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A Systematic Study of the Purification of
Oxalic Acid

A SYSTEMATIC STUDY OF THE PURIFICATION
OF OXALIC ACID

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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A C K N O W L E D G M E N T

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A SYSTEMATIC STUDY OF THE PURIFICATION OF OXALIC ACID
I N T R O D U C T I O N

It is necessary at times to obtain pure oxalic acid for use in the laboratory. Inasmuch as it is impossible to get absolutely pure acid on the market it becomes necessary to prepare the pure product. This is usually done either by purifying the commercial acid or by preparing a pure product from recrystallized sugar and redistilled nitric acid. The purification of commercial oxalic acid may be effected in either of two ways, by recrystallization from solvents, or by sublimation of the pure acid from the impurities.

It is the purpose of this investigation to study the purification of oxalic acid with the hope of obtaining some information which will be of service in the preparation of the pure product.

H I S T O R I C A L

Various authors prescribe different methods for the purification of oxalic acid. However, there seems to be no available data which gives an accurate idea of the purity of the product. Neither is there any data which enables one to compare the different methods used.

Siebold*, in a paper read before the Pharmaceutical Society of Great Britain in December, 1875, states that the standard of purity of oxalic acid required by the British Pharmacopoeia is unattainable by the official process, for the mere recrystallization of the commercial acid from its solution in boiling water never yields a product which is entirely dissipated by heat below 350°. The alkaline oxalates are less soluble in oxalic acid than in water and, therefore, crystallize out with the oxalic acid instead of remaining in the mother liquor. Some chemists have expressed a doubt that perfectly pure oxalic acid can be at all produced from the commercial article and prefer the acid prepared from sugar for quantitative analysis. Siebold recommends the following procedure:

"Agitate the produced commercial acid with five times its weight of distilled water at about a hundred degrees F. for some time, allow the mixture to stand in a cool place for about six hours and then filter the solution, evaporate it to about two-thirds of its original bulk and stir well while it is cooling. Collect and wash on a filter the crystals which have been

*Pharm. Jour. & Trans. (3) 6, 441 (1875-76).

formed, and purify them twice by recrystallization from boiling distilled water. The acid obtained leaves absolutely no residue on ignition in platinum." He also quotes Stolbe who recommends the recrystallization from hot HCl and then from boiling distilled water and adds that the product thus produced is less satisfactory than that produced by the method just outlined. Sublimation yields a very pure product but is an exceedingly wasteful process.

Schmatolla* describes the following procedure.

"Dissolve 50 grams of commercial oxalic acid in 120 grams of absolute alcohol on a water bath. Allow this to cool and settle. The solution is then filtered to remove any sludge which may separate out, and two or three drops sulphuric acid (1:2) is added. Allow this to stand over night and then distill off the alcohol. Dissolve the residue in 200-300 cc water and separate the heavy oil which is formed as an impurity by the action on the alcohol. Filter and crystallize out the oxalic acid. These crystals are absolutely pure."

Ruchelman# describes a method of preparation of pure crystals as follows:

"Crystallize the commercial acid once from ether and then once from water". He also states that comparatively large quantities of acid may be conveniently dissolved in ether by using a Soxhlet's extractor fitted with a Schliecher and Schull's cartridge.

* Apoth. Zeit. 16, 194 (1901)

#Zeit. Öffentl. Chemie. 3, 131.

T H E O R E T I C A L

From the preceding brief review of the literature on the purification of oxalic acid, it becomes apparent that the crystallization from solvents is the preferred method. Crystallization of the pure acid from the mother liquor containing the impurities is based upon a difference in degree of saturation of the substances present. The oxalic acid, being in such a large excess over the impurities, causes the solution to become saturated with respect to the oxalic acid before it becomes saturated with respect to any of the other constituents, and the pure acid separates out. Although this is the basic principle, other factors enter in. Crystals in general display the property of including, occluding or ~~a~~^d sorbing impurities. The term inclusion will be used to mean a mechanical including parts of the mother liquor having a composition the same as the mother liquor. Occlusion will be used to mean a selective including of impurities, namely, taking one constituent in larger amount than the others. By ~~a~~^d sorption will be meant a concentration of the constituents on the surface of the crystals.

