Determination of Less Than 40 PPM Calcium and Magnesium in Sodium Chloride

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ABSTRACT

The customary EDTA titration has been modified and improved to accurately detect and determine levels of calcium and magnesium between 2 and 40 ppm in salt. Based on 250 determinations, the standard deviation is ± 1 ppm calcium.

The modification in the procedure involves adding a small amount of calcium to the hydroxylamine hydrochloride solution and an equivalent amount of EDTA to the buffer. It is thus possible to detect as little as 10 micrograms of calcium in the titration at pH 12.5. Without this modification, it would not be possible to detect less than 120 micrograms of calcium at pH 12.5 with the calcium indicator used, and the magnesium would be overestimated by up to 76 micrograms.

Magnesium was determined on a number of salt samples both by this improved EDTA method and by the colorimetric Clayton-Yellow method. Excellent agreement was found between the two analytical methods.

INTRODUCTION

Many methods (Schwarzenbach, 1957, p. 21; Welcher, 1958) have been described for the analytical determination of calcium and magnesium by EDTA using one or another of numerous indicators. Usually, these methods have been developed for the analysis of the metal ions in dilute aqueous solutions. Several procedures have appeared for the analysis of calcium and magnesium in salt, brine or sea water solutions (Welcher, 1958, p. 110, 128) and are quite satisfactory for high levels of calcium and magnesium.

The general technique calls for the addition of solutions of hydroxylamine hydrochloride, potassium cyanide, ammonia-ammonium chloride buffer, and hardness indicator to the salt solution. This solution is then titrated for both Ca and Mg at pH 10. Calcium is determined separately by a titration at pH 12.5. Magnesium is obtained by difference. These techniques are usually satisfactory for analyzing crude rock salt, solar salt or vacuum pan salt.

This general procedure is not adequate for an accurate determination of very small quantities of calcium and magnesium in purified brine or reagent grade salt. When we started to analyze for less than 300 micrograms of calcium and magnesium, the magnesium values were too high. Reproducibility was poor. Even the color change of the indicator at the end point varied.

We tried different indicators. Unfortunately, each indicator has a little different hue and it is necessary for the analyst to become accustomed to the end point color. Different buffers and different masking agents were tried, but none were satisfactory.

Therefore, we selected two indicators, Betz # 290 for total calcium and magnesium and Cal Ver II for calcium. We did a systematic investigation using these two indicators. Both indicators

have a distinctive blue color in the absence of calcium or magnesium. We also chose to continue the use of hydroxylamine hydrochloride, potassium cyanide, and ammonia-ammonium chloride buffer.

Some knowledge of the physical and chemical properties of the indicators would be useful. Because many indicators for calcium and magnesium determination behave similarly, we can examine some of the physical and chemical properties of the indicators originally developed for the EDTA titration.

Figure 1 shows the color relationship between the reciprocal log of the Mg ion concentration (commonly referred to as pMg) and the pH for the Mg-Eriochromeschwarz T chelate system (reproduced by permission, Chaberek, 1959, pp. 242 and 245). We observe that there are a number of color changes depending upon pH and magnesium concentration. For instance, at pH 10 the color changes from red to blue as the magnesium concentration decreases, i.e., as the pMg increases. This is indicated by the vertical dashed line. We also see that the amount of magnesium remaining in solution at the end point is dependent upon pH; the higher the pH, the lower the level of magnesium in solution when the color change occurs. (Ringbom, 1963, p. 362.)

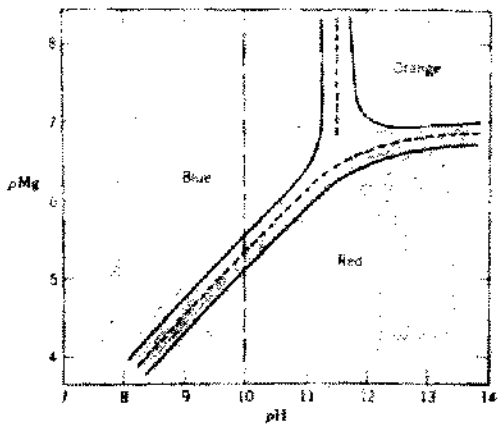

Figure 1. Color relationships between pMg and pH for the Mg (II)-Eriochromeschwarz T chelate system.

The calcium-purpurate chelate system behaves similarly. In this system it is also necessary to closely control the pH for analysis of small quantities of Ca.

EXPERIMENTAL PROCEDURES AND RESULTS

Titration Techniques

At pH 10. For the standardization of the solutions at pH 10.00 portions of a 40 ug/ml calcium solution are pipetted into beakers and diluted to 300 ml. One-half ml each of hydroxylamine hydrochloride and potassium cyanide and one ml of the NH_4 OH-NH_4 Cl buffer are added to the stirred solution. Three to five scoops of Betz # 290 hardness indicator (or a suitable amount for individual preference) are added to the solution. The final adjustment to the exact pH is made with 50% KOH solution using a pH meter.

A tungsten light or a microscope illuminator placed behind the beaker aids in detection of the end point. The solution is then titrated with the 0.4 g/l EDTA solution to the complete disappearance of the red color. The pH is adjusted, again, in case it has dropped and the titration continued. The color at the end point is a distinct blue with no tinge of red. When the blue color persists for five to ten seconds, the end point has been reached.

At pH 12.50. Standardization at pH 12.50 is similar to the procedure at pH 10, except that -- (1) no buffer is added; (2) Cal Ver II indicator is substituted for Betz # 290; and (3) the pH of the solution is adjusted to 12.50 with 50% KOH.

After adjustment of pH, the electrodes are rinsed and removed. The solution is then titrated with EDTA. Again, the end point is the complete disappearance of the last tinge of red. Readjustment of pH is not necessary at this high pH.

Standardizations

The techniques just described were used in all our titrations. These were carried out at ambient room temperature, with solution temperatures ranging from 18-28°C.

