SOLUBILITIES OF SOME CALCIUM MINERALS AND PREPARED CALCIUM COMPOUNDS IN EDTA (ETHYLENE DIAMINE TETRAACETIC ACID) SOLUTIONS

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SUMMARY. — In these studies, the solubilities of calcium minerals such as ulexite, colemanite, pandermite, gypsum, calcite, aragonite and marble and also, phosphate and oxalate compounds of calcium, in 0.1 and 0.2 N aqueous solutions of disodyum EDTA salt, were examined.

The solubility studies were made at room temperature under constant mixing.

During the studies, the calcination products, between 50-900°C, and original forms of the afore-mentioned calcium compounds were used. As a result of the studies it was seen that carbonate and borate minerals were completely dissociated and gypsum, phosphate and oxalate salts were partially dissociated, depending on the conditions. It was also put forward that the solubility occurred according to the principle of complex formation.

Further, by means of these solubility studies it was once more proved that Ca-carbonate minerals and precipitated CaCO3 were thermally decomposed during calcination over 650°C.

Calcination and solubility studies on solid CaC_2O_4 salt showed that this salt was decomposed as

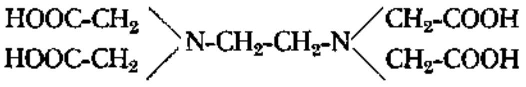
CaC_2O_4 $CaCO_3$ CaO

in detail.

As a result, the reality that the lattice energies of the compounds and the minerals which were examined in this study were overcome by the EDTA, and the EDTA's chelate-forming force was much more than dipole force of water, was put forward.

INTRODUCTION AND A SHORT HISTORY

Aminopolycarboxylic acids, which are generalized in an empirical formula $R\text{-}N(CH_2\text{-}COOH)_2$, are complex-forming compounds. Their most well-known and applicable compound is ethylene diamine tetraacetic acid. This compound is expressed shortly as EDTA with a formula:



EDTA, which has a limited solubility in water, is used in practice in the form of disodium salt. The most well-known names of these compounds are Titriplex III and Complexone III. Sometimes in literature EDTA is shown as H_4Y, too.

Similar to all other chelate-making organic compounds, EDTA also forms very strong complexes which can not be compared with inorganic chelate-making compounds.

Chelates which are formed by EDTA with metal cations are extraordinarily strong, due to the fact that they have many complex-forming functional ends and these complexes are formed by O and N atoms and also the formed rings are 5 membered. The aqueous solutions of complexes formed by EDTA have high thermal stabilities.

EDTA ionizes as

$$HY^{-3} \quad Y^{-4} \quad + \quad H^{+}$$

and lowers the pH of the solution by giving protons. Especially the chelates, which are formed by earth alkali, metals, are very typical and also extraordinarily strong.

In aqueous solutions disodium EDTA (Titriplex III) yields reactions with differently valenced metal cations as shown in the following:

$$Me^{+2} + H_2Y^{-2} \rightleftarrows MeY^{-2} + 2H^{+}$$
$$Me^{+3} + H_2Y^{-2} \rightleftarrows MeY^{-} + 2H^{+}$$
$$Me^{+4} + H_2Y^{-} \rightleftarrows MeY + 2H^{+}$$

In order to form this kind of complexes, the pH of the medium should be somewhat high. However, at very high pH values the equilibrium will shift to the right according to the reaction:

$$MeY^{(n-4)} + nOH^{-} \rightleftarrows Me(OH)_n + Y^{(n-4)}$$

and the efficiency in the complex formation will be reduced.

The chelates which Ca^{++} and $Mg++$ atom ions formed in aqueous solutions are so strong that it is impossible to precipitate these cations with known analytic reactions. If sufficient amount of EDTA exists in a solution containing $Ca++$ and $Mg++$ cations, it is impossible to precipitate these two ions in the forms of $CaCO_3$, $CaSO_4$, $Ca_3(PO_4)_2$, CaC_2O_4, $Mg(OH)_2$, $Mg_3(PO_4)2$, etc.

The principal object of these studies is to see whether the reverse of this typical peculiarity of aminopolycarboxylic acids is valid. That is, in other words, to see to what degree the aminopolycarboxylic acids (in this study EDTA) can dissolve the solid salts of $CaCO_3$, $CaSO_4$, CaC_2O_4, $Ca_3(PO_4)_2$ and Ca-borate which are insoluble in water because of the lower value of their solubility products.

In these solvation tests piece size of the dissolved matter, time, rate of stirring and temperature were chosen as parameters (alternative functions).

The minerals, which are used as materials in these solubility studies, are pandermite and colemanite, in Ca-hydroborate form, ulexite, im Na-Ca-hydroborate form, calcite, arogonite and marble, shown with the formula $CaCO_3$, and gypsum. In case of prepared compounds Ca-oxalate, Ca-phosphate and Ca-carbonate salts are used.

Although many important studies were made about the solubilities of the above minerals in water and other solvents, the researches made by using EDTA or Titriplex III are very limited. Amongst these E.D. Glover's research, in which he tried to extract calcite from clay, soil, etc., by using EDTA; W. E. Hill's and D.R. Evans' researches, in which they studied the comparing solubilities of about 20 minerals in sodium, potassium and ammonium EDTA, can be mentioned.

METHOD AND INSTRUMENTS

A. Obtaining and preparation of the samples

Samples of mineral and prepared compounds and their compositions and the ways in which they are obtained are shown in the following:

1. *Ulexite* ($Na_2O.2CaO.5B_2O_3.16H_2O$). — Completely pure crystals collected from the deposits of Ali Şayakçı Tic. Ltd. Şirketi near the town of Bigadiç in Western Anatolia. (Composition: 7.66 % Na_2O, 13.80 % CaO, 42.80 % B_2O_3 and 35.74 % H_2O.)

2. *Pandermite* ($4CaO.5B_2O_3.7H_2O$). — Completely pure crystals collected from the deposits of Türk Boraks Madencilik A.Ş. at a locality of Sultançayırı, near the town of Susurluk in Western Anatolia. (Composition: 30.48 % CaO, 52.34 % B_2O_3, 17.18 % H_2O.)

3. *Colemanite* ($2CaO.3B_2O_3.5H_2O$). — Completely pure crystals collected from the deposits of Bortaş Madencilik Şirketi at a locality of Kestelek near the town of M. Kemalpaşa in Western Anatolia. (Composition: 27.27 % CaO, 50.80 % B_2O_3, 21.91 % H_2O.)

4. *Gypsum* ($CaSO_4.2H_2O$). — Pure and clean crystals collected from the deposits belonging to Yakal Borasit Ltd. Şirketi at Bigadiç district. (Composition: 32.50 % CaO, 46.50 % SO_3 and 20.29 % H_2O).

5. *Aragonite, calcile, marble* ($CaCO_3$). — Original samples obtained from the collections of the Geology Department of M.T.A. Institute, Ankara.

6. *Calcium phosphate* ($Ca_5(PO_4)_3(OH)$). — Calcium carbonate ($CaCO_3$) and calcium oxalate (CaC_2O_4) compounds were brought from the Merck firm in their original packages.

