380
	3022	861-866	9678	9570
	3023	866-871	9654	9660
	3024	871-876	10062	9690
	3025	876-881	10485	8880
	3026	881-886	9748	8460
	3028	680-685	10227	9840
	3029	685-690	13542	10500
	3030	690-695	12965	11100
	3031	695-700	12507	10700
	3032	700-705	9992	9360
	3033	705-710	14576	10900
	3034	710-715	11599	9950
	3036	720-725	12437	10900
	3037	725-730	16258	12200
	3038	730-735	16448	13200
	3039	735-740	13767	10300
BC44	3040	0-1 surface scrape	36	200
	3041	1-2	47	200
	3042	0-1 subcore	7	200
	3043	1-2	101	200

TABLE V (Continued)

Core #	Sample #	Depth (cm)	Dissolved Mn (ppb) Extraction	Flame
BC44	3044	2-3	18	200
	3045	3-4	1314	200
	3046	4-5	81	200
	3047	5-6	42	200
	3048	6.5-8	1760	764
	3049	8-10	1044	243
	3050	10-11	2056	505
	3051	11-12	1826	1650
	3052	12-13	334	313
	3057	17-19	3629	2780
	3058	19-20	3593	2280
	3060	20-22	3961	3050
	3061	22-23	5962	5000
	3067	28-30	4253	2520
	3069	30-32	5732	5050
	3071	32-33	2984	5300
	3072	33-35	4885	4830