Figure 2 shows the average of duplicate calcium titrations in water at a pH of 9.8, 10.0, 12.3 and 12.5. We notice several things here: (1) the extrapolation of the data to the axis at

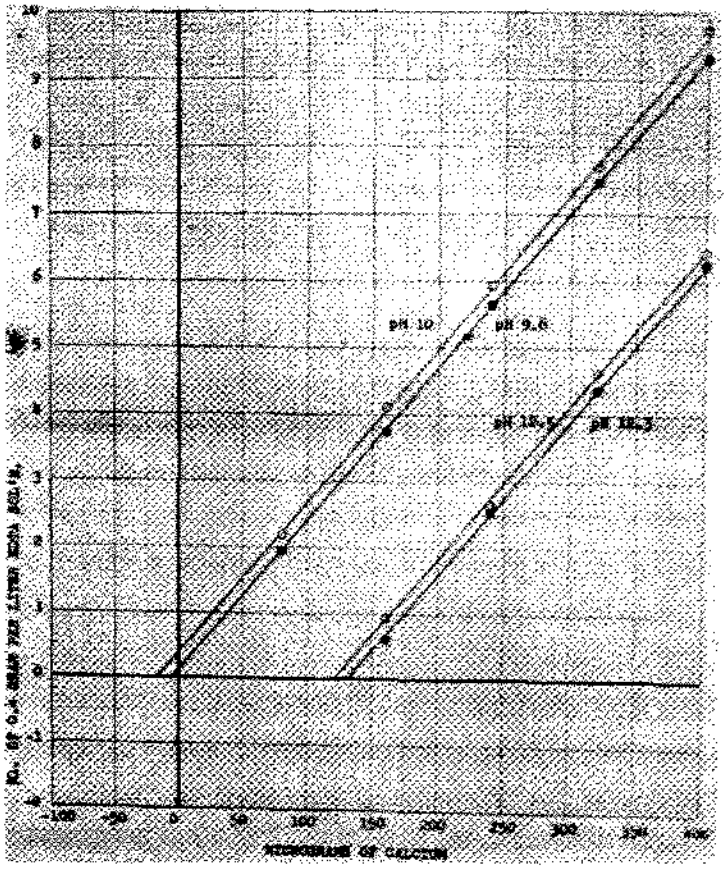

Figure 2. Comparison of calcium titration in water at pH of 9.8, 10.0, 12.3 and 12.5 (before adjustment of solutions).

pH 9.8 and 10.0 does not pass through the origin. The data indicate that there is the equivalent of 16 micrograms of calcium in solution at pH 10. At pH 9.8, there is the equivalent of 6 micrograms of calcium. This source of titratable ions in the blank is probably due to free magnesium ions in the Mg-EDTA which was added to the buffer. If there is a slight excess of Mg in the Mg-EDTA salt, then this excess Mg will be titrated. (Chaberek, 1959, p. 253.) (2) When the titration is carried out at pH 12.5, 120 micrograms of calcium cannot be detected. At pH 12.3, 130 micrograms of calcium cannot be detected. This is due to the stability constant of the calcium-indicator complex at pH of 12.5. The data shows that a small change of pH in the solution being titrated has a definite effect on the quantity of the ions that can be detected. Therefore, the pH must be closely controlled and in our titrations we control the pH to $\pm$ 0.01 pH units in order to obtain reproducible results.

The titration at pH 10 shows the presence of free ions in solution equivalent to 16 micrograms of calcium. We want the extrapolation to pass through the origin. Therefore, we can add sufficient EDTA to the buffer solution so that every ml of the buffer will contain EDTA equivalent to 16 micrograms of calcium.

Then, when one ml of the buffer is added to the solution to be titrated, the EDTA will tie up the free metallic ions in solution. The titer will be exactly equal to the quantity of calcium or magnesium in the unknown, and there will be no need for a blank.

At pH 12.5 we cannot detect 120 micrograms of calcium. Thus, if our unknown contained less than 120 micrograms of calcium, we could not detect any of it. If the hydroxylamine solution is made up to contain 120 micrograms of calcium per one-half ml, then when one-half ml is added to the solution to be titrated, we will be able to detect a few micrograms of calcium in the unknown. Since the hydroxylamine is added to the unknown solution at pH 10.0 also, it is necessary

to add additional EDTA to the buffer to complex the calcium ions added with the hydroxylamine solution.

Replicate Titrations of Known Calcium Solutions

Titration with Strong EDTA Solution. Having standardized the solutions, we determined the analytical error of the EDTA titration of calcium and magnesium. Table I presents the data for the titrations at exactly pH 10.00. All the figures shown here represent titrations using standardized solutions, that is, solutions to which calcium and EDTA had been added for reasons previously described.

TABLE I

TITRATION OF CALCIUM IN WATER, 3 AND 6% SALT SOLUTION AT pH 10.0 (AFTER ADJUSTMENT OF SOLUTION)

ugCa	#1	#2	#3	#4	#5	#6	Ave.	Std. Dev.
				In H_2O				
80	1.96	1.86	1.77	1.97	2.00	1.95	1.91	0.087
160	3.71	3.71	3.67	3.81	3.79	3.81	3.75	0.061
240	5.60	5.52	5.66	5.60	5.66	5.73	5.63	0.071
320	7.48	7.45	7.58	7.56	7.57	7.57	7.53	0.056
400	9.40	9.39	9.34	9.46	9.53	9.40	9.42	0.066
						Pooled Estimate of Std. Dev.		0.070
				In 3% NaCl				
80	2.30	2.02	1.89	1.84	1.84	2.14	2.01	0.186
160	4.13	3.97	3.85	3.82	3.58	3.82	3.86	0.182
240	5.83	5.83	5.82	5.88	5.50	5.92	5.80	0.150
320	7.90	7.70	7.95	7.80	7.45	7.55	7.73	0.197
400	9.78	9.62	9.72	9.77	9.35	9.26	9.58	0.225
						Pooled Estimate of Std. Dev.		0.190
				In 6% NaCl				
80	2.87	2.14	2.52	2.13	2.29	2.24	2.37	0.285
160	4.79	4.53	4.34	4.25	4.46	4.25	4.44	0.206
240	6.43	5.95	6.50	5.95	6.67	6.23	6.29	0.298
320	8.33	8.08	8.50	8.03	8.55	8.13	8.27	0.223
400	10.11	9.90	10.18	9.63	10.48	10.26	10.09	0.296
						Pooled Estimate of Std. Dev.		0.264