If the impurities are ~~a~~^d sorbed, the large crystals will have a smaller percentage of impurities than the small ones because the larger crystals have a smaller total surface for a given mass than the smaller ones. If the impurities were included or occluded, this would not be true. The crystals would then have either the same amount of impurities independent of the size of the crystal because the impurities are distributed

throughout the entire volume of the crystal and therefore the phenomenon is a volume phenomenon and not a surface phenomenon, or the larger crystals would have the great percentage of impurities because of the possibility of the formation of larger pockets, which would contain impurities, in the larger crystals. In either case of occlusion or inclusion the smaller crystals would contain either the same amount of or a smaller amount of impurities than the large crystals.

By an analysis of crystals prepared so that one portion was made up of large crystals while another was made up of small crystals, it could be determined how the impurities were taken up, or at least, whether they were ^d absorbed or not.

Oxalic acid has the property of a greatly increased solubility with an increase of temperature.

TABLE I*

Solubility of Oxalic Acid is 100 Parts of Water.

Temperature (Centigrade)	Parts of Oxalic Acid
0	3.45
10	5.55
20	8.75
25	11.36
30	13.77
40	21.15
50	31.53
60	45.55
70	63.82

*Seidell. Solubilities of Inorganic and Organic Compounds.

From the above table it is evident that if a solution saturated at a high temperature were allowed to cool the crystals of acid would separate out. This property is made use of in the purification by recrystallization.

E X P E R I M E N T A L

The above theoretical discussion suggested the following procedure:

First, the temperature at which to begin crystallization was determined. Siebold mentions crystallization from boiling water.

A quantity of commercial acid was dissolved in an evaporating dish on a hot plate and the temperature measured. It was found that when a temperature above 80°C . was reached some of the oxalic acid sublimed off from the hot sides of the container and made the air in the room almost unbearable. It was also found, and this was more important, that when the acid crystallized out from a solution at 100°C . the quantity of mother liquor remaining was so small that there was great probability that some of the impurities would separate out and contaminate the crystals. At 70 to 75°C ., however, the quantity of liquid was great enough to contain all of the impurities and the probability of contamination was greatly reduced. For this reason the crystallizations were carried on at from 70 to 75°C .

With this in mind a quantity of commercial acid was dissolved in distilled water so that the solu-

tion after filtering to remove any undissolved solids was divided into two parts. One part was cooled rapidly stirring continually while crystallization was taking place in order to produce the very fine crystals commonly known as "crystal meal", the other portion was allowed to cool slowly without any stirring, thus producing large crystals. Here it was thought advisable to compare the thoroughness of draining with a centrifuge and draining through a Büchner funnel. Consequently, each of the above portions was divided into two smaller portions. One of each, large and small crystals, was drained with centrifuge running (800 R. P. M.) while the other portions were drained in a Büchner funnel. The drained crystals were spread out on paper covered with paper to prevent contamination by dust particles and allowed to dry in the air for several days, stirring frequently to break up any crust which formed. When the crystals were thoroughly air dried they were crushed with a glass tube so as to pass a twenty mesh sieve. The mass was then "conned and quartered" until the two opposite quarters weighed approximately two hundred fifty grams. This sample was then put into a clean glass stoppered bottle and labeled. These samples were analyzed for non-volatile residue by igniting in a porcelain crucible over a low

Bunsen flame and the following results were obtained:

TABLE II

Per cent non-volatile residue

Original commercial acid .15

	Fine Centrifuge	Fine Büchner	Coarse Centrifuge	Coarse Büchner
First	.057	.047	.059	.056
Recrystallization	.057	.047	.052	.056

These results showed that the Büchner funnel was about as good as the centrifuge as a draining agent and that the "crystal meal" is somewhat purer than the coarse crystals.

Because of the small percentage of impurities a new set of samples was prepared. Some commercial acid was dissolved in water until saturated at 70 - 75° C. and the following impurities were added CaCl_2 , NaCl , FeSO_4 , $\text{Fe}(\text{NO}_3)_2$. The impurities were added so that the residue after ignition could be more readily analyzed and more accurate data could be obtained. Calcium and sodium were selected because previous writers claimed that the alkali metals were difficult to remove. Iron was added because it was found to be present in the original acid. The SO_4^- , Cl^- , NO_3^- ions were added so that data concerning their removal could be obtained. The above saturated solution was filtered to remove any undissolved solids, and then cooled. The crystals obtained were used as the starting

point for purification. They were air dried and sampled and then dissolved in distilled water forming a saturated solution at 70°C. This solution was divided into two parts and crystallized and drained exactly as described above. After sampling each portion the remainder was again dissolved in distilled water and crystallized exactly as it had been before. This was repeated as far as possible giving the following samples:

Original Crystals			
"Crystal Meal"		Coarse Crystals	
Centrifuge	Büchner	Centrifuge	Büchner
First Recrystallization	First Recrystallization	First Recrystallization	First Recrystallization
Second Recrystallization	Second Recrystallization	Second Recrystallization	Second Recrystallization
Third Recrystallization	Third Recrystallization	Third Recrystallization	Third Recrystallization
etc.	etc.	etc.	etc.

The samples obtained were analyzed for non-volatile residue, chloride, sulphate, nitrate and sodium.

The analysis for non-volatile residue was made on approximately fifty gram samples. A porcelain crucible weighing approximately 8 or 9 grams was ignited to constant weight and then filled nearly full with the sample and ignited slowly over a Bunsen burner. Great care was taken to prevent loss by dissolving in its water of crystallization and spattering. When this portion had been decomposed or sublimed off another portion from the same weighing bottle was added and the ignition con-

tinued. After the whole sample had been decomposed the residue was ignited to constant weight over a Meeker burner. The results are shown in the following table:

TABLE III

Percentages Non-volatile Residue.

Original sample .639
.645

	"Crystal Meal"		Coarse Crystals	
	Centrifuge	Büchner	Centrifuge	Büchner
First	.42	.40	.36	.46
Recrys.	.39	--	--	.35
Second	.058	.14	.14	.24
Recrys.	.059	.14	.12	.17
Third	.033	.012	.017	.061
Recrys.	.030	.012	.017	.12
Fourth	.027	.0029	----	.0075
Recrys.	.035	.0019	----	.013
Fifth		.0000		
Recrys.		.0000		

The above table indicates that oxalic acid free from non-volatile residue can be prepared by recrystallization from water. Also that "Crystal meal" seems to give a purer product than the coarse crystals which indicates that these impurities are either included or occluded but are not ^d absorbed.

The residues from the above ignitions were dissolved in hydrochloric acid and tested for iron with ammonium sulphocyanate and for calcium in the spectroscope. The results showed that iron and calcium were not removed until recrystallized four times. There was a little insoluble residue left

in the crucible which may have been either dissolved from the crystallizing dishes or formed by the action of the oxides on the crucible.

Analysis for chlorine showed such a small amount present that the ordinary gravimetric and volumetric methods could not be used. In order to make a quantitative determination of the chlorine present a nephelometer was used. Solutions of the samples having a known concentration were compared with solutions containing known amounts of chlorine. For this purpose a .0001 N. sodium chloride solution was prepared by dissolving 5.8500 grams in one litre of solution and diluting this 1000 times. One hundred cc volumetric flasks were calibrated at room temperature and then portions of the oxalic acid samples approximating six grams were weighed accurately and put into them and made up to a hundred cc each. For nephelometer tubes hard glass test tubes all of the same size were used. These after thorough cleansing were filled with distilled water and calibrated against one tube as a standard. The difference in turbidity was used as a glass correction. The procedure followed was that prescribed by T. W. Richards and R. C. Wells*. To each tube was added one cc of redistilled nitric acid free from chlorides and two cc of .02 N silver nitrate. A little distilled water was added and then ten cc of each of the solutions of the samples were added. The tubes were filled to within one-eighth inch from the top and stirred well, thoroughly mixing the solution. The standard tubes were made up in the

* Am. Chem. Jour. 31, 235.

same way except that instead of adding ten cc of the unknown, varying amounts of the standard sodium chloride solution were added. All tubes were allowed to stand in a dark room for about twelve hours and then the turbidities were measured. The results are shown in Table IV.

TABLE IV.

Table Showing Percentages of Chlorine in Various Samples.

	Original Sample (----.0155 ----.0160)	First Crystallization	Second Crystal.	Third Crystal.
Fine Centrifuge		.000775 .000775	.000468	none
Fine Büchner		.000663 .000657	None	"
Coarse Centrifuge		.000372	"	"
Coarse Büchner		.000373	"	"

From this table it may be concluded that the chlorine ion is easily removed none being present after the second re-crystallization. Further, that since the percentage of chlorine is greater in the small crystals than in the large ones, the chloride ion is ^d absorbed by the crystal.

