THE EFFECT OF HYDROGEN ION CONCENTRATION 
UPON THE DETERMINATION OF CALCIUM.

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McCrudden’s (1, 2) method has come to be recognized as the best for the accurate determination of calcium. The method is to precipitate the calcium as oxalate in the presence of sufficient ammonium chloride to hold the magnesium oxalate in solution, and of sufficient acid to hold the calcium oxalate partly in solution. Sodium acetate is then added to decrease the acidity and to precipitate the rest of the calcium oxalate on the crystals already formed. Thus, large crystals are made which are easy to filter and are not contaminated with occluded magnesium or calcium phosphate.¹ The amount of acetate is selected so as to give a solution not acid enough to dissolve the calcium oxalate, nor alkaline enough, if cold, to allow calcium phosphate to precipitate. These directions are empiric and must be followed accurately, as the author cautions.² Just what determines the amount of acetate is not definite, for he states that in the ash of feces 15 instead of 8 cc. are required.³

The sodium acetate added regulates the acidity of the solution. Unfortunately, at the time McCrudden wrote his article, Sörensen’s (3), Michaelis’ (4), and Clark’s (5) monographs on hydrogen ion concentration were not published. In 1913, Hildebrand (6) of the Bureau of Standards showed the necessity of a systematic investigation of analytical methods with regard to the hydrogen ion concentration. Such information is not as yet available for

² McCrudden (1), p. 100.
³ McCrudden (2), p. 198.
many types of analysis. Except that of Kramer and Tisdall (7) there is none for calcium. We have, therefore, critically examined McCrudden's method in relation to hydrogen ion concentration.

Theory Underlying the Precipitation of Calcium as Oxalate.

The determination of calcium in the presence of magnesium and phosphate depends primarily upon the solubility product of the various precipitates involved; secondarily, upon the hydrogen ion concentration. As a development of the last 30 years in the chemistry of solutions, the theory of ionization has been applied to the problem of precipitation of nearly insoluble substances with great success.

Solubility Product.—Stieglitz (8) and Noyes (9) have presented very carefully in their manuals of qualitative analysis the relation between ionization and precipitation. The basic principle is the mass law, which can be stated.

\[
\frac{(A^+)(B^-)}{(A\text{ }B)} = K
\]

In non-mathematical terms, when a substance is present in water an equilibrium is established between the concentration of the undissociated salt in solution and the concentration of the ions. The value, \(K\), is a constant depending upon the nature of the particular salt. Or, when there are two ions present which form an insoluble compound, precipitation occurs until the product of the concentration of the ions divided by the concentration of undissociated salt is a constant which is the \(K\) for that salt.

A simpler relation which holds with sufficient accuracy for practical purposes is that the product of the ions is a constant. This constant is known as the "solubility product."

\[
(A^+)(B^-) = K
\]

Obviously, we decrease the amount of either ion present by increasing the other ion. If we double \(A^+\) we halve \(B^-\). Hence, adding more \(A^+\) causes more and more complete precipitation

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4 The question of the problem of occlusion and the conditions for obtaining large crystals have been discussed by McCrudden (1), p. 99.

6 Parentheses about a symbol mean concentration. Thus, \(\text{H}^+\) means hydrogen ion; \((\text{H}^+)\) means hydrogen ion concentration.
of $B^-$. Thus, one adds an excess of oxalate ions, so that the calcium is more completely precipitated. The value of the solubility constant is very important for it determines which salt will precipitate. The salt having the smaller solubility product will precipitate and the other will remain in solution. If all the factors are known a quantitative expression can be calculated rigorously from the mass law. The solubility product determines whether calcium will be precipitated as a phosphate or carbonate or oxalate in solutions containing these acids. The solubility products of the various salts to be considered are given in Table I.

Effect of Hydrogen Ion Concentrations.—Acids on dissociation always give hydrogen ions, $H^+$. The extent of the acidity depends upon the concentration of the hydrogen ions, $(H^+)$ (10). The effect of hydrogen ions in precipitation can best be discussed under three heads: (a) the effect on basic salts, (b) the change in the ionization constant of the acid radicals, and (c) the suppression of ionization of weak acids.

The effect of acid on basic salts is to depress the ionization of the hydroxyl ions; for substances in solution are related to the ionization of water. Water itself gives $H^+$ ions and also $OH^-$ or basic ions. The relation of the ions is expressed by the mass law:

$$\frac{(H^+)}{(OH^-)} = 10^{-14}$$

When one adds $H^+$ ions to water one depresses the ionization of the hydroxyl ions since the product of these ions is a constant. Thus, in the case of magnesium hydroxide, by adding acid one decreases $(OH^-)$ to such an extent that in acid solution its solubility product is never reached and hence no magnesium hydroxide can precipitate.

