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# *The (Ethylenedinitrilo)-tetraacetate Titration of Calcium and Magnesium in Ocean Waters*

## *II. Determination of Magnesium*

John B. Pate<sup>1</sup> and Rex J. Robinson

*Department of Chemistry  
University of Washington  
Seattle 5, Washington*

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### ABSTRACT

Modifications of the EDTA titration of total hardness have been evaluated for use in determining magnesium in sea water. In this procedure EDTA is the titrant, Eriochrome Blue Black B the indicator, and ethanolamine the buffer. Various conditions necessary for accurate sea water titrations have been established. A mean magnesium-chlorinity ratio of 0.06689 was obtained when 30 sea water samples were titrated.

Determination of calcium in ocean waters by (ethylenedinitrilo)tetraacetate (EDTA) titration has been reported by Pate and Robinson (1958), and determination of magnesium in ocean waters by EDTA titration is now reported. De Sousa (1954) determined magnesium by subtracting the calcium hardness from the total hardness obtained by titrating with EDTA; although he indicated satisfactory results in sea water analyses, he included no results in his paper. Voipio (1957), al Kadhim (1957) and Carpenter (1957) further explored application of the method to sea water samples; al Kadhim determined magnesium after separation of calcium by oxalate precipitation, and Carpenter used a spectrophotometric method for magnesium estimation after ion exchange separation of calcium.

### REAGENTS AND INDICATORS

All chemicals, unless otherwise indicated, were of reagent grade.

*Calcium Standard Solution.* After drying at 105°C, dissolve 1.0009 g of Mallinckrodt primary standard calcium carbonate in a minimum of 2 N HCl and dilute the solution to one liter.

<sup>1</sup> Present address: Robert A. Taft Sanitary Engineering Center, USPHS, Cincinnati 26, Ohio.

*Calcium and Magnesium Standard Solution.* Dissolve calcium carbonate (1.0009 g) in HCl, as above, and dilute to about 600 ml; dry 12.324 g of magnesium sulfate heptahydrate over a mixture of hydrates according to Lott and Cheng (1958), dissolve, add to the calcium solution, and dilute to one liter.

*Magnesium Standard Solution.* Dissolve J. T. Baker Purified Magnesium Turnings (0.2432 g) in hydrochloric acid and dilute the solution to one liter.

*Synthetic Sea Water.* Dissolve 1.3 g potassium bisulfate, 12.9 g magnesium sulfate heptahydrate, 1.82 g sodium sulfate, 1.0 g calcium carbonate, 45.7 ml 12 N hydrochloric acid and 21.04 g sodium hydroxide in distilled water and titrate the solution with standard 1 N sodium hydroxide to a methyl orange end point. Then dilute the solution to one liter.

*Ammonia Buffer.* Dissolve 67.5 g of ammonium chloride in 570 ml of 15 N ammonium hydroxide and dilute the solution to one liter.

*Ethanolamine Buffer.* Dilute 27.5 ml of 12 N hydrochloric acid with 200 ml of distilled water, add 155 ml of monoethanolamine (2-amino-ethanol) while stirring and dilute to one liter after cooling.

*EDTA (0.0150 M).* Dissolve 5.585 g of disodium dihydrogen (ethylenedinitrilo)-tetraacetate dihydrate, assaying 100.0%, in water and dilute to one liter. This solution was used as a primary standard, to which all secondary standards were referred. Use either the commercial assayed reagent, or follow the Blaedel and Knight (1954) preparation.

*EDTA-Mg (0.0149 M).* Dissolve 5.585 g of disodium dihydrogen (ethylenedinitrilo)-tetraacetate dihydrate and 0.1 g of magnesium chloride hexahydrate in water and dilute to one liter.

*Erio T.* Dissolve 1.5 g of Eriochrome Black T in a filtered solution of 13.5 g of hydroxylamine hydrochloride in 300 ml of 95% ethanol.

*Erio B.* Dissolve 1.0 g of Eriochrome Blue Black B (K and K Laboratories) in 50 ml of anhydrous methanol.

#### PROCEDURE FOR MAGNESIUM

Pipet 10 ml of the sea water sample into a 125 ml flask, add 25 ml of water, 2 ml of ethanolamine buffer and three drops of Erio B solution, then mix. Titrate the solution with EDTA solution to a true blue end point under incandescent light. Calculate the milliequivalents per liter of alkaline earth present from the titer of the EDTA.

