

# A New Preparation Method of Barium Hydroxide By Extractive Electrolysis Using Hydrophobic Organic Solvent.

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## 1. Introduction

Recently, studies on the electrolysis of metals in organic media are much found in papers. (1~4) Also, M. A. Qazi and L. Leja reported on work which electrolysed manganese salts in a diaphragmic cell using various amide solution of manganese salts as catholyte and aqueous solution of ammonium chloride as anolyte. (5)

The authors, too had interest in the electrolysis using hydrophobic organic solvent, especially in the extractive electrolysis which electrolysed between the cathode dipped in organic phase and the anode in aqueous phase, contacted each other. Few instances of such electrolysis can be seen. As results of our experiment, it seems that the said extractive electrolysis may have the following characteristics: (1) It requires comparatively high voltage, but as the catholyte does not mix readily with anolyte. Consequently, diaphragmic effects are expected. (2) The solubility of inorganic salts in an organic solvent is generally low. Products which are hard to crystallize in the electrolysis of aqueous solution can often be obtainable as crystalline by the extractive electrolysis.

This report is on the extractive electrolysis of barium salts using hydrophobic alcohol and other solvents. The product is identified to be barium hydroxide which could not be obtained as solid by the conventional electrolysis of aqueous solution unless the catholyte was concentrated by evaporation.

## 2. Experimental

**Apparatus.** As for the current source, BA-8-2type, a high voltage current supplier for the electrophoresis made by Toyo Kagaku Sangyo Co., Ltd. was used. The cell was of fraction funnel type measuring 5 cm in diameter and 8 cm in depth, as shown in fig. 1. The cathode, a stainless steel plate (18/8) with a diameter of 35 mm was fixed at the position where its top was unit cm above the boundary between the aqueous phase and the organic phase, while that of the anode, a platinum wire of 0.1 mm in diameter and 5 mm length, was that its top was unit cm under the boundary. Furthermore, in order to prevent the mixing of the gases, produced at both electrodes, the anode was surrounded with a little bigger size of glass tube so that the gas at the anode might directly be let out of the cell. The cell enclosed in a plastic film was immersed in a tank whose temperature was kept at 20°C.

For the X-ray analysis, D-3F type, for the thermalanalysis YGHDtype, both made by Rigaku Denki Co., Ltd. and for determination of water content in the organic phase, Karl

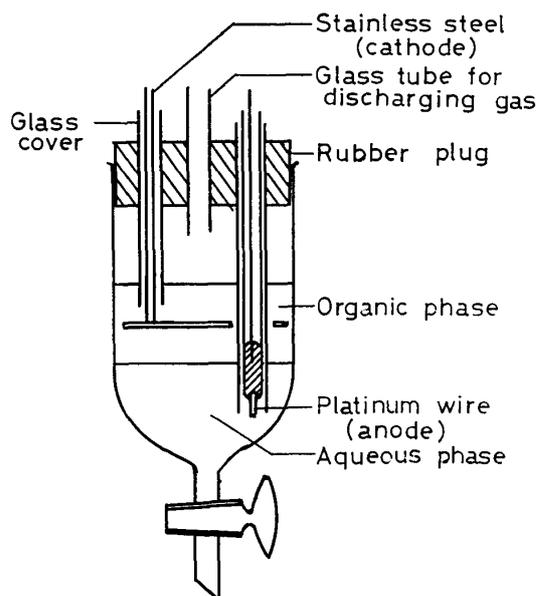


Fig. 1. Cell diagram.

Determination of barium in aqueous solution. The quantity of barium in aqueous solution was determined by chelatometric titration at pH 10 using Mg-EDTA and eriochrom black T indicator. The decrease of barium content in aqueous solution during the electrolysis was determined by comparing the content of barium in aqueous solution before and after the electrolysis.

Reagent. The reagents were of special grade. The organic solvents were used without distilling. In order to pour in the cell, aqueous solution and hydrophobic alcohol were previously shaken in a large fraction funnel for a plentiful time, and after separating, the concentration of salt in aqueous and organic phase before the electrolysis were determined. In the electrolysis, aqueous solution, thus prepared, was into contact with the alcohol and the electrolysis was conducted.