Sets of calcium solutions were titrated in three media -- water, 3% salt solutions and 6% salt solutions. Each set consists of five calcium levels -- 80, 160, 240, 320 and 400 micrograms. All sodium chloride used here was specially purified (see appendix). The 3% salt solutions contained 10 grams of salt per 300 ml. Therefore, in 3% salt solutions, 80 micrograms of calcium represents 8 ppm in salt.

The individual titers, the means, and the standard deviations are indicated for each calcium level. The standard deviations for each calcium level in a particular medium are essentially equal and for each medium the best estimate of the standard deviation was calculated from the pooled sums of squares. We see that the standard deviation is lowest for the titration in water and highest for the titration in the 6% salt solution.

Figure 3 presents a graphical plot of this data. There are six determinations at each calcium level, some of which are plotted on top of one another. The center line represents the best straight line thru all the points while the outer lines represent the 95% confidence limits. The 95% confidence limits indicate that on the average 95 observations out of 100 will fall inside the two outer lines when the center line represents the true value. For example, when titrating

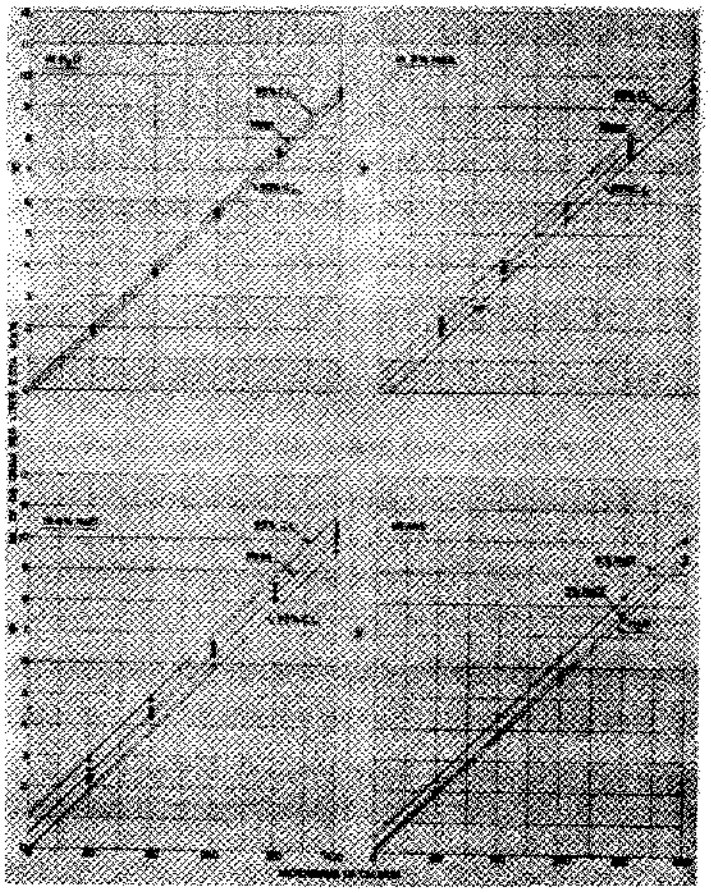

Figure 3. Titration of calcium at pH 10.00.

160 micrograms of calcium in water, a titer of 3.76 ml of 0.4 g/l EDTA solution is expected. However, 2.5 times out of a hundred a titer greater than 3.92 ml and 2.5 times out of a hundred a titer less than 3.60 ml is obtained. This occurs when the true value is 3.76 ml and is due to the errors in all the manipulations involved when making a titration.

The extrapolation of the data for the titration in water passes close to the origin, indicating that the original titrations were good and the addition of EDTA to the buffer and calcium to the hydroxylamine solutions worked well.

The mean line for the 3 and 6% salt solutions does not intercept the origin. This might indicate that the salt contains calcium or magnesium but it is more likely that this anomaly is a salt effect. More will be said about this later.

From this data, we see that if the solutions are standardized in water and then the calcium determined in a 3% salt solution, using 10 g of salt, the estimate of the true calcium value will on the average be high by 7 micrograms or 0.7 ppm based on salt. If calcium is determined in a 6% salt solution, the estimate will be high by 28 micrograms or 1.4 ppm based on 20 grams of salt. If magnesium were determined, the overestimation in the 3 and 6% salt solutions will be high by 0.43 and .85 ppm respectively.

Figure 4 illustrates similar graphical plots obtained from the titration of calcium with EDTA at a pH of exactly 12.50. For the titration in the salt solutions, the pH was adjusted to indicate 12.45 to compensate for the sodium ion effect.

The titer for the 3% salt solution is about the same as that for water, while the titer for the 6% salt solution is much more than for water. It appears that 10 grams of salt contains no free calcium, while the 20 g of salt contains about 80 micrograms of calcium. Evidently, this is a salt effect. The 95% confidence interval for the 3% salt solution is quite small while it is higher for water and much higher for the 6% salt solution.