Titrate an additional aliquot of the sea water sample to determine the milliequivalents per liter of calcium and strontium, using the procedure given by Pate and Robinson (1958). Subtract this value from the milliequivalents per liter of total alkaline earths previously determined. The residual value is the magnesium content of the sample.

In titrating sea water samples which have been diluted by appreciable quantities of land water, the presence of interfering ions is probable. Inter-



ference may be eliminated by using one or more masking agents, as reported in monographs in the field (Schwarzenback, 1957; Welcher, 1958; Barnard, 1956, 1957).

#### INVESTIGATION OF THE METHOD

As commonly performed, an ammonia buffer is used to obtain a pH of 10 and the sample is titrated with EDTA to a blue end point using Eriochrome Black T as the indicator. The present work was undertaken to determine if the numerous proposed modifications of this method would enhance its applicability to the titration of sea water samples. A brief summary of the investigation follows.

The results were evaluated statistically by the procedures outlined previously by Pate and Robinson (1958).

*Selection of Buffer.* The strong ammonia odor of the usual concentrated ammonia buffer has led investigators to examine various alternate buffer systems. Patton and Reeder (1956) proposed the use of Thies and Kallinich's (1953) ethanolamine-hydrochloric acid buffer; this seemed to offer promise since it possesses no odor, has good keeping qualities and yields sharp end points.

Results of preliminary titrations with this buffer are given in Tables I and II. The results found when titrating synthetic sea water were comparable to those obtained with the ammonia buffer. The low results obtained with calcium standards were later found to be due to indicator characteristics. Similarly, the anomalous low result found when titrating the magnesium standard (Table I) is explained as being due to precipitation prior to titration (see following discussion).

TABLE I. EVALUATION OF ERIO T AS AN INDICATOR.

	<i>Titrant</i>	<i>Buffer</i>	<i>Meq Found</i>
Synthetic Sea Water Meq Ca and Mg Taken: 1.303	EDTA + Mg	Ammonia	1.303
		Ethanolamine	1.302
	EDTA	Ammonia	1.303
		Ethanolamine	1.303
Magnesium Standard Meq Taken: 0.5000	EDTA + Mg	Ammonia	0.4994
		Ethanolamine	0.4995
	EDTA	Ammonia	0.5005
		Ethanolamine	0.4982
Calcium Standard Meq Taken: 0.5000	EDTA + Mg	Ammonia	0.5000
		Ethanolamine	0.4998
	EDTA	Ammonia	0.5000
		Ethanolamine	0.4952

TABLE II. EVALUATION OF ERIO B AS AN INDICATOR.

	<i>Titrant</i>	<i>Buffer</i>	<i>Meq Found</i>
Synthetic Sea Water Meq Ca and Mg Taken: 1.303	EDTA + Mg	Ammonia	1.299
		Ethanolamine	1.300
	EDTA	Ammonia	1.300
		Ethanolamine	1.303
Magnesium Standard Meq Taken: 0.5000	EDTA + Mg	Ammonia	0.4999
		Ethanolamine	0.4995
	EDTA	Ammonia	0.4998
		Ethanolamine	0.5001
Calcium Standard Meq Taken: 0.5000	EDTA + Mg	Ammonia	0.5000
		Ethanolamine	0.4998
	EDTA	Ammonia	0.5000
		Ethanolamine	0.4952

*Indicator Selector.* Erio T (Eriochrome Black T), CI 203 sodium 1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulfonate and Erio B (Eriochrome Blue-black B), CI 201 sodium 1-(1-hydroxy-2-naphthylazo)-2-naphthol-4-sulfonate were the metal indicators evaluated in this study. Erio T, although it is commonly used to determine the end point in total hardness titrations, is highly unstable in solution. Suggestions by various authors as to methods of avoiding rapid oxidation of the indicator solution have been summarized in several reviews (Barnard, 1956, 1957; Welcher, 1958); these reviews have also listed other indicators proposed as substitutes for Erio T. Of these, Erio B was selected for evaluation in this study.

Table I may be compared with Table II for an evaluation of the use of Erio T and Erio B as indicators. Results obtained were sufficiently accurate to warrant further investigation of Erio B.

*Titrant Selection.* A poor end point is obtained in the total hardness of calcium. Since the presence of 5% magnesium sharpens the end point, this amount is normally added to the titrant (Diehl, *et al.*, 1950) or the sample. The titrant must be standardized after the magnesium addition, and a second titrating solution is then required for calcium determinations.