B. Calcination

In order to compare the solubilities of original minerals and compounds these samples were calcined at 50°, 100°, 150°, 200°, 250°, 300°, 400°.......900°C.

For calcination studies the static method was applied. For this reason the samples were heated at particular temperatures until they came to a fixed weight and then weighed after cooling.

Usually a Hereaus furnace was used. Every time 5.0000 gr from each sample, at aforementioned temperatures, were heated for five hours.

C. Solvation studies

Each time 0.5 gr original and calcined minerals and compounds were taken and put in a 400-ml beaker and then on it 50 ml 0.1 and 0.2 N Titriplex III (ethylene diamine tetraacetic acid disodium salt) solution was added.

The contents of the beaker were mixed by means of a magnetic mixer for 20 minutes and then firstly the pH of the contents was measured; subsequently, if there existed any undissolved residue, it was dried at 105°C for three hours, after filtering from a $2G_4$ crucible and then weighed. These solvation studies were made at normal temperatures. The amount of Titriplex III in the filtered solution was found by back-titrating with n/10 $CaCl_2$ solution and then the amount of spent reagents was confirmed. By this process, gravimetrically obtained solvation results were also confirmed by volumetric methods.

For comparison, the solubilities of these samples in distilled water, under the same conditions were also obtained by gravimetric and volumetric methods.

RESULTS AND DISCUSSION

I. Calcination

As a result of the calcination studies, made by the above process, the losses of mase that the mineral and compound samples undergo at a followed sequence of temperatures, are given in Table 1.

Table - 1

t°C	Ulexite	Pandermite	Colemanite	Gibbsite	Calcite	Aragonite	Marble	Pre. $CaCO_3$	CaC_2O_4	$Ca_5(PO_4)_3(OH)$
50	0.98	0.04	0.04	0.02	0.02	0.02	0.02	0.24	0.04	0.38
100	8.28	0.22	0.13	15.34	0.04	0.02	0.02	0.37	0.10	0.88
150	18.75	0.51	0.22	19.73	0.05	0.04	0.03	0.40	4.93	1.28
200	24.29	0.60	0.22	20.86	0.06	0.05	0.03	0.44	8.84	1.52
250	28.56	1.82	0.36	20.86	0.07	0.06	0.04	0.49	11.98	1.80
300	30.87	5.07	1.47	20.86	0.08	0.07	0.04	0.63	12.00	1.80
350	32.12	5.95	3.09	20.86	0.09	0.07	0.04	0.72	12.40	1.80
400	33.67	9.51	11.20	20.87	0.10	0.07	0.05	0.97	12.92	1.80
450	34.81	15.05	20.08	20.97	0.14	0.08	0.06	1.50	28.96	1.80
500	35.15	17.21	21.88	20.87	0.16	0.09	0.07	1.56	30.88	1.80
550	35.26	17.45	21.88	20.88	0.22	0.10	0.08	1.76	30.94	1.80
600	35.36	17.45	21.88	20.88	0.36	0.47	0.50	2.52	31.20	1.80
650	35.40	17.46	21.88	20.88	2.05	2.10	1.45	5.28	31.82	1.80
700	—	17.46	21.88	20.90	6.75	6.00	7.49	14.71	32.20	1.80
750	—	—	—	20.90	33.01	30.97	31.97	42.02	60.20	1.80
800	—	—	—	20.90	43.87	43.74	43.74	43.44	—	1.80
850	—	—	—	20.90	43.93	43.78	43.78	43.51	—	1.80
900	—	—	—	20.90	43.96	43.78	43.80	43.71	—	1.80

In studying this table, it is seen that:

a. The calcination of the minerals pandermite, colemanite and ulexite is completed almost at the same temperature (500°C) by reaching a fixed weight.

b. The mineral of gypsum is transformed into a fixed compound (anhydride) after 200°C.

c. Calcite, aragonite, marble and precipitated $CaCO_3$ begin to decompose at 650°C.

d. CaC_2O_4 compound, since it is an organic salt, after 700°C by carbonation and oxidation reactions, completely transtorms into CaO.

e. The Ca-phosphate mineral, with the formula $Ca_5(PO_4)_3(OH)$, in its calcination at temperatures to 900°C, transforms into a product with the formula $3Ca_3(PO_4)_2.CaO$ by losing H_2O only.

The main object of calcination of these minerals and compounds is not to investigate their thermal decompositions in detail, because this type of researches was made many times. The object is to obtain destructured minerals and compounds as materials for solubility studies.

The graphics drawn by utilizing the values taken from Table 1, instead of being given independently, will be presented together with the solubility curves.

Since at the calcination of pandermite, colemanite, ulexite and gypsum minerals and $Ca_5(PO_4)_3(OH)$ compound, H_2O, and at the decomposition of calcite, aragonite, marble and precipitated $CaCO_3$, CO_2 are given off, from mass losses shown in Table 1, by a simple computation, it can easily be calculated at what composition these minerals and compounds can be at particular calcination temperatures.

II. Solubility

A. The solubilities of ulexite, colemanite and pandermite minerals in their original and calcined forms, at a sequence of temperatures in distilled water and in 0.1 N and 0.2 N Titriplex III solutions, were measured comparably and the results were shown in Tables 2, 3 and 4.

All of these three minerals, whether in original form or in calcined product form, dissociate completely in 0.1 N and 0.2 N Titriplex III solutions.

Table - 2

pH of the distilled water	: 5.50
pH of the 0.1 N solution	: 4.58
pH of the 0.2 N solution	: 4.50

Temp. °C	*Solubility in distilled water*		*Solubility in 0.1 Titriplex III solution*		*Solubility in 0.2 Titriplex III solution*	
	pH	*% solubility*	*pH*	*% solubility*	*pH*	*% solubility*
Original	9.20	34.00	6.02	100.00	5.30	100.00
50	9.20	33.00	6.02	100.00	5.40	100.00
100	9.20	31.10	6.20	100.00	5.40	100.00
150	9.20	29.20	6.20	100.00	5.40	100.00
200	9.20	29.20	6.20	100.00	5.40	100.00
250	9.20	29.20	6.20	100.00	5.50	100.00
300	9.20	29.20	6.20	100.00	5.50	100.00
350	9.20	29.20	6.20	100.00	5.60	100.00
400	9.20	29.00	6.20	100.00	5.60	100.00
450	9.20	29.00	6.20	100.00	5.60	100.00
500	8.92	28.80	6.20	100.00	5.60	100.00
550	8.80	28.50	6.20	100.00	5.60	100.00
600	8.80	28.00	6.20	100.00	5.60	100.00
650	8.80	28.00	6.20	100.00	5.60	100.00

Table - 3

pH of the distilled water	: 5.50
pH of the 0.1 N solution	: 4.58
pH of the 0.2 N solution	: 4.50