By adding acid one changes the ionization constant of the acid. Thus, in the case of the tri-basic phosphate the addition of $H^+$ ions gives the following reaction:

$$\text{PO}_4^2- + H^+ = H\text{PO}_4^- + H^+ = H_2\text{PO}_4$$

The tri-basic salt can only exist in alkaline solution and as one increases the hydrogen ion concentration the di-basic and monobasic salt must be formed. Thus, in an acid system there is no calcium phosphate but only the more soluble di-basic and mono-
basic calcium phosphates. The solution, if quite acid, about pH 3.0, will have the same effect on calcium oxalate.

\[ \text{H}^+ + (\text{C}_2\text{O}_4) \rightleftharpoons (\text{H}_2\text{C}_2\text{O}_4) \]

By adding acid to a solution containing ions of a weak acid one converts the highly ionized salt into a slightly ionized acid, according to the equation:

\[ 2\text{H}^+ + (\text{C}_2\text{O}_4) \rightleftharpoons \text{H}_2\text{C}_2\text{O}_4 \]

Thus one removes oxalate ions from the solution by adding acid. If the ionization is repressed below the solubility product no precipitate is formed.

Each of these factors: the effect on basic salts, the change in the ionization constant of the acid, and the suppression of ionization, influence the precipitation. Therefore, we shall consider each of the salts that may be formed in the course of the analysis of calcium in the presence of magnesium and phosphates, in an acid solution of pH 4.0 to 6.2.

**Calcium Oxalate and Magnesium Oxalate.**—These salts are precipitated in the presence of an excess of oxalate ions. The question is whether there is any danger of precipitating magnesium with the calcium. This has been discussed in part by Kramer and Tisdall (7). The solubility product of these salts is sufficiently different so that Gooch (11) recommends that even in the presence of ten times the amount of magnesium it is not necessary to carry out double precipitation. In acid solution this difference in solubility product is even more marked.

Acid added to a solution of calcium and magnesium oxalates favors the precipitation of the calcium in two ways. It forms the acid salts which are more soluble. The acid salt of calcium oxalate, at this acidity (pH 4.0 to 6.2) is not formed in sufficient amount to have any appreciable effect on the solubility. No study of the magnesium salts has been made, but from general evidence it is concluded that this would be more readily affected by acids and hence more soluble.

Second, the addition of acid suppresses ionization, in this case from about 40 to about 30 per cent. The diminished ioniz-
tion affects the calcium oxalate much less than the magnesium oxalate as the former has a much smaller solubility product. Any acidity not great enough to form acid calcium oxalate will be a factor in preventing the formation of magnesium oxalate and in favoring the precipitation of calcium oxalate.

*Magnesium Hydroxide and Magnesium Ammonium Phosphate.*—

Both salts are extremely insoluble but since they do not occur in acid solutions they do not precipitate. Hildebrand (6) says that the former precipitates at pH 7.4 to 8.0 and that the latter first appears at pH 6.6.

*Mono-, Di-, and Tri-Basic Calcium Phosphate.*—The salts of calcium form a very difficult problem since as found by Cameron (12) and his collaborators and many others, these salts vary in their composition according to the source, are decomposed by water, and take months to come to equilibrium.

For orientation we attempted to find the pH of saturated solutions of the mono-, di-, and tri-basic salts of calcium phosphate. These salts (Baker’s analyzed) were washed with distilled water. The acidity of the supernatant liquids, determined by the colorimetric method (5), became roughly constant at room temperature in 24 hours and gave the following values:

\[
\begin{align*}
\text{CaH}_4(\text{PO}_4)_2 & = \text{pH 5.0} \\
\text{CaH}_2\text{PO}_4 & = \text{pH 7.4} \\
\text{Ca}_2(\text{PO}_4)_2 & = \text{pH 6.8}
\end{align*}
\]

We found that no calcium solution more acid than pH 4.0 which contained phosphates yielded a precipitate after boiling, but Patten and Mains (13) report a precipitate at pH 2.3 at 26°. But the more acid the point at which these salts precipitate, the greater is the proportion of phosphate to calcium. And, as one can see by glancing at Table I, the more acid the salt the greater is the solubility product. Therefore, at pH 4.0 to 6.4 there is no danger of any calcium being present as phosphates. At this acidity the calcium phosphates have a solubility product more than a million times as great as calcium oxalate. Breazeale (14) remarks it is quite safe to precipitate calcium phosphate quantitatively as calcium oxalate by adding oxalic acid. Therefore, there is no danger of the precipitation of calcium acid
pH and Determination of Calcium

phosphate if the precipitation of calcium oxalate is carried out at the proper acidity.