Since all sea water samples contain an appreciable amount of magnesium as well as calcium, no added magnesium is required when an actual sample is to be titrated. By use of a combined calcium and magnesium standard, pure EDTA solution is usable as a titrant in the total hardness determination. Tables I and II show that there is no loss of precision or accuracy.

*Effect of Ionic Strength of the Sample Upon Titration.* When ethanolamine buffer was added to a sample of undiluted sea water, a precipitate slowly formed.



TABLE III. EFFECT OF VARYING IONIC STRENGTH OF SAMPLE. TITRANT: EDTA+  
Mg. BUFFER: ETHANOLAMINE.

Sample	NaCl Molarity		Meq Taken	Meq Found	95 % CI ±	% Dev.
	Before Titr.	After Titr.				
Erio T as Indicator						
Ca + NaCl . . . . .	0.487	0.325	0.5000	0.5002	0.0002	0.0
Mg + NaCl . . . . .	0.487	0.325	0.4974	0.5118	0.0035	+ 2.9
	0.428	0.081	1.239	1.241	0.001	+ 0.1
	0.122	0.055	1.239	1.240	0.001	+ 0.1
Sea Water . . . . .	0.462	0.118	1.118	1.111	0.001	- 0.6
Erio B as Indicator						
Ca + NaCl . . . . .	0.487	0.325	0.5000	0.5001	0.0001	0.0
Mg + NaCl . . . . .	0.487	0.325	0.4970	0.5033	0.0005	+ 1.3
	0.428	0.081	1.240	1.240	0.001	0.0
	0.122	0.055	1.240	1.240	0.001	0.0
Sea Water . . . . .	0.462	0.118	1.118	1.111	0.001	- 0.6

Since this precipitate formed only in the presence of magnesium, it was assumed to be a magnesium-hydroxyl-ethanolamine complex. When indicator was added, it was absorbed on the precipitate, coloring it a magenta-purple. Upon titrating, the precipitate dissolved, the solution turned its normal red, and the usual end point behavior was observed. Dilutions of the sample at various stages of titration were made as shown in Table III. From the results it is seen that, with either of the indicators used, the sample must be diluted so that the sodium chloride molarity of the titrated sample is 0.1 M or less. Results also show that samples with sufficient sodium chloride (0.4-0.5 M in Table III) to form a precipitate upon addition of ethanolamine buffer may be accurately titrated if they are diluted prior to completion of the titration.

Fivian and Moser (1951) showed that a concentrated sample containing alkali salts gave a false end point with Erio T whereas Schneider and Emmerich (1951) found that Erio B was free of this effect. However, results (Table III) indicate that the ionic strength of sea water is not great enough to show a difference between these two indicators.

Buffer capacity was checked under varying conditions of dilution. With maximum dilution (10 ml sea water diluted to 50 ml, 87 ml final volume after titration), 1 to 5 ml of buffer yielded a final pH of 9.8 to 10.3.

*Conditions Required to Avoid Precipitation.* In examining conditions required for the ethanolamine complex to precipitate, a relationship was found between the magnitude of the error introduced thereby and the elapsed time after addition of the buffer. Results of a series of titrations, performed to check this relationship, are shown in Table IV. Accurate results are found upon addition of the buffer to the sample immediately prior to titration. Results

TABLE IV. EFFECT OF TIME INTERVAL BETWEEN BUFFER ADDITION AND TITRATION. TITRANT: EDTA. INDICATOR: ERIO B.

<i>Buffer</i>	<i>Buffer Added</i>	<i>Meq Found</i>	95 % <i>CI</i> ±
Meq Ca + Mg Taken: 1.243			
Ammonia.....	Immediately before titration	1.242	
	"	1.241	
	"	1.241	
	Mean	1.241	0.023
Ethanolamine .....	Immediately before titration	1.241	
	"	1.243	
	Mean	1.241	0.061
Ethanolamine .....	30 min. before	< 0.3	
Meq Mg Taken: 0.5208			
Ethanolamine .....	Immediately before titration	0.5218	0.0004
	3 min. before	0.5208	
	5 " "	0.5211	
	8 " "	0.5205	
	10 " "	0.5151	
	25 " "	0.5075	
	30 " "	0.4970	

TABLE V. EFFECT OF DILUTING SAMPLE. TITRANT: EDTA. Meq Ca + Mg STANDARD TAKEN: 1.243.