Temp. °C	*Solubility in distilled water*		*Solubility in 0.1 Titriplex III solution*		*Solubility in 0.2 Titriplex III solution*	
	pH	*% solubility*	*pH*	*% solubility*	*pH*	*% solubility*
Original	9.08	5.50	4.92	100.00	4.50	100.00
50	9.14	6.78	4.92	100.00	4.60	100.00
100	9.14	6.80	4.92	100.00	4.60	100.00
150	9.14	6.88	4.98	100.00	4.60	100.00
200	9.14	7.14	4.98	100.00	4.60	100.00
250	9.08	7.38	4.98	100.00	4.60	100.00
300	9.08	8.80	4.98	100.00	4.60	100.00
350	9.08	15.68	4.98	100.00	4.60	100.00
400	9.08	26.54	5.20	100.00	4.60	100.00
450	9.14	38.00	5.30	100.00	4.82	100.00
500	9.14	39.00	5.40	100.00	4.82	100.00
550	9.14	39.00	5.40	100.00	4.84	100.00
600	9.14	39.00	5.40	100.00	4.84	100.00
650	9.14	39.00	5.40	100.00	4.84	100.00
700	9.14	39.00	5.40	100.00	4.84	100.00

Table - 4

pH of the distilled water : 5.50
pH of the 0.1 N solution : 4.58
pH of the 0.2 N solution : 4.50

Temp. °C	Solubility in distilled water		Solubility in 0.1 N Titriplex III solution		Solubility in 0.2 N Titriplex III solution	
	pH	% solubility	pH	% solubility	pH	% solubility
Original	9.60	4.00	4.80	100.00	4.60	100.00
50	9.60	4.20	4.80	100.00	4.60	100.00
100	9.60	4.20	4.80	100.00	4.60	100.00
150	9.60	4.30	4.80	100.00	4.60	100.00
200	9.60	4.40	4.80	100.00	4.60	100.00
250	9.60	4.52	4.80	100.00	4.60	100.00
300	9.60	8.70	4.80	100.00	4.60	100.00
350	9.66	8.80	4.80	100.00	4.60	100.00
400	9.60	18.40	4.80	100.00	4.60	100.00
450	9.60	24.30	4.80	100.00	4.60	100.00
500	9.80	26.00	5.10	100.00	4.68	100.00
550	9.80	27.20	5.10	100.00	4.68	100.00
600	9.80	39.00	5.10	100.00	4.68	100.00
650	9.80	39.80	5.10	100.00	4.68	100.00
700	9.80	39.80	5.10	100.00	4.68	100.00

This shows that these minerals, which have Ca-borate and Na-Ca-borate crystal structures and a particular lattice energy, can no more keep their crystal line structure in the presence of a complexion which has an extraordinarily high complex-forming ability. In other words, the lattice energy of these three minerals reduces to zero against the complex-forming strength of EDTA complexion.

The solubilities in water of all these three minerals are limited (-30-39%). On account of this, it is possible to say that the 100 % solubility in Titriplex III comes completely from the complex-forming ability of the EDTA complex.

The investigation of the pH values of the aqueous, and 0.1 N and 0.2 N Titriplex III solution in the tables produces interesting results.

a. While the pH of the used distilled water was 5.50, the pH of the aqueous was about 9. This shows that as the result of dissociation, basic Ca^{++} and Na^{+} ions have passed into the solution.

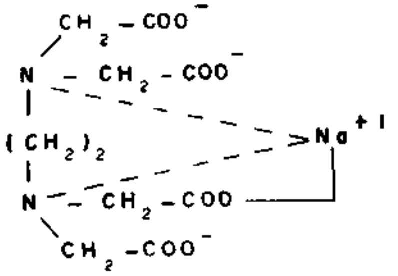
b. While the pH values of 0.1 N and 0.2 N Titriplex III solutions were approximately 4.50 at the end of the dissociation experiments, these solutions had higher pH values. This can be explained like this: As a result of disodium EDTA dissociation which takes place as

$$H_2Y^{--} \rightleftarrows HY^{---} + H^{+}$$

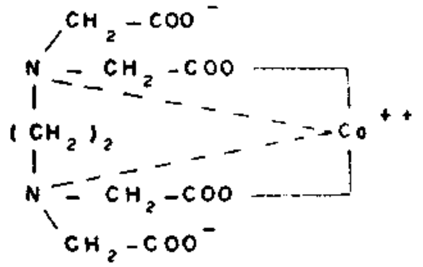
and

$$HY^{---} \rightleftarrows Y^{-4} + H^{+}$$

the protons are given off. These protons are held by oxygen atom ions, which are given off by ulexite ($Na_2. 2CaO. 5B_2O_3.16H_2O$), colemanite ($2CaO. 3B_2O_3. 5H_2O$) and pandermite ($4CaO. 5B_2O_3. 7H_2O$), as they are producing chelates having the following formula:



and



and as a result the pH of the medium naturally increases.

However, since whether in colemanite or in pandermite the number of chelate-forming metal cations are less than in the ulexite, the pH values obtained in solubility studies are found to be lower than in the solubility studies done with ulexite.

B. The solubility of gypsum mineral, its original and calcined form at a sequence of temperatures, in distilled water, and in 0.1 N and 0.2 N Titriplex III solutions are comparably shown in Table 5.

Table - 5

pH of the distilled water : 5.50
pH of the 0.1 N solution : 4.58
pH of the 0.2 N solution : 4.50

Temp. °C	*Solubility in distilled water*		*Solubility in 0.1 N Titriplex III solution*		*Solubility in 0.2 N Titriplex III solution*	
	pH	*% solubility*	*pH*	*% solubility*	*pH*	*% solubility*
Original	6.00	55.22	3.40	100.00	3.20	100.00
50	6.00	55.00	3.40	100.00	3.20	100.00
100	6.00	54.00	3.40	100.00	3.20	100.00
150	6.00	52.00	4.00	100.00	3.40	100.00
200	6.00	49.00	4.00	92.14	3.40	100.00
250	6.00	47.00	4.00	92.00	3.40	100.00
300	6.00	46.00	4.00	91.60	3.40	96.00
350	6.10	46.00	4.20	90.00	3.40	92.10
400	6.10	44.80	4.20	90.00	3.40	92.10
450	6.10	44.80	4.20	88.00	3.40	91.00
500	6.10	44.80	4.20	88.00	3.40	90.00
550	6.10	44.80	4.20	86.00	3.40	89.00
600	6.10	44.80	4.20	86.00	3.40	89.00
650	6.10	44.80	4.20	84.00	3.40	88.60
700	6.10	44.80	4.20	80.00	3.40	88.00
750	6.10	44.00	4.20	80.00	3.40	87.60
800	6.10	44.00	4.20	78.00	3.40	87.40
850	6.10	44.00	4.20	76.00	3.40	87.00
900	6.10	43.60	4.20	72.00	3.40	87.00

It is noticeable that the solubility of $CaSO_4.2H_2O$ mineral in water decreases by increasing calcination temperature. Because of the structural property of the gypsum mineral it shows a higher solubility with respect to borate minerals in water. As a result of this, it can also be said that gypsum mineral crystals have lower lattice energies than borate minerals. So, the fact that the mineral hardness of gypsum is lower compared to the afore-mentioned borate minerals helps us in suggesting an explanation in this way.

It is noticeable that the mineral sample, in its original form, dissociates completely in 0.1 N and 0.2 N Titriplex solutions, but then this solubility decreases parallel to the increase of calcination temperature. However, from 200°C, at which the anhydride begins to form, it is seen that the solubility is in a small amount proportional to the concentration of the solvent.