### 3. Results and Discussion

#### 3.1. Constant current extractive electrolysis of barium salts.

Effects of current. It was examined how current changed with the voltage of the extractive electrolysis. Fig. 2 shows the hourly change of voltage when 0.5 M aqueous solution of barium chloride was extractively electrolysed at several constant current using isobuthylalcohol. In the electrolysis, as barium ion decreases abruptly to be hydroxide without supplying not so much as consumed in the organic phase and then current is hard to flow so that voltage rises its peak taking time in inverse proportion to current, and fall down, as temperature rises with the progress of the electrolysis. Also, Fig. 3 shows the hourly change of the concentration of barium and chloride ions in the organic phase. As above-illustrated, the concentration of salt in organic phase decreases, until it apparently reaches a constant concentration. Furthermore, it was discovered that main species of barium compound in the organic phase

Fischer Titrator MK-S type made by Kyoto Denshi Co., Ltd. were used.

Electrolysis. In order to prepare for the electrolysis, 25 ml of aqueous solution was poured into the cell and the anode was let in. Then, 25ml of organic solvent was poured into the cell and the cathode was let in. Thus prepared, the electrolysis was carried out at constant current.

Weighing of the product. The electrode with the product was on a watch glass. On the other hand, the organic phase was filtered through a glass filter and the residue was collected. Then these two gathered, were exposed to carbon dioxide gas to obtain barium carbonate. After drying, weight of that was measured.

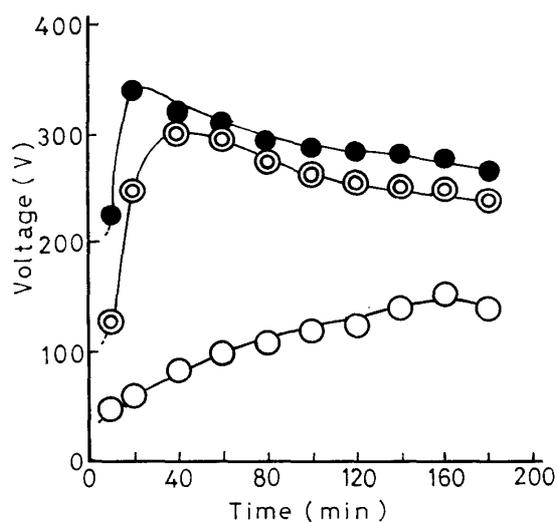


Fig. 2. Time-voltage curve on extractive electrolysis at various current.

○ 10 mA      ⊙ 30 mA      ● 50 mA

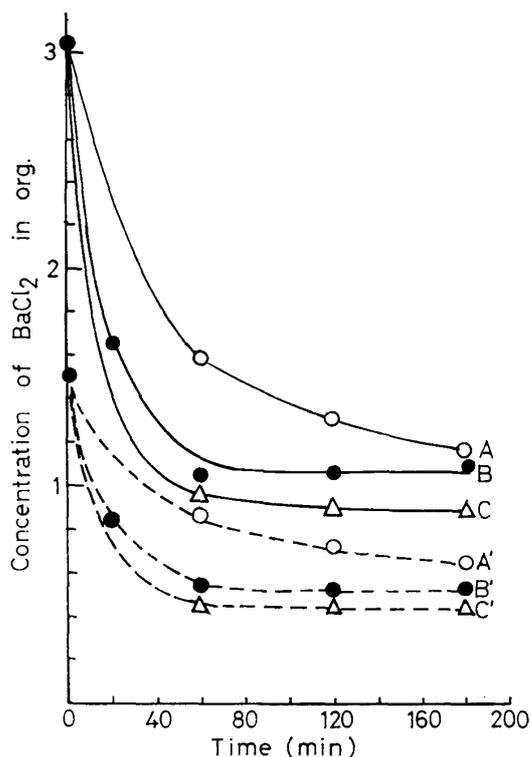


Fig. 3. Relation between time and concentration of barium and chloride ion in organic phase.

A: Cl<sup>-</sup> at 10 mA, B: Cl<sup>-</sup> at 20 mA, C: Cl<sup>-</sup> at 50 mA.  
A': Ba<sup>++</sup> at 10 mA, B': Ba<sup>++</sup> at 20 mA, C': Ba<sup>++</sup> at 50 mA.