<i>Buffer</i>	<i>Buffer Added</i>	<i>Meq Found</i>	95 % <i>CI</i> ±
25 ml Water Added			
Ammonia.....	Immediately before titration	1.238	
"	"	1.241	
	Mean	1.240	0.019
Ethanolamine .....	Immediately before titration	1.242	
"	"	1.241	
"	"	1.242	
	Mean	1.242	0.001
Ethanolamine .....	30 min. before titration	less than 1.0 meq	
50 ml Water Added			
Ethanolamine .....	30 min. before titration	1.242	
"	"	1.241	
"	"	1.244	
	Mean	1.242	0.004



are proportionally lower as the time interval between addition of the buffer and titration increases.

The time relationship of the precipitate formation is modified by dilution of the sample, as shown in Table V. A five-fold dilution of the sample will permit a half-hour delay in titrating after the buffer is added. A  $2\frac{1}{2}$ -fold dilution is insufficient to prevent formation of the precipitate; therefore immediate titration following addition of the buffer is required.

As a matter of convenience, appropriate amounts of indicator and buffer were mixed in order that both could be added in a single operation prior to titration. If these mixtures were used within several hours, precision and accuracy were maintained, although the alkalinity promoted oxidation of the indicator. The discolored solution was therefore discarded and a fresh mixture was prepared daily.

#### MAGNESIUM CONTENT OF OCEAN WATERS

Thirty water samples from three ocean stations have been analyzed for magnesium using the procedure described. The chlorinities were determined by Mr. Ralph W. Riley, chemist, Oceanography Department, University of Washington. The method described by Knudsen was followed except that

TABLE VI. MAGNESIUM CONTENT OF SEA WATER.

Cruise: Brown Bear No. 179. Station: No. 26 (49° 12' N, 127° 17' W). Date: November 9, 1957.

Depth (m)	Temp. (°C)	Chlorinity (‰)	Meq Mg/l* (Calc.)	Meq Mg/l (Found)	% Dev.	Mg/Cl
0	13.28	17.927	120.3	120.2	-0.1	0.06680
10	13.28	17.931	120.4	120.2	-0.1	0.06675
20	12.96	17.925	120.3	120.2	-0.1	0.06677
30	11.74	17.973	120.7	120.7	0.0	0.06691
50	7.46	18.069	121.3	121.3	0.0	0.06688
75	7.02	18.102	121.5	121.7	+0.1	0.06701
100	6.70	18.215	122.3	122.5	+0.2	0.06703
125	6.93	18.404	123.6	123.8	+0.1	0.06702
143	6.83	18.583	125.0	125.0	0.0	0.06696
167	6.85	18.690	125.7	125.6	-0.1	0.06678
182	6.84	18.706	125.8	125.9	0.0	0.06690
271	5.98	18.780	126.3	126.2	-0.1	0.06684
448	4.90	18.873	127.0	126.6	-0.3	0.06665
678	4.22	18.941	127.5	127.7	+0.2	0.06710
918	3.61	19.007	127.9	128.0	+0.1	0.06696
1267	2.99	19.071	128.3	128.4	0.0	0.06691
1559	2.44	19.100	128.6	128.4	-0.1	0.06680
				Mean		0.06689
				Standard Deviation:		±0.00012

\* Calculated from Mg/Cl ratio of 0.06695 (Thompson and Wright, 1930).



fluorescein was used as the indicator, as recommended by Miyake (1939). The authors verified these values by using the regular Knudsen method. Representative results of a single series are presented in Table VI. The mean magnesium-chlorinity ratio (by weight) found for the 30 samples analyzed is 0.06689, with an average percent deviation of 0.1%.

Thompson and Robinson (1932) summarized the magnesium-chlorinity ratios reported in 12 previous papers. They concluded that these results were unreliable because of the analytical techniques used. Thompson and Wright (1930), by gravimetric determination of the magnesium as the phosphate, found a ratio of 0.06694 in 30 samples. Their value of 0.06695 (corrected for changes in the atomic weight of phosphorus) has since been accepted as the most valid magnesium-chlorinity ratio of ocean water. Miyake (1939) reported a value of 0.06763 for the ratio of 18 samples by a gravimetric method, and Carpenter (1957) reported a ratio of 0.0667 for 24 samples of Chesapeake Bay water corrected for dilution by an EDTA titration method.

The magnesium-chlorinity ratio as ascertained from the present work is within 0.1% agreement with the ratio of Thompson and Wright, although it was obtained by a radically different analytical method. The speed and simplicity of the EDTA titration method should encourage its usage in the determination of magnesium in sea water.

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