Due to the fact that the SO4^{--} anion passes into the solution and makes it acidic after Ca^{++} atom, ions in the crystalline structure form chelates, as a result of the partial or complete dissociation of the samples having the formula $CaSO_4.2H_2O$ or $CaSO_4$ in 0.1 N and 0.2 N Titriplex III solutions, the pH values are notably low. As a result of this, because of the excess H$^+$ ions in the reaction,

$$H_4Y \rightleftarrows H_2Y^{-2}+2H^+$$

the equilibrium shifts to the left and mostly the EDTA crystals, which have a very low solubility, precipitate.

C. The solubilities of aragonite mineral in its original and calcined torms at a sequence of temperatures, in distilled water, and in 0.1 N and 0.2 N Titriplex III solutions are comparably shown in Table 6.

Table - 6

pH of the distilled water : 5.50
pH of the 0.1 N solution : 4.58
pH of the 0.2 N solution : 4.50

Temp. °C	*Solubility in distilled water*		*Solubility in 0.1 N Titriplex III solution*		*Solubility in 0.2 N Titriplex III solution*	
	pH	*% solubility*	*pH*	*% solubility*	*pH*	*% solubility*
Original	8.20	0.96	5.50	100.00	4.90	100.00
50	8.22	1.14	5.50	100.00	4.90	100.00
100	8.22	1.14	5.52	100.00	4.90	100.00
150	8.22	1.14	5.52	100.00	4.90	100.00
200	8.22	1.14	5.52	100.00	4.98	100.00
250	8.22	1.22	5.66	100.00	4.98	100.00
300	8.22	1.22	5.72	100.00	5.00	100.00
350	8.22	1.24	5.76	100.00	5.00	100.00
400	8.22	1.24	5.82	100.00	5.00	100.00
450	8.22	1.24	5.88	100.00	5.00	100.00
500	8.22	1.26	5.96	100.00	5.20	100.00
550	8.22	1.26	5.96	100.00	5.20	100.00
600	8.22	1.26	6.40	100.00	5.40	100.00
650	11.00	1.48	8.00	100.00	5.80	100.00
700	12.30	1.50	11.00	100.00	6.40	100.00
750	12.30	1.50	11.20	100.00	6.60	100.00
800	12.42	1.58	11.30	100.00	6.60	100.00
850	12.46	1.62	11.30	100.00	6.60	100.00
900	12.60	1.64	11.40	100.00	6.70	100.00

Since the results obtained from the experiments done with the calcite, marble and precipitated $CaCO_3$ samples are entirely the same as the results obtained for aragonite, here only aragonite was taken into consideration.

a. Whether in original form or in calcined form, aragonite samples completely dissociate in Titriplex III solutions.

b. The solubilities of the same samples in distilled water are very low.

c. pH values of the solutions which were obtained by treating the samples, calcined over 650°C with distilled water, were very high compared to the former solutions. This shows that the aragonite decomposes over that temperature as follows:

$$CaCO_3 \longrightarrow CaO + CO_2$$

because CaO reacts with water $CaO + H_2O \quad Ca(OH)_2$ and begins to give OH ions to the medium. Thus, this fact is confirmed by the loss of mass values of aragonite at which these values show a prominent increase over 650°C.

d. The 0.5-gr aragonite sample, calcined at 700°C, has not completely dissociated in 50 ml 0.1 N Titriplex solution. In order to obtain a complete dissociation 17 ml more of the 0.1 N solution was spent.

This shows that at that temperature the aragonite sample, having the formula $CaCO_3$, begins to decompose by the reaction $CaCO_3 \quad CaO + CO_2$. Because the amount of CaO that 50 ml 0.1 N Titriplex III solution can dissolve is 50x5.6—280 mg. The amount of CaO in 500-mg aragonite sample is 500x0.56— 280 mg.

The fact that the 50-ml 0.1 N Titriplex III solution is not sufficient to dissolve a 500-mg sample calcined over 700°C shows that the amount of CaO in these samples is more than 280 mg. In this way, it becomes possible to say that $CaCO_3$ begins to decompose from 650°C on.

The additional amounts of 0.1 N Titriplex solution in order to dissolve 50 mg portion taken from the samples which are calcined at 700°, 750°, 800°, 850° and 900°C are 17, 19, 22, 25 and 27 ml, respectively. These additions should be made to the 50 ml 0.1 N Titriplex solution which is, normally, enough for the 500 mg portions below 650°C.

In this way, as a result of some simple calculations, it was proved that 43.28 % $CaCO_3$ thermally decomposes at 700°C; 48.40 % at 750°C; 56.00 % at 800°C; 63.60 % at 850°C and 68.80 % at 900°C.

If we carefully examine the second pH column of Table 6, a sudden increase after 650°C can easily be recognized. This is considered to be another sign which shows that $CaCO_3$ begins to decompose after 650°C. Because in this way CaO, which has begun to form, increases the pH value of the medium by the reaction:

$$CaO + H_2O \qquad Ca\,(OH)_2$$

D. The solubilities of the CaC_2O_4 compound in its original and calcined forms, at a sequence of temperatures in distilled water, and in 0.1 N and 0.2 N Titriplex solutions, are comparably shows in Table 7.

The close examination of the solubility and pH values of Table 7 shows that Ca-oxalate compound begins to decompose by the reaction $CaC_2O_4 \quad CaCO_3 \quad CaO$ from 450°C on. Because, while the solubilities both in distilled water and in 0.1 N and 0.2 N Titriplex solutions are increasing, the pH values of the solutions also show a noticeable increase.

E. The solubilities of $Ca_5(PO_4)_3(OH)$ in its original and calcined forms, at a sequence of temperatures in distilled water, and in 0.1 N and 0.2 N Titriplex solutions, are comparably shown in Table 8.

The $Ca_5(PO_4)_3(OH)$ compound does not dissociate in distilled water. However, the samples calcined over 550°C show a very slight dissociation, so this is necessarily attributed to a structural change of the sample in a way to give H_2O. The solubilities in 0.1 N and 0.2 N Titriplex solution, contrary to the solubility in water, show a prominent decrease reversely proportional to calcination temperature.