Table 1. Extractive electrolysis at various constant current

Current (mA)	Quantity of Ba <sup>++</sup> * decreased (mM)	Quantity of product (g)	Product per unit farady (mole/farady)
10	0.2725	0.0524	0.2435
20	0.3025	0.0607	0.0900
50	0.6075	0.1042	0.0945

\* in a aqueous phase

was barium chloride. Also, table 1 shows the quantity of the product in the electrolysis, continued for three hours. A low current brings much product per unit farady. It seems that low current results in high concentration of barium ion in the organic phase so that hydroxide ion combines effectively with barium ion to be barium hydroxide. Also, water content in the organic phase were determined before and after the electrolysis. The organic phase contained in every electrolysis 95 mg of water per unit ml over duration of the electrolysis.

**Effects of concentration.** The relation between the concentration and the quantity of extracted barium chloride in the aqueous phase examined. The result are shown in table 2. The concentration of barium chloride reaches about constant 0.0005 M usually, using higher concentration of aqueous solution than 0.25 M, whereas mechanical shaking lets bring different concentration, which can be applied the distribution law. The quantity of barium extracted,

Table 2. Extractive electrolysis at various concentration

Mole/l	Ba <sup>++</sup> decreased (mM)	Product (g)	Ba <sup>++</sup> in org.* (mM/l)	Ba <sup>++</sup> in org.** (mM/l)
1.0	0.860	0.0894	2.382	0.501
0.75	0.383	0.0768	1.961	0.544
0.5	0.303	0.0607	1.530	0.528
0.25	0.290	0.0534	0.911	0.571
0.1	0.256	0.0503	0.361	0.286

\* before electrolysis

\*\* after electrolysis

that is, decreased in the aqueous phase and that of the product increased with the concentration of aqueous phase. These results apparently show that higher concentration of aqueous phase are used, more barium ion is extracted electrically, that is more current is carried by barium ion.

Electrolysis using various salts. Fig. 4 shows the hourly change of voltage when 0.5 M aqueous solution of barium salts were extractively electrolysed at 30 mA. It is shown that current flows easily in acetate, following in nitrate and chloride. Also, table 3 shows quantities, related to the electrolysis. Nitrate distributes excell-

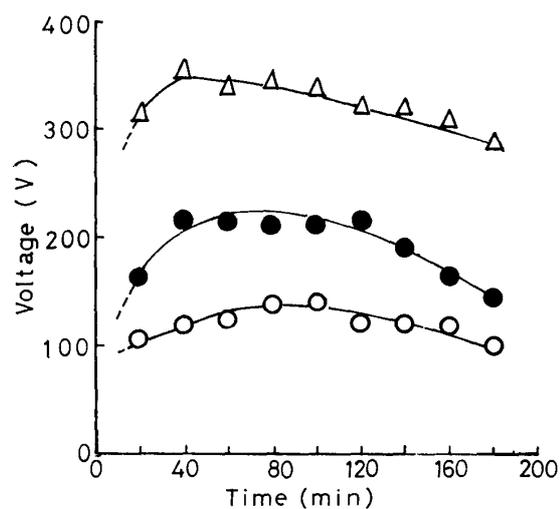


Fig. 4. Time-voltage curve on extractive electrolysis using various salts.

○Ba(CH<sub>3</sub>COO)<sub>2</sub>, ●Ba(NO<sub>3</sub>)<sub>2</sub>, △BaCl<sub>2</sub>.

Table 3. Extractive electrolysis using various salts

Salts	Ba <sup>++</sup> in org.		Ba <sup>++</sup> decreased (mM)	Product (g)
	(mM/l)*	(mM/l)**		
BaCl <sub>2</sub>	0.911	0.571	0.290	0.0534
Ba(NO <sub>3</sub> ) <sub>2</sub>	2.015	0.593	0.253	0.0549
Ba(CH <sub>3</sub> COO) <sub>2</sub>	1.008	0.803	0.681	0.1368

\* before electrolysis

\*\* after electrolysis

ently barium in the organic phase, mechanically, whereas acetate keeps high concentration of barium after current was applied. It seems that, using acetate, acetic acid produces in the anolyte, containing a little hydronium ion, so that barium ion is attracted effectively to the cathode in the organic phase, whereas in nitrate and chloride current are carried by other ions such as hydroxide ion and hydronium ion as well as barium ion. It is reason that acetate produces much deposit, maybe.