The presence of nitrates was detected by the test described by Merck*. On overlaying 10 cc of a solution of dephenylamine in concentrated sulphuric acid with 10 cc of a (1:10) aqueous solution of oxalic acid a blue zone will appear

*Merck. Chemical Reagents, Their Purity and Tests, (1914).

if nitrates are present. This test showed the complete absence of nitrate even in the original crystals which, as was stated before was crystallized from solution to obtain even crystals. This indicates that nitrates are removed immediately on one recrystallization.

The test for sulphate ion with BaCl_2 according to Merck* showed the presence of a trace of sulphate in the product which had been recrystallized once. After the second recrystallization there was none present.

In testing for sodium the spectroscope could not be used because of a continual bright sodium line. The flame test showed the presence of an appreciable quantity of sodium in the original sample which was completely eliminated after the third recrystallization. The first and second recrystallizations showed a decreasing amount. In the second recrystallization there was only the slightest trace. This indicates that sodium is not so difficult to remove as are calcium and iron.

An experiment was set up to test the efficiency of sublimation as a means of purifying oxalic acid. Several pieces of apparatus were designed and tried out but none would give any quantity of acid and yet permit regulation of the pressure and testing of the gases. As reduced pressure helps distillation and even makes possible the distillation of some easily decomposed substances, it was thought that perhaps oxalic acid would decompose less if sublimed in a vacuum than if sublimed at atmospheric pressure. After many unsuccessful attempts to get any results the apparatus shown in the sketch was designed.

*Merck. Chem. Reagents, Their Purity and Tests. (1914).



Apparatus for Testing the Sublimation of Oxalic Acid.

(a) $\text{Ca}(\text{OH})_2$, (b) H_2O , (c) Preheater, (d) Boat, (e) Iron pipe, (f) Sand, (g) Glass tube, (h) Thermometer, (i) HCl , (j) $\text{Ca}(\text{OH})_2$, (k) H_2O , (l) Manometer, (m) Lead to pump.

A boat full of oxalic acid was placed in the glass tube as shown and the tube evacuated. The furnace was then heated evenly all around and when it reached about 80° the air was allowed to enter the tube in a very slow stream, first passing through the $\text{Ca}(\text{OH})_2$, to remove the carbon dioxide, and then through the preheater where it was heated to about 170° . The pressure in the manometer ranged between twelve and forty millimeters. It was noticed in earlier experiments that it was extremely difficult to get the acid to pass for any length of the tube so it would be allowed to separate out pure. The current of hot air it was thought, would make this possible. However, it was not wholly successful since the acid still deposited itself right above the boat. The temperature in the furnace was increased up to 180° . Even at this temperature and forty millimeters pressure no decomposition could be noticed. Had any decomposition taken place there would have been a precipitate of CaCO_3 in the $\text{Ca}(\text{OH})_2$ solution. Whereas, if any oxalic acid

came over it would remain in the dilute HCl.

The precipitate was wholly absent. From this it may be concluded that oxalic acid is pretty stable and may be heated above its sublimation temperature without decomposition.

SUMMARY AND CONCLUSIONS

From the results of this investigation it may be concluded:

First, that pure oxalic acid can be prepared by recrystallization of the commercial acid from distilled water.

Second, that iron and calcium are more difficult to remove than sodium.

Third, that the sulphate, chloride and nitrate ions are readily removed, the nitrate in one recrystallization, the chloride in two recrystallizations and the sulphate in three crystallizations. The number of crystallizations may vary, however, with the amounts present.

Fourth, that the non-volatile residues are included throughout the mass, the larger crystals having a larger percentage than the smaller ones.

Fifth, that the chlorine appears to be ^{absorbed} since the small crystals have the larger percentage of chlorine present.

Sixth, that the Büchner funnel is about as efficient for draining the crystals as a low speed centrifuge (about 800 R.P.M.).

Seventh, that oxalic acid is stable even at 180° and twelve to forty millimeters pressure.

B I B L I O G R A P H Y

1. Phar. Jour. and Trans. (3) 6, 441, (1875-76).
2. Apoth. Zeit. 16, 194, (1901).
3. Zeit. Offentl Chemie 3, 131.
4. Solubilities of Inorganic and Organic Compounds, Seidell.
5. Am. Chem. Jour., 31, 235.

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