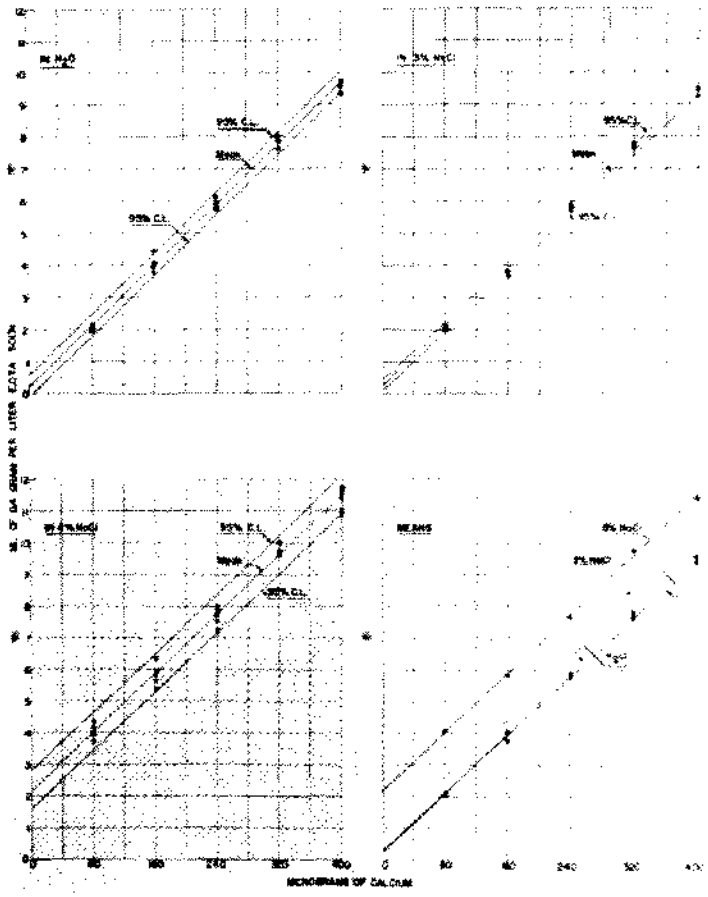

Figure 4. Titration of calcium at pH 12.50.

Titrations with Weak EDTA Solution. Similar titrations were made with a weak, 0.1 g/l EDTA solution. The standard deviation for the titration using the weak EDTA solution was four times higher than the strong EDTA. This is when the standard deviation is expressed in ml of titer. However, when expressed in ppm calcium in salt, the standard deviations are the same for the titrations with the two solutions.

Triethanolamine as a Masking and Buffering Agent. Triethanolamine was used as a masking and buffering agent in another group of experiments. It was used in place of the hydroxylamine hydrochloride, the potassium cyanide and the ammonia-ammonium chloride buffer. Known calcium solutions were titrated in duplicate with the strong and weak EDTA. These titrations give results identical to those obtained with the other masking and buffering agents.

Comparison of Magnesium Determination by the EDTA and Clayton-Yellow Methods. From these studies we concluded that we would standardize the EDTA solution in water, add calcium to the hydroxylamine hydrochloride in order to detect a few micrograms of calcium at pH 12.50, add a corresponding quantity of EDTA to the buffer for the titration of calcium and magnesium at pH 10.0, and then determine calcium and magnesium in 3% salt solutions. Since magnesium is obtained by difference it may be subject to a greater error than calcium which is titrated directly at pH 12.50. Therefore, magnesium was determined on unknown samples by the colorimetric, Clayton-Yellow, method and compared to the EDTA method. Table II presents such data.

In this series of salt samples, the calcium level ranged from 10 to 300 ppm based on salt, or a total of 100 to 3,000 micrograms of calcium. This range of calcium is far beyond what one would ever expect to find in C.P. salt. If good magnesium results are obtained over this range, we would be satisfied that the EDTA method for calcium and magnesium is good.

TABLE II

COMPARISON OF MAGNESIUM DETERMINATION BY THE EDTA DIFFERENCE METHOD AND THE CLAYTON-YELLOW COLORIMETRIC METHOD OVER THE CALCIUM RANGE OF 100-3,000 MICROGRAMS

	Calcium and Magnesium By The EDTA Method (ppm in 10 g of Salt)				Magnesium By The Clayton-Yellow Method (ppm in 10 g of Salt)
Sample No.	Ca		Mg		Mg
306-10-17	9.6	9.8	13.5	12.7	12.7
-18	6.1	9.1	12.0	9.9	11.3
-19	307	313	6.9	4.0	9.2
-20	168	--	4.9	--	6.5
-21	78.3	79.1	2.6	2.8	3.9
-22	25.7	26.4	3.3	3.0	2.8
-23	10.1	11.2	2.5	2.2	2.1
-24	8.0	9.5	2.2	1.8	2.1

Here we see the data for calcium and magnesium by the EDTA method and for magnesium alone using the Clayton-Yellow method. The EDTA titration was run in duplicate, while only a single magnesium determination was made by the Clayton-Yellow method.

We see that there is good agreement between the magnesium values determined by the two methods when the calcium level is below 300 micrograms. In fact the results were better than expected. The agreement between the two methods was not as good when the calcium level was above 30 ppm.

Temperature Effect

Frequently during the analysis of salt solutions by the EDTA method, it was observed that the color of the salt solutions at the end point varied when the titration was carried out at a pH of 12.50. At times the color was a pure blue and at other times it was green. Frequently, the color varied between the two extremes. This was puzzling.

Fortunately, we titrated duplicate samples one morning when the temperature of two solutions was about 19 and 25°C. The difference in titer for the duplicate samples was about 1.5 ml. This led us to believe that the difference in the titer was due to a temperature effect, which we subsequently investigated.

Table III shows quadruplicate titrations of 400 micrograms of calcium at pH 10.00 and 12.50 in water, 3 and 6% salt solutions for the temperatures, 20, 25 and 30°C. Also tabulated are the means and standard deviations of the quadruplicate titrations. Several worth-while observations can be made from examination of this data: (1) The reproducibility of the titrations at constant temperature is very good as evidenced by the data and the standard deviations. The best estimate of the standard deviation is $\pm$ 0.04 ml. The 95% confidence interval based on calcium is $\pm$ 0.3 ppm. For magnesium it is $\pm$ 0.2 ppm. (2) We also see evidence of a definite salt-temperature-pH effect. But, this relationship can be seen more clearly in Fig. 5.