Table - 7

pH of the distilled water : 5.50
pH of the 0.1 N solution : 4.58
pH of the 0.2 N solution : 4.50

Temp. °C	*Solubility in distilled water*		*Solubility in 0.1 N Titriplex III solution*		*Solubility in 0.2 N Titriplex III solution*	
	pH	*% solubility*	*pH*	*% solubility*	*pH*	*% solubility*
Original	8.34	1.90	4.00	4.18	3.50	6.00
50	8.38	3.00	4.10	4.18	3.50	6.00
100	8.48	3.00	4.10	4.18	3.60	6.00
150	8.48	4.00	4.10	6.00	3.60	8.00
200	8.48	4.00	4.10	6.00	3.60	9.00
250	8.48	4.80	4.10	7.00	3.60	9.00
300	8.80	5.00	4.10	7.20	3.60	9.80
350	8.80	6.00	4.10	7.40	3.50	10.00
400	8.80	6.00	4.50	8.00	3.80	14.00
450	8.80	6.00	5.00	30.00	4.20	38.00
500	9.00	8.16	5.00	100.00	4.20	100.00
550	9.00	8.16	5.00	100.00	4.20	100.00
600	9.00	7.16	5.00	100.00	4.20	100.00
650	9.00	8.16	5.00	100.00	4.20	100.00
700	9.00	8.16	5.00	100.00	4.20	100.00

Table - 8

pH of the distilled water : 5.50
pH of the 0.1 N solution : 4.58
pH of the 0.2 N solution : 4.50

Temp. °C	*Solubility in distilled water*		*Solubility in 0.1 N Titriplex III solution*		*Solubility in 0.2 N Titriplex III solution*	
	pH	*% solubility*	*pH*	*% solubility*	*pH*	*% solubility*
Original	6.00	0.00	3.88	100.00	3.60	100.00
50	6.10	0.00	3.88	100.00	3.60	100.00
100	6.10	0.00	3.90	100.00	3.60	100.00
150	6.20	0.00	3.90	96.00	3.60	100.00
200	6.20	0.00	3.90	91.80	3.60	96.30
250	6.20	0.00	3.90	90.90	3.60	94.00
300	6.20	0.00	3.90	89.90	3.60	94.00
350	6.20	0.00	3.90	89.50	3.60	94.00
400	6.30	0.00	3.90	89.50	3.60	93.00
450	6.40	0.00	3.90	89.50	3.60	92.00
500	6.40	0.00	3.92	89.10	3.60	91.00
550	6.50	0.00	3.92	83.80	3.60	88.50
600	6.50	0.00	3.92	80.00	3.60	86.00
650	6.50	0.00	3.92	71.40	3.66	82.00
700	6.60	0.00	3.92	70.00	3.66	78.00
750	6.60	0.00	3.92	66.00	3.66	72.70
800	6.60	0.00	3.92	62.60	3.66	69.50
850	6.60	0.00	3.92	57.10	3.66	66.00
900	6.60	0.00	3.92	56.80	3.66	64.10

III. Comparisons of thermal decompositions and solubilities of the studied mineral and compound samples are given in graphics Fig. 1 to 7. By examining these graphics it is prossible to demonstrate to what degree the solubilities of the samples are related to their structural changes.

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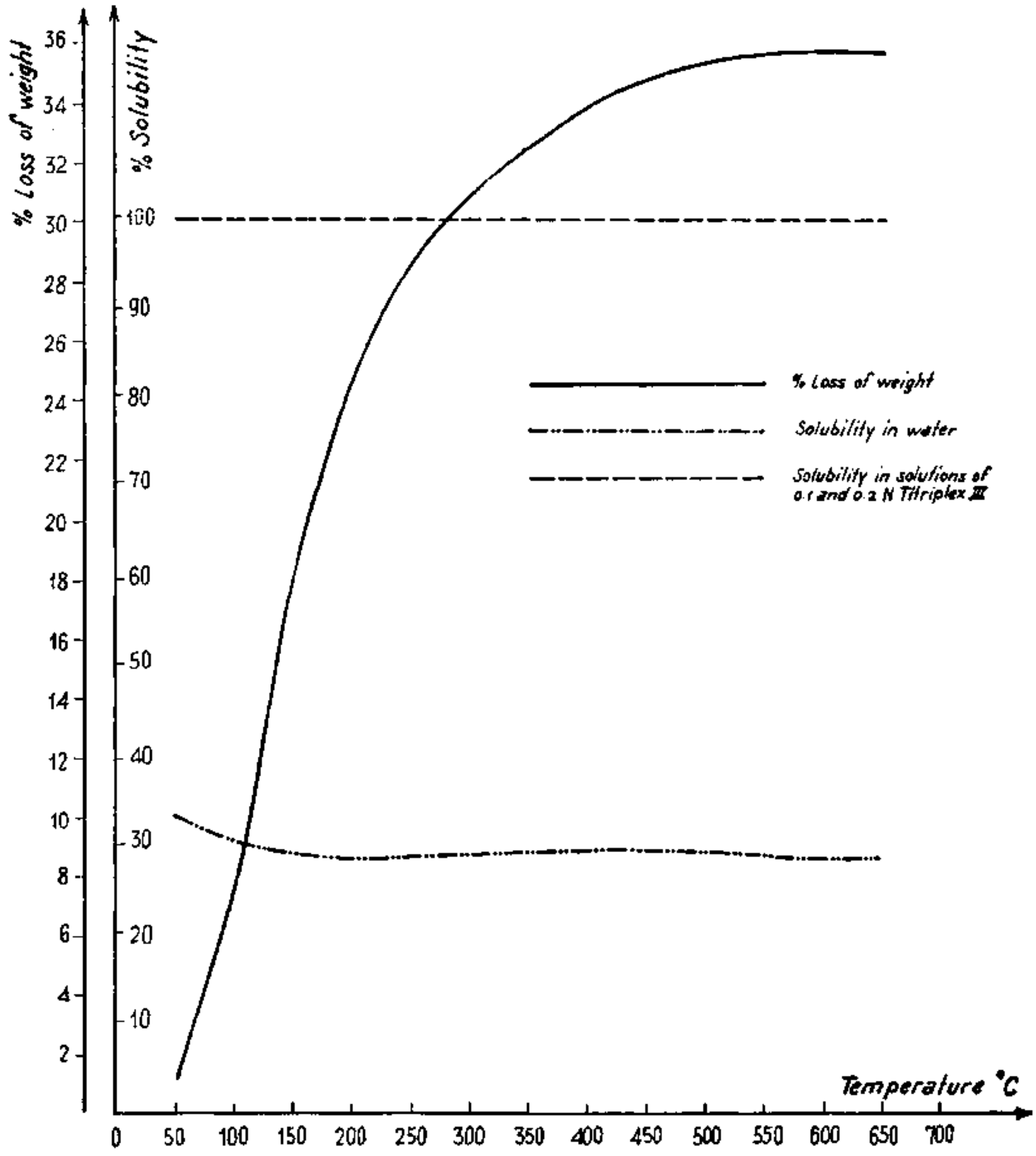

Fig. 1 - Ulexite.