Effect of alcohols as organic phase. Time-voltage curves, using various alcohols are shown

in Fig. 5. In isobuthylalcohol, curve rises at first and following falls down gradually, while in other alcohol, they tend to fall down, following rise and fall down again. The result perhaps, means that isobuthylalcohol can transmit ions and water readily, but in other alcohols, some solution structure which inhibit the transportation of ions and water is present and the structure is destroyed gradually by current being applied. Furthermore to rise means the decrease of barium salt in the organic phase by the electrolysis and to down again means rising of temperature in the cell. Table 4 indicates various quantities about the electrolysis. In mechanical shaking, barium chloride distributes in tert-amylalcohol as well as isobuthylalcohol, but current is difficult to

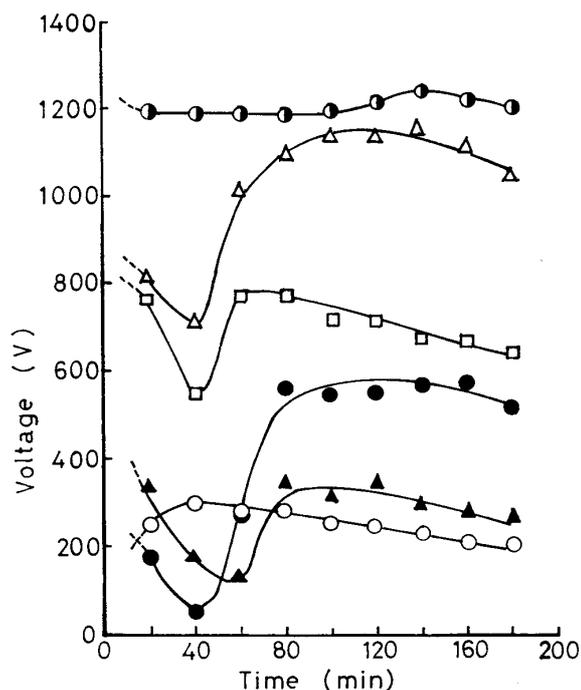


Fig. 5. Time-voltage curve on extractive electrolysis using various alcohol.

○ iso-butyl alc.,      ▲ n-amyl alc.,  
● tert-amyl alc.,    □ iso-amyl alc.,  
△ n-hexyl alc.,     ● sec-hexyl alc.

Table 4. Extractive electrolysis using various alcohol

Alcohol	Ba <sup>++</sup> in org.		Water in org.		Ba <sup>++</sup> decreased (mM)	Product (g)
	(mM/l)*	(mM/l)**	(mg/ml)*	(mg/ml)**		
iso-butyl	1.530	0.529	100.8	100.4	0.304	0.0607
iso-amyl	0.291	0.237	54.82	52.96	0.175	0.0295
n-amyl	0.393	0.318	59.38	56.29	0.236	0.0457
tert-amyl	1.767	0.733	112.0	112.7	0.090	0.0105
n-hexyl	0.03	0.03	58.03	52.35	0.078	0.0105
sec-hexyl	0.162	0.03	56.42	44.70	0.060	0.003

n-hexyl: at 5mA.

sec-hexyl: at 1mA

\* before electrolysis.

\*\* after electrolysis

transmit comparatively and so a little product is only observed.

Judging from these results shown in table 4, isobuthylalcohol was better solvent of the extractive electrolysis.

### 3.2 Constant voltage extractive electrolysis of barium salts.

Extractive electrolysis of barium salts. Concerning the extractive electrolysis using various barium salts, the relation between the kind of barium salts and the quantity of the product at the cathode and those between the latter and the quantity of current were examined. Fig. 6 shows the hourly change of electric current when 0.2M aqueous solution of barium chloride,