Here we see that there is a large salt-temperature effect when the titration is carried out at pH 12.50. A larger deviation occurs in the 6% salt solution than in the 3% salt solution. The slopes for the titers in the two solutions are also different. The salt-temperature effect is also present in the salt solutions at pH 10.00, but it is not pronounced as at pH 12.50. In 3% salt solutions and at pH 10.00, the salt effect is much less than in 6% salt solution. We would expect that the effect would be even less pronounced in more dilute salt solution.

We also see that there is a very small temperature effect when the titration is carried out in water -- either at pH 10.00 or 12.50. In water, the titer is somewhat higher at pH 12.50 than at pH 10.00, indicating a slight excess of calcium. This source of calcium is evidently from the

TABLE III

TITRATION OF 400 MICROGRAMS OF CALCIUM IN WATER, 3% AND 6% NaCl SOLUTIONS AT pH 10.00 AND 12.50 AND SOLUTION TEMPERATURES OF 20, 25 AND 30°C

pH				10.00					
Solution	Water			3% NaCl			6% NaCl		
Temp. °C.	20	25	30	20	25	30	20	25	30
Replicate # 1	9.26	9.29	9.31	9.08	9.38	9.62	9.78	9.85	9.99
# 2	9.32	9.27	9.33	9.02	9.42	9.57	9.79	9.92	10.13
# 3	9.24	9.28	9.36	9.10	9.35	9.62	9.72	9.86	10.05
# 4	9.35	9.26	9.36	9.07	9.34	9.55	9.75	9.91	10.02
Average	9.288	9.275	9.340	9.068	9.372	9.590	9.760	9.885	10.048
Std. Dev.	0.043	0.013	0.024	0.034	0.036	0.036	0.032	0.037	0.060

pH				12.5					
Solution	Water			3% NaCl			6% NaCl		
Temp. °C.	20	25	30	20	25	30	20	25	30
Replicate # 1	9.31	9.36	9.46	8.64	9.79	11.30	10.88	11.58	12.35
# 2	9.36	9.38	9.48	8.66	9.84	11.34	10.82	11.53	12.32
# 3	9.42	9.41	9.49	8.71	9.90	11.27	10.85	11.60	12.37
# 4	9.37	9.42	9.50	8.66	9.87	11.19	10.90	11.55	12.40
Average	9.365	9.392	9.475	8.668	9.850	11.275	10.862	11.565	12.36
Std. Dev.	0.045	0.028	0.024	0.030	0.047	0.063	0.035	0.046	0.034

Best Estimate of Standard Deviation = ± 0.039 ml of 0.4 g/l EDTA Sol'n.
95% Confidence Interval = ± 0.078 ml of 0.4 g/l EDTA Sol'n.
95% Confidence Interval Based on Calcium = ± 3.3 ugCa.
95% Confidence Interval Based on Calcium in Salt = ± 0.3 ppm.

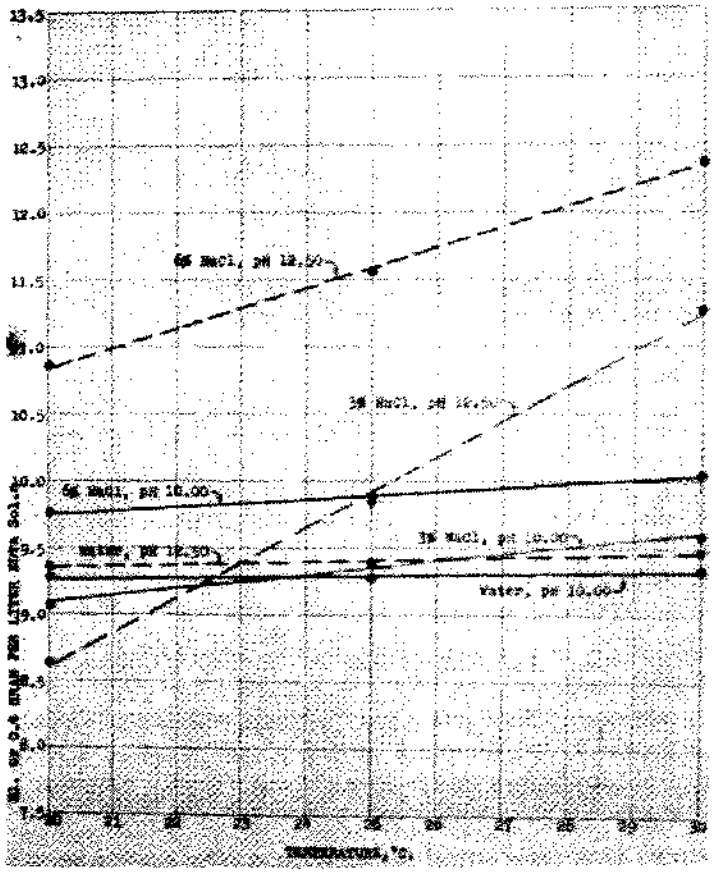

Figure 5. Titration of 400 micrograms of calcium in water, 3% and 6% NaCl solutions at pH 10.00 and 12.50 and solution temperatures of 20, 25 and 30° C.

hydroxylamine to which we had previously added calcium in the standardization of the reagents. Now that the titrations are more precise, the small excess is detected. There is a small temperature effect at pH 10.00 in 3% salt solution and a larger effect in the 6% salt solutions.

From this plot, it is conclusive that there is a definite salt-temperature effect at both pH levels. However, the salt temperature effect may not be a hindrance if all the titrations are carried out at a temperature of about 23.5°C because at this temperature the titers for 400 micrograms of calcium in water and a 3% salt solution at pH 10.00 and 12.50 are all about the same.