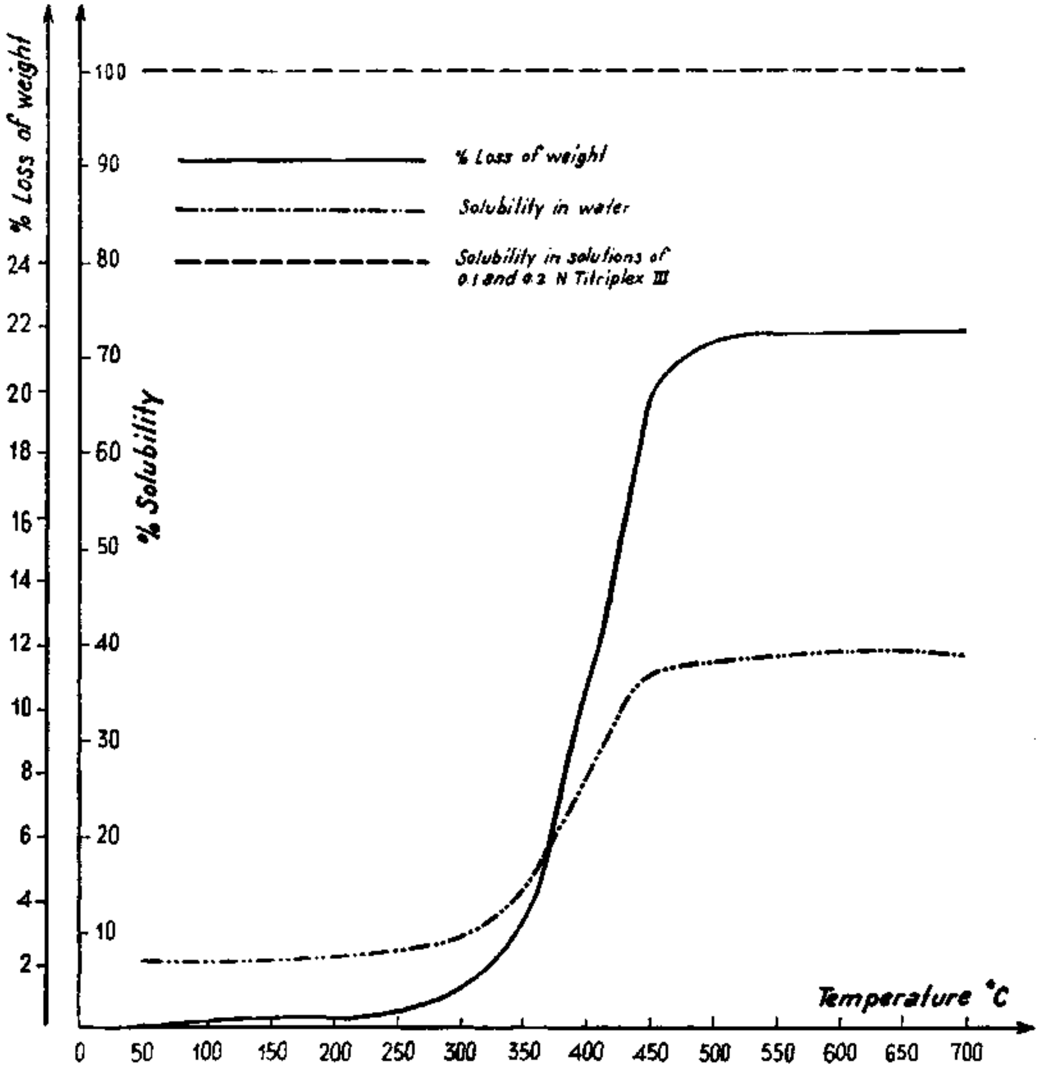

Fig. 2 - Colemanite.

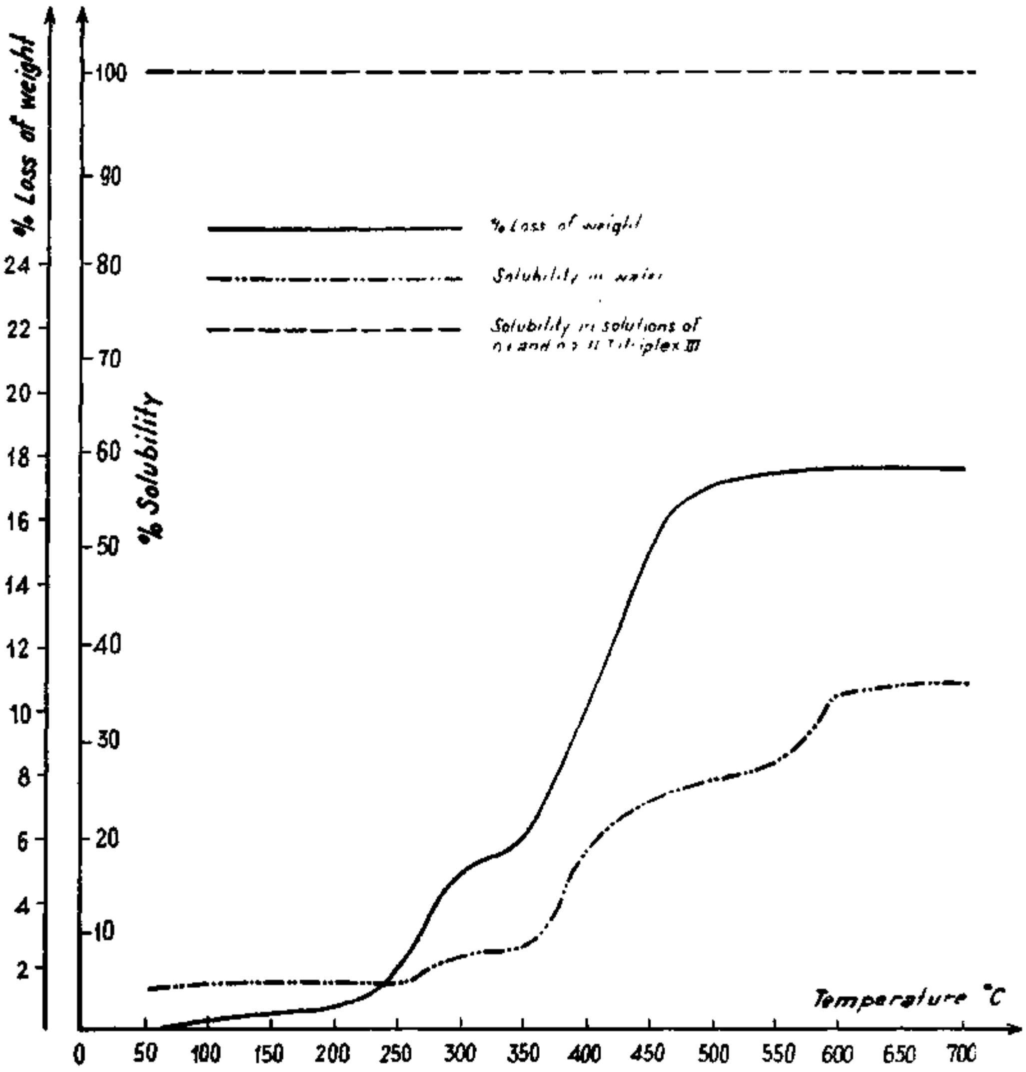

Fig. 3 - Pandermite.