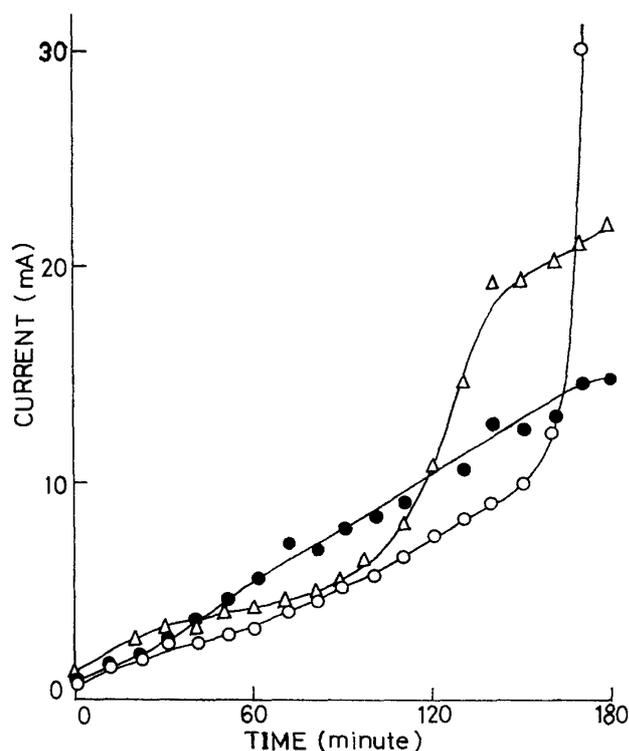


Fig. 6. Time-Current curve for extractive Electrolysis using various salts.

thylalcohol phase. It is expected that the easier the solubilization of the barium salt in organic phase is the greater is the quantity of the hydroxide produced. So it perhaps seems that as barium acetate dissolves more easily and fast in isobuthylalcohol, the acetate produces the greatest quantity of barium hydroxide.

Relation between time and quantity of barium, decreased in aqueous solution. It was examined how barium and chloride ion in the aqueous solution decrease with the passage of time.

25 ml of the aqueous solution of 0.1 M barium chloride was brought in contact with 25 ml of isobuthylalcohol and it was extractively electrolysed at 500 volt for 30 ~ 240 minutes. Then the aqueous phase was eliminated. Thus the total quantity of barium and chloride ion in the aqueous solution were measured. Comparing the quantity with that obtained before the electrolysis, the quantity decreased was determined. The results are shown in figure 7. Up to 150 minutes after the commencement of the electrolysis, the decrease of the quantity of chloride ion is greater than that of barium. It is judged that this is due to the fact that some chloride ion is oxidized at the anode into chlorine gas and expelled, and then the other

nitrate and acetate were extractively electrolysed at 500 volt using isobuthylalcohol. As the figure shows, a little difference is observed in each case of barium salts, but totally almost same quantity of current is carried out. Furthermore, the quantity of current, the quantity of the product and the decrease of barium content in aqueous solution were shown in table 5. As for the quantity of the product at the cathode, the acetate is the greatest, nitrate and chloride following in the order. It is concluded for plating out of barium hydroxide at the cathode that water first is dissolved or extracted in the organic phase, is reduced and produces hydroxide ion, which forms barium hydroxide by combining with barium ion in isobuthylalcohol phase.

Table 5. Extractive electrolysis using various salts.

salt	decreased quantity of barium (mole)	weight of Product (mg)	quantity of current (C)
BaCl <sub>2</sub>	$8.0 \times 10^{-5}$	12.0	98.38
Ba(NO <sub>3</sub> ) <sub>2</sub>	$2.6 \times 10^{-4}$	29.3	83.81
Ba(CH <sub>3</sub> COO) <sub>2</sub>	$4.5 \times 10^{-4}$	36.4	79.48

goes into the organic phase and there it is extracted as barium chloride, while barium is also extracted in the organic phase in the same equivalent as chloride and remains in it, but at the beginning of electrolysis, barium is not eliminated as barium hydroxide at the cathode so much as chlorine at the anode, for low concentration of barium in the organic phase prevents effectively to make barium hydroxide. This fact accounts for the above-mentioned difference between chloride and barium ion in their decreasing quantities,

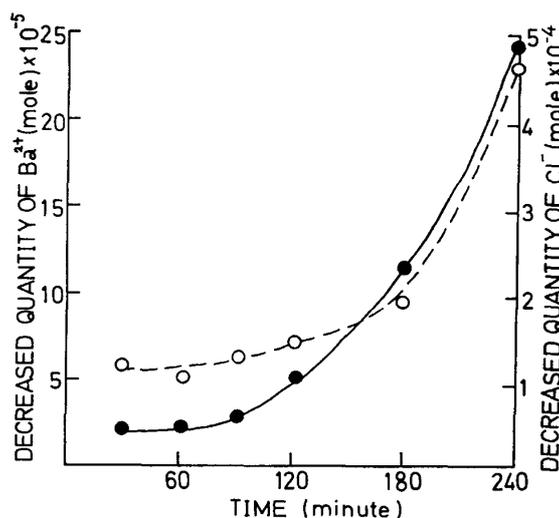


Fig. 7. Relation between time and decreased quantity of barium and chloride in aqueous solution. : ○ Cl<sup>-</sup>, ● Ba<sup>2+</sup>

When the barium chloride in the organic phase become saturated with the progress of electrolysis, the concentration of chloride ion in the organic phase keeps constant and then the same equivalent barium as chloride which is expelled at the anode moves from aqueous solution to the organic phase and there it is eliminated as barium hydroxide.