Table IV presents the data for the titration of 80, 160, 240, 320 and 400 micrograms of calcium under the above conditions. We see that the data for the titrations in water and 3% salt solutions at pH 10.00 and 12.50 are very similar.

TABLE IV

TITRATION OF CALCIUM IN WATER AND 3% NaCl SOLUTION WITH 0.4 g/l EDTA SOLUTION AT pH 10.00 AND 12.50 (SOLUTION TEMPERATURE = 23.5°C)

WATER

	pH = 10.00		pH = 12.50	
ugCa	#1	#2	#1	#2
80	1.82	1.81	1.88	1.84
160	3.62	3.64	3.64	3.90
240	5.53	5.50	5.58	5.64
320	7.30	7.40	7.45	7.42
400	9.33	9.34	9.67	9.38

3% SALT-10 g

	pH = 10.00		pH = 12.50	
ugCa	#1	#2	#1	#2
80	1.79	1.86	2.03	1.83
160	3.58	3.62	3.63	3.74
240	5.53	5.55	5.60	5.54
320	7.42	7.46	7.41	7.49
400	9.29	9.36	9.33	9.37

Standard Deviation At Each Level	
80 ugCa	0.0751
160 ugCa	0.1030
240 ugCa	0.0452
320 ugCa	0.0564
400 ugCa	0.1190
Best Est.	0.0844

Standard Deviation = 0.084 cc of 0.4 g/l EDTA sol'n.
95% Confidence Interval = ± 0.17 cc of 0.4 g/l EDTA
95% Confidence Interval Based on Calcium = ± 7.3 ugCa
95% Confidence Interval Based on Calcium in Salt = 0.73 ppm

All the titration data at pH 12.50 seems to be slightly higher than that at pH 10.00. This was observed in Table III and can be compensated for in the future analysis. Since the standard deviations are essentially equal, we calculated the best estimate from the sums of squares.

When running a calcium determination in water or salt solution, the 95% confidence interval is 0.17 ml of the standard EDTA solution. In terms of calcium it is 7.3 micrograms of calcium. If the solution contains 10 grams of salt, the 95% confidence interval is $\pm$ 0.73 ppm Ca. But, most of the time it will be less than this value. Based on magnesium the 95% confidence interval is 0.44 ppm.

Figure 6 shows the graphical plot of this data. The best line and 95% confidence limits are drawn from the data.

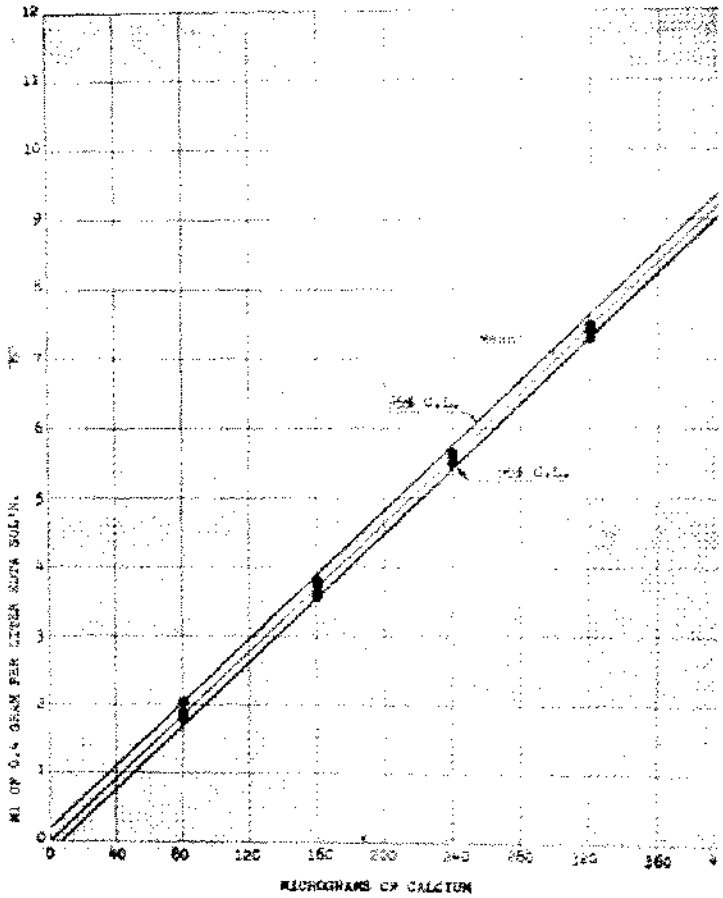

Figure 6. Titration of calcium in water and 3% NaCl solution at pH 10.00 and 12.50 (solution temperature = 23.5° C).

SUMMARY

The procedure described is very good for determining calcium and magnesium in high purity salt. To obtain reproducible results, it is necessary to (1) precisely adjust the pH, (2) standardize the chemical reagent solutions, and (3) titrate the unknown brine solutions at a temperature of 23-24°C.

APPENDIX

Preparation of Pure NaCl

It is difficult to obtain sodium chloride with very low and known impurity levels. In fact, to my knowledge, it is not possible to commercially purchase such a sample. This leaves the purification to the individual who desires such a pure sample.

One way of positively determining whether or not a salt sample has been sufficiently purified with respect to one or more ions is to add radioactive tracers to the salt solution. The salt is purified and then the activity of the salt sample is measured to determine if all of the impurity has been removed. Many people do not have such facilities or such equipment and one must resort to other methods.

In our laboratory, we use bromine analysis as an index of the degree of purification. Bromine forms a solid solution with salt. If the salt contains little or no bromine after purification, we feel that the other impurities have been reduced to very low levels.

The following is the method used in this laboratory for the purification of the salt, which was used for standardization of the solutions for the EDTA determination of Ca and Mg.