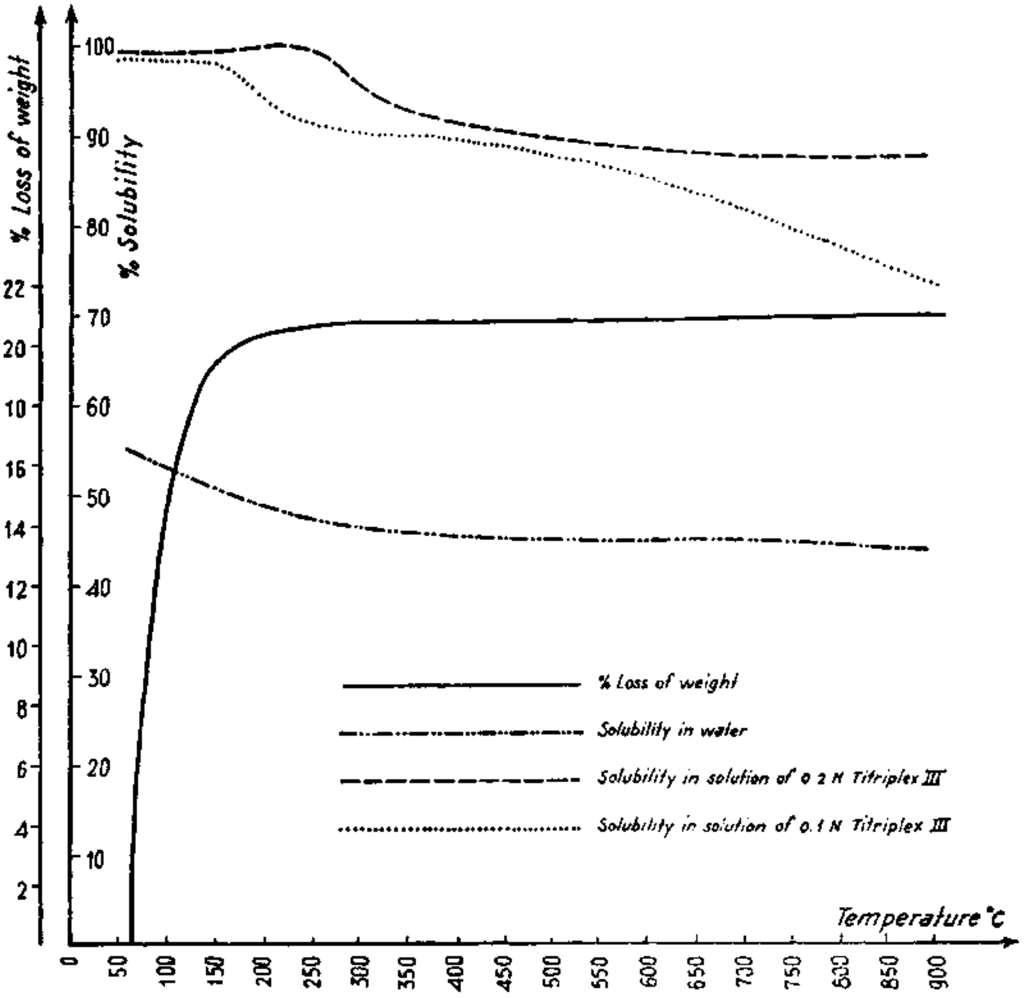

Fig. 4 - Gibbsite.

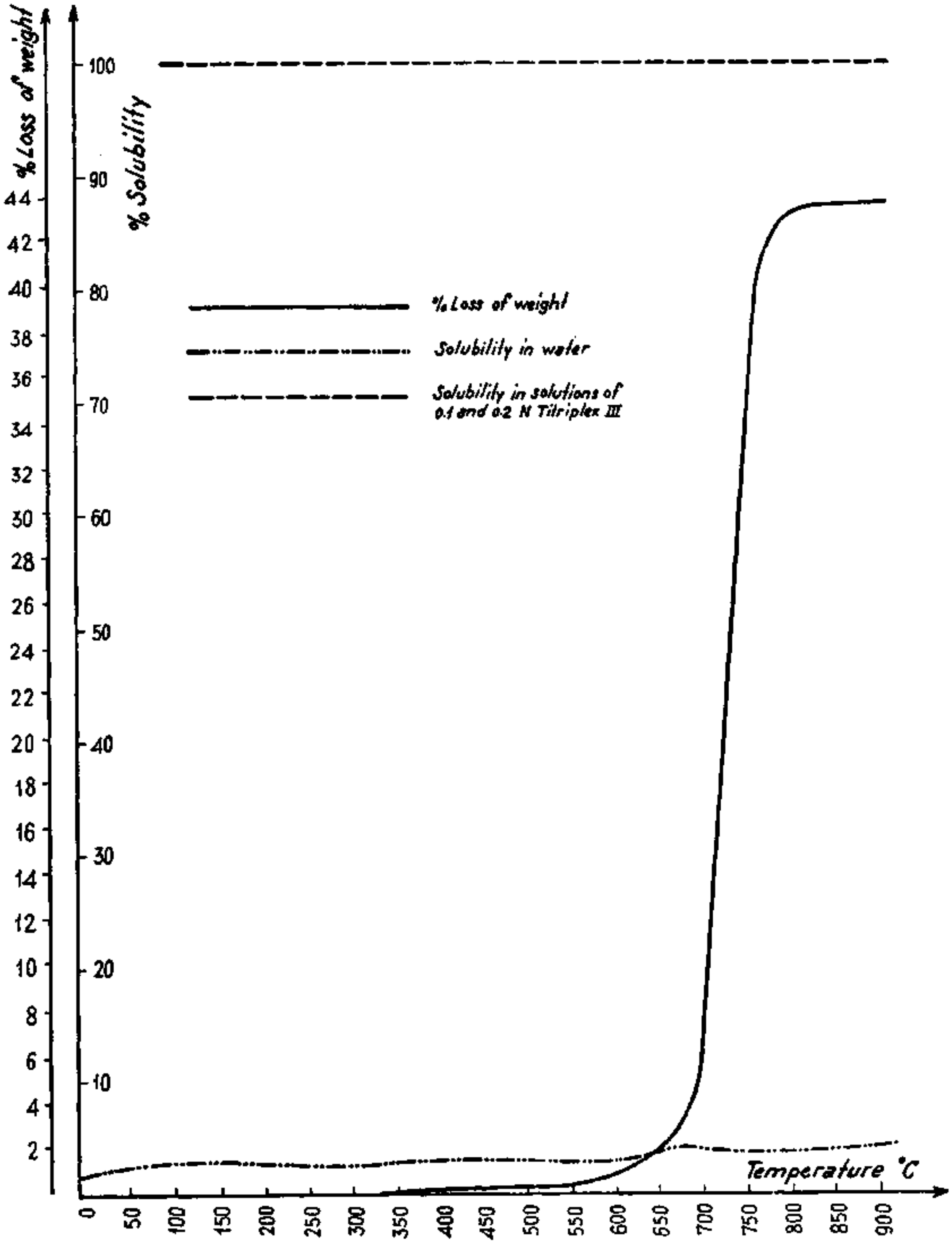

Fig. 5 - Aragonite.