It may be considered that this explains why the decreased quantity of chloride ion and barium ion become almost equal in over 100 minutes after the commencement of electrolysis. Furthermore, at this stage, it is considered that the solvated quantity of chloride effects seriously for the quantity of chloride in the aqueous phase and it is reason that the curve of chloride is a little under the curve of barium in 150 minutes.

When a dilute aqueous solution of barium chloride was extractively electrolysed, the organic phase was eliminated the organic phase was dried by evaporation, and then the quantities of barium and chloride ion contained in it were measured, it was found that the ratio of barium to chloride ion was 1 to 2. This indicates that the species of barium compound in the organic phase was BaCl<sub>2</sub>.

Extractive electrolysis using various organic solvents. It was examined how the quantity of barium hydroxide varied with the organic solvent used. In this experiment, a stainless plate was used in place of the platinum wire to obtain effective current flux, because most organic solvents have poor conductivity. The stainless plate was fixed at the position where its top was unit cm above the boundary, but the above-mentioned platinum wire was used as the anode in aqueous solution.

The results of the electrolysis for three hours are shown in table 6. As the table shows, the quantity of the product at the cathode for three hours electrolysis, was very much when alcohols were used as organic phase, and MIBK, cyclohexanone, caproic acid, ethylacetate, etc. were used, a trace of crystalline was plated out, while it was not observed when toluene, isopropylether, chloroform, aniline etc. were used, for these solvents have poor conductivity for electric current.

Table 6. Extractive electrolysis using various solvents.

organic solvent	decreased quantity of barium(mole) $\times 10^{-4}$	quantity of product (mg)	quantity of current (C)
isobuthylalcohol*	15.5	108.9	411.0
isoamylalcohol	9.8	44.9	197.0
n-hexylalcohol	5.8	11.0	16.5
isopropylether	2.5	0	—
toluene	2.5	0	—
MIBK	2.5	trace	6.4
cyclohexanone	2.5	trace	4.9
n-caproic acid	4.8	trace	9.8
ethyl acetate	4.4	trace	11.6
diethyl ether	7.8	0	10.3
monochlorobenzene	2.5	0	—
aniline	5.1	0	8.8
tr cresyl phosphate	2.5	0	—
tetrachloroethylene	5.8	0	—
trichloroethylene	3.3	0	—
carbon tetrachloride	2.8	0	—
chloroform	3.3	0	—

\* 300 volt

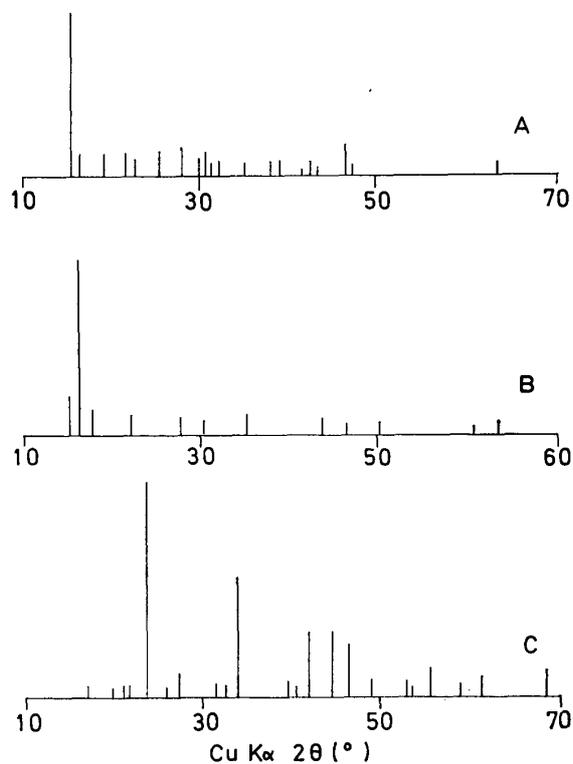


Fig. 8. X-ray diffraction pattern  
 A Product at 20°C, B Product at 80°C,  
 C Product dried in CO $_2$  gas.