**TABLE I.**

*Data on Solubilities.*

<table>
<thead>
<tr>
<th>Salt,</th>
<th>Per liter</th>
<th>Mols per liter</th>
<th>Solubility product</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaC₂O₄</td>
<td>0.0055</td>
<td>0.000044</td>
<td>1.9 × 10⁻⁹</td>
</tr>
<tr>
<td>Mg(OH)₂</td>
<td>0.009</td>
<td>0.00015</td>
<td>3.5 × 10⁻¹²</td>
</tr>
<tr>
<td>MgNH₂PO₄</td>
<td>0.05</td>
<td>0.0068</td>
<td>3.0 × 10⁻⁷</td>
</tr>
<tr>
<td>MgC₂O₄</td>
<td>0.302</td>
<td>0.0027</td>
<td>4.8 × 10⁻⁶</td>
</tr>
<tr>
<td>Ca₃(PO₄)₂</td>
<td>0.01</td>
<td>0.00033</td>
<td>2.8 × 10⁻¹⁸</td>
</tr>
<tr>
<td>CaH₂PO₄</td>
<td>0.2</td>
<td>0.00147</td>
<td>2.0 × 10⁻⁸</td>
</tr>
<tr>
<td>CaH₄(PO₄)₂</td>
<td>16.0</td>
<td>0.77</td>
<td>4.0 × 10⁻¹</td>
</tr>
</tbody>
</table>

* The figures are compiled from Landolt-Börnstein, Physikalisch-Chemische Tabellen; A. Seidell, The solubilities of inorganic substances; The Chemische Kalender, 1914—Dictionary of Solubilities, etc.

**EXPERIMENTAL APPLICATION OF THE THEORY.**

It is important to verify, first, the most acid limit of acidity; second, the least acid limit; and third, the best method of obtaining the desired acidity.

*Most Acid Limit.*—The most acid limit is the point at which calcium oxalate begins to be converted into the more soluble acid calcium oxalate. McCrudden has determined the amount of sodium acetate, which, under the conditions of his procedure will prevent the solution of calcium oxalate.⁶ We determined colorimetrically the hydrogen ion concentration of solutions precipitated according to his directions. In all solutions more acid than pH 4.4, which contain less than 6 cc. of sodium acetate, the results are low. Further experiments in Table II show that correct determinations are made at pH 4.0, which is, therefore, the most acid limit for the determination of calcium oxalate.

*The Least Acid Limit.*—The least acid limit is the point at which magnesium ammonium phosphate and magnesium hydroxide precipitate. According to Hildebrand this is pH 6.6 to 7.6. To fix this point experimentally we carried out the precipitation

⁶ McCrudden (1), p. 90.
TABLE II.

The Amount of Sodium Acetate and the Resulting Acidity.*

<table>
<thead>
<tr>
<th>No.</th>
<th>20 per cent sodium acetate</th>
<th>pH calculated</th>
<th>pH determined</th>
<th>Calcium.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cc.</td>
<td></td>
<td></td>
<td>mg.</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1.3</td>
<td>2.8</td>
<td>30.1</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>2.8</td>
<td>2.8</td>
<td>32.0</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>4.0</td>
<td>4.0</td>
<td>33.1</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>4.4</td>
<td>4.4</td>
<td>33.1</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>4.8</td>
<td>4.8</td>
<td>33.3</td>
</tr>
<tr>
<td>6</td>
<td>20</td>
<td>5.3</td>
<td>5.2</td>
<td>33.1</td>
</tr>
<tr>
<td>7</td>
<td>50</td>
<td>5.7</td>
<td>5.6</td>
<td>33.2</td>
</tr>
<tr>
<td>Theory...</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* In solutions more acid than pH 4.0 the results are low; 50 cc. of sodium acetate are not an excess and give correct results.

of calcium at varying acidities and determined the amount by both the gravimetric and volumetric methods. By this procedure it is possible to determine faulty results and also the cause of error. Titration with permanganate determines the oxalates. If phosphates are present and contaminating the calcium oxalate they will not affect the result. By the gravimetric method one determines the calcium as oxide and the oxalates are destroyed. Phosphates will cause the results to be too high. Reasoning thus, one can deduce the following:

<table>
<thead>
<tr>
<th>Precipitate consisting of:</th>
<th>Method.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium oxalate alone....</td>
<td>Gravimetric.</td>
</tr>
<tr>
<td>&quot; &quot; and calcium phosphate</td>
<td>Correct.</td>
</tr>
<tr>
<td>&quot; &quot; magnesium ammonium phosphate</td>
<td>High.</td>
</tr>
<tr>
<td>Calcium oxalate and magnesium oxalate</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot; &quot; &quot; &quot; &quot; hydroxide.</td>
<td>Correct.</td>
</tr>
<tr>
<td>&quot; &quot; &quot; &quot; &quot;</td>
<td>Correct.</td>
</tr>
</tbody>
</table>

Therefore, we took samples of calcium chloride. To these we added phosphates and made determinations by both volumetric and gravimetric methods at pH 7.4. Correct results were obtained by both. To a second sample we added magnesium sul-
fate and made determinations by both methods at pH 7.4. Correct results were obtained by both. Then to a third series of samples we added both phosphates and magnesium. The acidity was adjusted by ammonia to pH 5.6 to 7.4. The results are given in Table III.

From these data it is clear that in the precipitation of calcium oxalate, neither magnesium oxalate nor hydroxide give false results if no phosphate is present. Calcium phosphate does not give false results even in slightly alkaline solution when no magnesium is present; but if magnesium is also present, magnesium ammonium phosphate precipitates if the solution is more alkaline than pH 5.6.

<table>
<thead>
<tr>
<th>Substance present.</th>
<th>pH</th>
<th>Gravimetric Ca.</th>
<th>Volumetric Ca.</th>
<th>Ca present.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca and PO₄</td>
<td>7.4</td>
<td>84.9</td>
<td>84.4</td>
<td></td>
</tr>
<tr>
<td>Ca and Mg</td>
<td>7.4</td>
<td>84.8</td>
<td>84.4</td>
<td></td>
</tr>
<tr>
<td>Ca, Mg, and PO₄</td>
<td>5.6</td>
<td>84.9</td>
<td>84.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>86.0</td>
<td>84.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.6</td>
<td>92.0</td>
<td>84.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.0</td>
<td>94.3</td>
<td>84.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.4</td>
<td>100.2</td>
<td>84.8</td>
<td>84.6</td>
</tr>
</tbody>
</table>

* The least acid limit for the determination of calcium oxalate by the gravimetric method is pH 5.6. At points less acid magnesium ammonium phosphate is precipitated.

The Best Method of Obtaining the Desired Acidity.—When sodium acetate is added to a mixture of hydrochloric and oxalic acids, the stronger acids form salts with sodium and there remains in the solution acetic acid in the presence of acetates. This is an excellent buffer mixture and regulates the hydrogen ion concentration. If one knows the ratio of the acetic acid to the sodium acetate, with Walpole's (15) chart, one can estimate the pH. This is given in Table II under the column "pH calculated." How closely this approximates the pH as actually determined is shown by comparing these values with those given in the same table under the column "pH determined." As the ratio of acetic acid to sodium acetate becomes smaller the pH approaches 7.0 as a limit.
McCrudden's fear that calcium phosphate would precipitate unless there were between 6 and 10 cc. of sodium acetate is groundless. To test this point experimentally we made up a solution containing 2 cc. of 10 per cent calcium chloride, 2 cc. of 10 per cent magnesium sulfate, and 2 cc. of 10 per cent sodium acid phosphate. These we precipitated according to McCrudden's directions: 10 cc. of 0.5 N hydrochloric acid, 10 cc. of 25 per cent oxalic acid, 10 cc. of 3 per cent ammonium oxalate, cooled and to them added varying amounts of 20 per cent sodium acetate solution. The results are shown in Table II. Thus, even 50 cc. of acetate are not an excess and give correct results.

We found, by experiment, that it makes no difference whether one regulates the acidity by acetic acid and sodium acetate mixtures or more conveniently and quite as accurately by adding ammonia to the acid phosphates present. We have, therefore, developed a method based upon this conclusion, the details of which are given in the following paper.

Limits of Acidity.—From the above discussion it is clear that the limits of acidity for the precipitation of calcium by oxalic acid in the presence of magnesium and phosphates are determined. The most acid limit is pH 4.0. If the solution is more acid than this the calcium oxalate is partly converted into acid calcium oxalate which is so soluble that it is not quantitatively precipitated. The least acid limit is pH 5.6. If the solution is less acid appreciable amounts of magnesium ammonium phosphate precipitate and contaminate the calcium oxalate.

SUMMARY.

The hydrogen ion concentration is an important factor in making a calcium determination. If the solution is more acid than pH 4.0 calcium oxalate is dissolved. If the solution is less acid than pH 5.6, magnesium ammonium phosphate is precipitated.

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