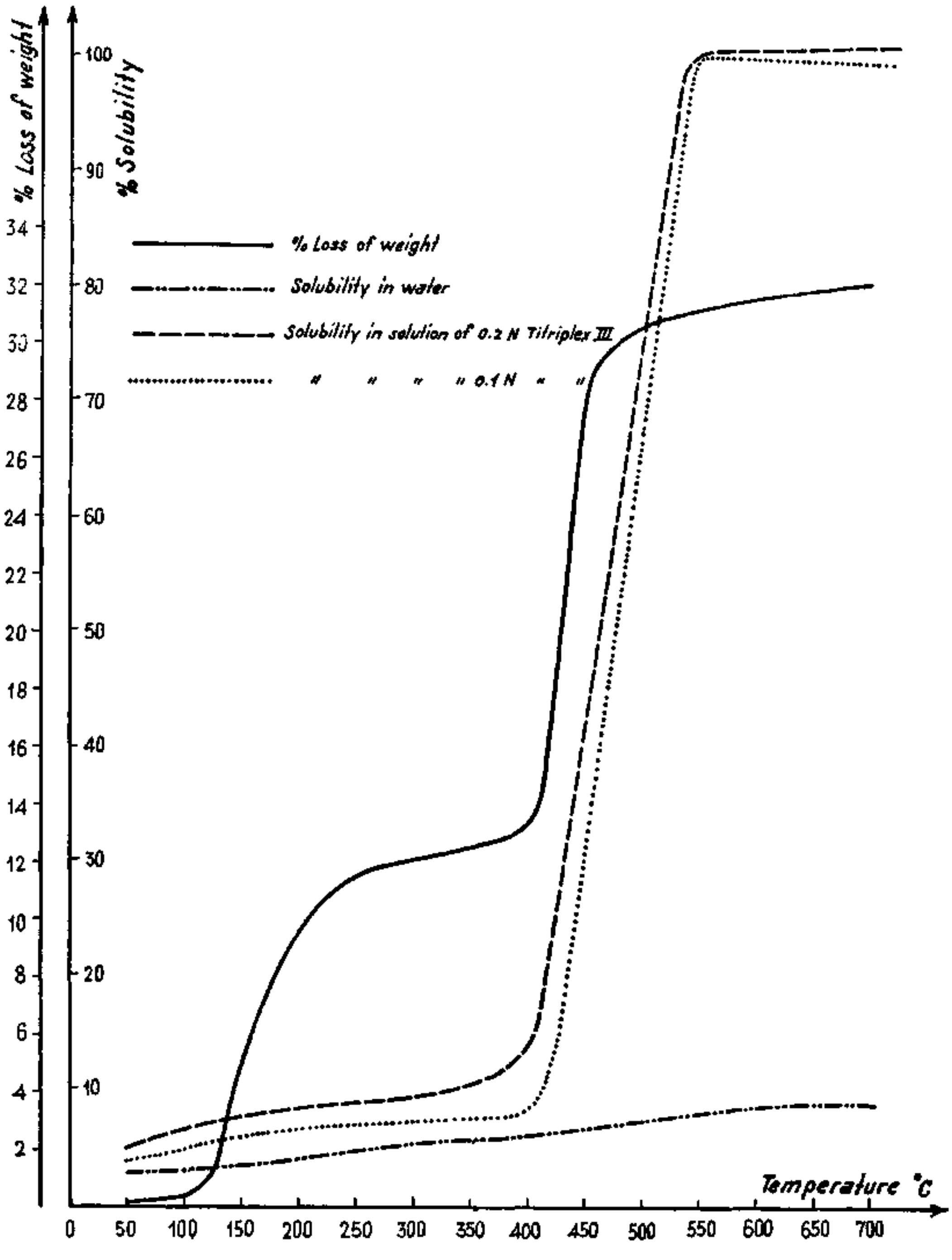

Fig. 6 - Calcium oxalate.

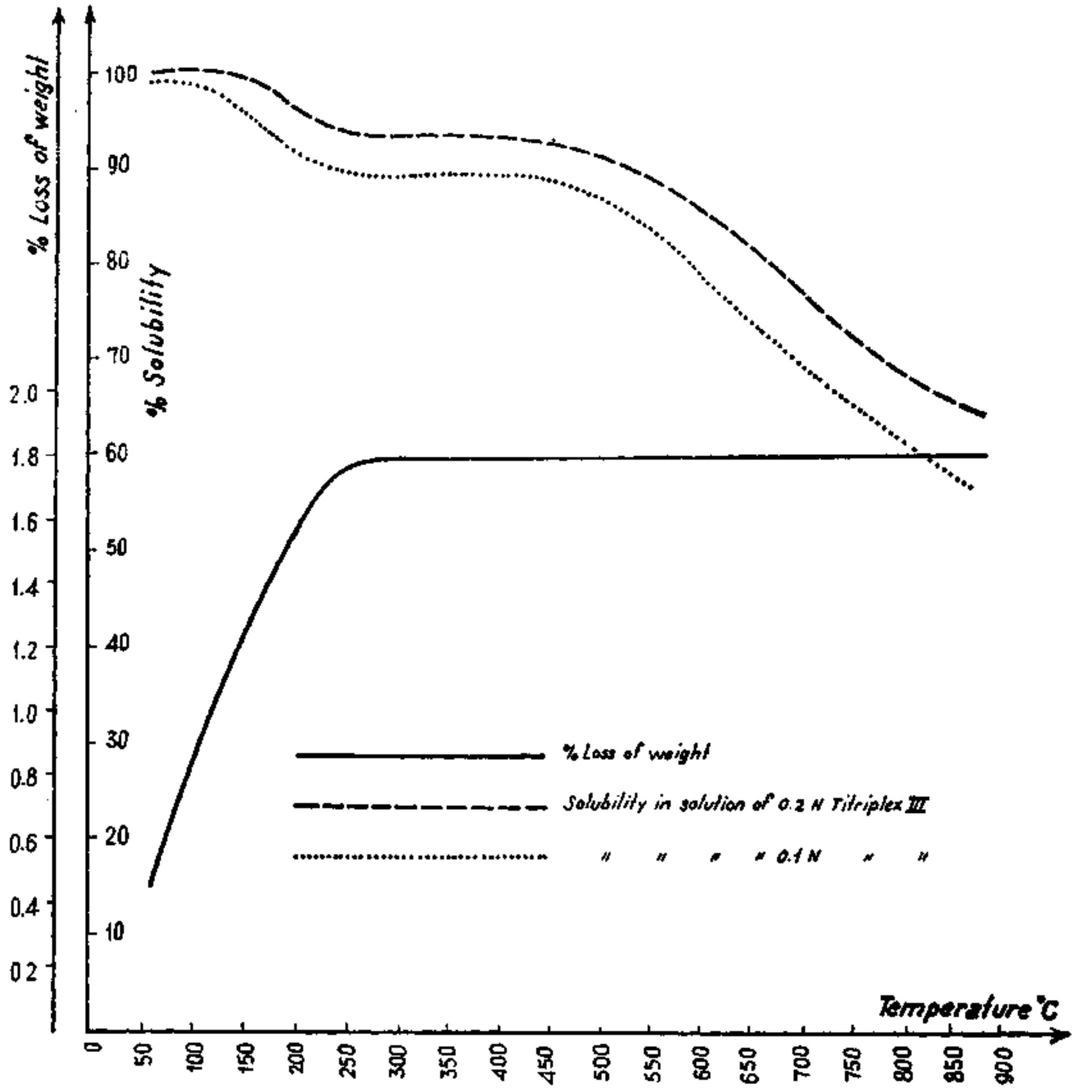

Fig. 7 - Calcium phosphate.