Ten thousand grams of reagent grade NaCl are placed in a table top buchner funnel fitted with filter paper. The funnel opening is plugged with a rubber stopper and 2% HCl solution is added to just cover the salt. After the salt has soaked for one-half hour, the acid is removed by applying suction to a suction flask connected to the funnel. De-ionized water is then added to the salt, to barely cover the salt. After soaking for one-half hour the water is removed by suction.

The salt is dissolved in water and the resulting solution is filtered through # 42 filter paper. The filtered solution is transferred to a 22-liter round bottom flask equipped with a heating mantle, a mechanical paddle stirrer and a condenser.

The solution is continuously stirred while boiling. After one liter of water has evaporated, the heat is turned off and the solution allowed to cool. The crystals are filtered and discarded. The solution is returned to the flask and the water evaporated until a thick slurry of solution and crystals is formed. Heating is discontinued but the agitation is continued until the slurry has cooled. The continued agitation prevents the caking of the crystals during cooling.

The crystals are separated by filtration and are washed twice by flooding the crystals twice with water. Suction is applied to remove the water each time. The crystals are dried in porcelain or pyrex dishes at 50-110°C. Occasionally the crystals are mixed to keep caking to a minimum.

A typical analysis of starting salt, washed salt and recrystallized salt is given below:

	Ca (ppm)	Mg (ppm)	Br (ppm)
Reagent Grade Salt	6.4	0.2	4
Acid Washed Salt	1.8	0.1	
After Crystallization	Not Measured		Not Detectable

We assumed that the calcium and magnesium levels were very low in the recrystallized salt because the bromide ion, which forms a solid solution with salt dropped from 4 ppm to an undetectable level.

Solutions, Indicators, Chemicals and Equipment

Below are the solutions, indicators, chemicals and equipment used in this laboratory in determining trace amounts of calcium and magnesium in salt. The solutions are prepared with reagent grade chemicals and deionized water.

Solutions

5% KCN solution -- Dissolve 25 g and dilute to 500 ml.

10% $NH_2OH \cdot HCl$ -- Dissolve 50 g and dilute to 500 ml.

Buffer solution -- Mix 5 g magnesium EDTA, 67.5 g NH_4Cl and 570 ml concentrated NH_4OH and dilute to one liter.

50% KOH -- Dissolve 500 g KOH in 500 ml of H_2O. Store in plastic container. Dispense from 250 ml polyethylene wash bottle.

20 g/l EDTA solution -- Dissolve 10 grams and dilute to 500 ml.

4 g/l EDTA solution -- Dilute 200 ml of 20 g/l solution to one liter.

0.4 g/l EDTA solution -- Dilute 100 ml of 4 g/l EDTA solution to one liter.

4,000 ppm Ca solution -- Dry the $CaCO_3$ at 285°C for 2 hours and weigh 2.4973 grams. Place in 250 ml erlenmeyer, add 100 ml of H_2O, cover with funnel and slowly add HCl through funnel until $CaCO_3$ is completely dissolved. Gently boil to expel CO_2 and dilute to 250 ml in volumetric flask. This solution contains 4,000 ppm Ca.

400 ppm Ca solution -- Dilute 100 ml of preceding solution to one liter. This solution contains 400 ppm Ca or 400 ug/ml.

40 ppm Ca solution -- Dilute 100 ml to one liter. This solution contains 40 ug Ca/ml.

Indicators and Other Chemicals

Hardness Indicator (Ca and Mg at pH 10) -- Betz # 290
Betz Laboratories, Gellingham and Worth Sts.,
Philadelphia, Penn.

Calcium Indicator -- Calver II, Catalogue # 281
Hach Chemical Co., Box 597, Ames, Iowa

EDTA -- Titra Ver, Catalogue # 204
Hach Chemical Co., Box 597, Ames, Iowa

Magnesium EDTA -- Catalogue # 242
Hach Chemical Co., Box 597, Ames, Iowa

$CaCO_3$ -- Primary Standard (for standardizing EDTA solutions)
Mallinckrodt Chemical Works, St. Louis, Mo.

Equipment

Beckman Model 76 Expanded Scale pH Meter

Beckman Type E-2 Glass Electrode # 41260

Beckman Fiber Type Calomel Electrode # 39970

Beckman pH 10 Buffer Solution # 3505

Beckman pH 12.45 Packaged Buffer # 22326
Beckman Instruments Inc.
7360 North Lincoln Ave.
Lincolnwood 46, Illinois

Magnetic stirrer and Teflon covered magnetic bar

Illuminator AO Spencer, Model 370A (Sargent # S-58075)
E. H. Sargent and Co.
Chicago, Illinois

10 ml-Microburette

Notes on the Titrations

1. Titrations are carried out in about 300 ml of solution contained in 400 ml pyrex beakers. Stirring is accomplished by a magnetic stirrer. A 1/4-inch styrofoam sheet placed between the beaker and the stirring motor minimizes heating the solution which is being titrated.

2. When titrating for total Ca and Mg at pH 10.00 the electrodes are standardized with a pH 10 buffer. When titrating for Ca at pH 12.50, the electrodes are standardized at pH 12.45 with the packaged buffer. Standardization of the electrodes is necessary at both pH levels because the potentials of the electrodes change with use and abuse.

3. The titrations, for standardizing the solutions in water, are always done at pH 10.00 and 12.50. The titrations, in 300 ml of salt solutions containing 10 grams of salt, are carried out at pH 10.00 and 12.45. This compensation is necessary at the higher pH to correct for the sodium ion effect. With a glass electrode different than the E-2, the compensation may be much higher. It is recommended that only E-2 electrodes be used.

4. The masking agent used depends on the ions to be masked. Cyanide will mask Hg^{+2}, Cd^{+2}, Zn^{+2}, Ni^{+2}, Co^{+2}, Mn^{+2}, Ag^{+1} and Cu^{+1}. Triethanolamine will mask Fe, Al and Mn. Many other masking agents will be found in Welcher's book (Welcher, 1958, p. 71, 75).

5. During the titrations, the pH electrodes should be removed from the basic solution or they will fatigue and indicate the wrong pH. When not in use, the electrodes are stored in about a 1% HCl solution (pH of solution is about 0.5 to 2).

6. In the determination of unknown Ca and Mg in salt solutions, the solutions are acidified prior to adding the reagents. The pH is then adjusted to about 6 with 50% KOH and the reagents added. The final pH adjustment is made with 50% KOH. Salt solutions that are titrated for Ca and Mg at pH 10.00 can be titrated immediately with the EDTA solution. Salt solutions that are titrated for Ca in the presence of Mg at pH 12.50 must be allowed to stand for 20 minutes after the pH adjustment. This is to allow traces of Mg to precipitate. Final pH adjustment is made just prior to titration.

Notes on the Standardization

The techniques described so far have been the techniques used by us in developing the analytical method for determining Ca and Mg in NaCl. We feel that certain changes would improve and simplify the procedure. For example, instead of adding 1/2 ml each of hydroxylamine hydrochloride and of potassium cyanide, we would prefer to add one ml. Therefore, instead of dissolving 25 grams of potassium cyanide in 500 ml of H_2O, we would dissolve 25 grams in one liter. The same applies to the hydroxylamine. Instead of diluting to exactly one liter, we dilute to about 1,100 ml so that we will have exactly one liter to which to add the calcium and EDTA. This procedure simplifies measuring exact volumes.

By making this change, it is not necessary to add as much calcium to the hydroxylamine hydrochloride in the standardization. Also, there is less chance of error in pipetting one ml rather than one-half ml.

Addition of Ca to $NH_2OH \cdot HCl$

In the standardizations of the reagents, titrations are first made at pH 10.00 and 12.50. These titrations should be carried out at 25°C $\pm$ 5°C to improve the precision. The data obtained would be similar to Fig. 1. The equation of the lines can be calculated by the method of least squares and the intercepts calculated. The intercepts can also be readily obtained by a graphical plot similar to Fig. 1. From the intercepts it is a simple matter to calculate the quantity of Ca to add to the hydroxylamine hydrochloride and the quantity of EDTA to add to the buffer. We use the following equations for the calculations:

$$\frac{A \cdot B}{C+A} = D$$

Where A = ml of 4,000 ug/ml Ca solution to add to $NH_2OH \cdot HCl$

B = strength of Ca solution = 4,000 ug/ml

C = ml of hydroxylamine hydrochloride solution

D = micrograms of Ca to add to each ml of $NH_2OH \cdot HCl$

In our example (Fig. 1), 120 micrograms of Ca could not be detected. Therefore:

$$\frac{A \cdot 4,000}{1,000 + A} = 120$$

or A = 30.93 ml of the 4,000 ppm Ca solution.

If 30.93 ml of the 4,000 ppm Ca solution is added to one liter of hydroxylamine solution, each ml of hydroxylamine will contain 120 micrograms of Ca. Therefore, we will be able to detect a few micrograms of calcium in an unknown.

Addition of EDTA to the Buffer

Using Fig. 1 again for our example, we see that we have to add sufficient EDTA solution to the buffer to complex the free metallic ions equivalent to 16 micrograms of Ca which is contained in the various solutions. We also have to add sufficient EDTA to the buffer to complex the 120 micrograms that will be added with the $NH_2OH \cdot HCl$. Therefore, we will have to add EDTA to the buffer to complex 136 micrograms of Ca.

From the slope we calculate that one ml of 0.4 g/l EDTA solution will complex 43.37 micrograms of Ca. However, since we will be adding a 20 g/l EDTA solution to the buffer, the calcium equivalency of this strong solution is 43.37 × 50 = 2,169 micrograms of calcium. We can use a formula similar to the one preceding to calculate the quantity of EDTA to add to exactly one liter of buffer.

$$\frac{W \cdot X}{Y+W} = Z$$

Where W = ml of EDTA equivalent to 2,169 ug Ca per ml EDTA solution to add to buffer

X = strength of EDTA solution, 2,169 ug Ca/ml EDTA

Y = ml of buffer solution

Z = micrograms of calcium equivalent to EDTA required

In our example (Fig. 1), we need sufficient EDTA equivalent to 136 micrograms of calcium per ml of buffer.

Therefore,

$$\frac{W \cdot 2,169}{1,000 + W} = 136$$

or W = 66.90 ml of the 20 g/l EDTA solution.

When the additions have been made, the titrations at pH 10.00 and 12.50 should be identical and should pass through the origin. These standardized solutions should be stored in polyethylene bottles and aliquots of about 200 to 250 ml should be used as working solutions. These standardized solutions are sufficient for well over 1,000 determinations. If very many determinations are contemplated it may be advisable to prepare 2-5 liters of standardized solutions and of EDTA solutions.

After standardizing the solutions, it may be well to titrate 400 micrograms of Ca in water and 3% salt solution (10 grams of pure NaCl in 300 ml of water) at pH 10.00 and 12.45 and at 20, 25 and 30°C to determine the temperature where the titers are equivalent. This would be equivalent to obtaining data similar to Table III and Fig. 5. Once the temperature has been determined unknowns may be determined with confidence.

BIBLIOGRAPHY

Chaberek, S., Martell, A. E., 1959, Organic Sequestering Agents, New York, John Wiley and Sons, 616 p.

Ringbom, A., 1963, Complexation in Analytical Chemistry, New York, Interscience Publishers, 395 p.

Schwarzenbach, G., 1957, Complexometric Titrations, New York, Interscience Publishers, 132 p.

Welcher, F.J., 1958, The Analytical Uses of EDTA, Princeton, Von Nostrand, 336 p.