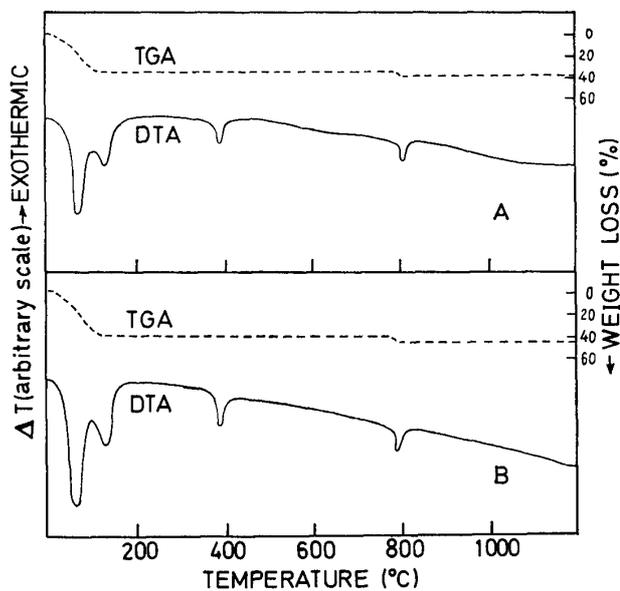


Fig. 9. DTA, TGA curves of product and Ba(OH) $_2$ ·8H $_2$ O.  
 A Product of extractive electrolysis.  
 B Ba(OH) $_2$ ·8H $_2$ O of market.

### 3.3 Identification of the product

For the purpose of identifying the product, it was subjected to X-ray analysis and the result was shown in Fig. 8. The deflection pattern varied with temperature of electrolysis and the compound corresponding to those pattern could be found neither in the A. S. T. M card nor in other hand books. But the deflection pattern of the substance which was left in the room after the electrolysis agreed with that of barium carbonate. From this it may be judged that the original product was either barium hydroxide or barium oxide which is the dehydrated product of barium hydroxide hydrate and that the substance changed to barium carbonate by absorbing carbon dioxide in the air. Accordingly the product was immediately washed in ether according to the decantation method and it was left in the decicator, introducing air which removed carbon dioxide, to dry in room temperature. The dried substance was subjected to defferential thermal analysis and the result was shown in Fig. 9. As the figure shows, the curves of these two, that is, the product and the barium hydroxide octahydrate were almost same in quality, although the difference in peak height and percent of decreased quantity over range of tepmerature,  $40 \sim 150\text{C}^\circ$  was observed. It maybe shows that in the process of the electrolysis, temperature in the cell rises considerably by Joule energy so that some part of crystalline water in the product is eliminated off. Also it was found that the pyrolysis of barium hydroxide octahydrate at market and the product of extractive electrolysis. at  $150\text{C}^\circ$  gave the same composition product, barium hydroxide monohydrate. It was therefore judged that the product of the extractive electrolysis was  $\text{Ba}(\text{OH})_2 \cdot \text{XH}_2\text{O}$  and that the X was lower than 8. Accordingly to this judgement, the product was analysed and the percentage of barium contents was calculated. The result was shown in table 7. As the table shows, the product is a substance which comes between 6 and 7 hydrate in its percentage of barium contents. Judging from these results. there can be no mistake in it that the product is barium hydroxide hydrate.

Table 7. Analysis of barium content in the product

substance	quantity of sample (mg)	barium content (mg)	percentage of barium (%)
product 1	0.3528	0.1657	46.96
peoduct 2	0.2441	0.1180	48.38
product 3	0.1490	0.0692	46.44
product 4	0.1946	0.0954	49.02
$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ at market	0.3332	0.1458	43.75

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## A New Preparation Method of Barium Hydroxide by Extractive Electrolysis using Hydrophobic Organic Solvent.

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Aqueous solution of barium salts were brought into contact with hydrophobic organic solvent, and the anode was dipped in aqueous phase and the cathode in organic phase. Barium was extractively electrolysed under this condition at comparatively high voltage, 200~700 volt.

Barium in aqueous solution was extracted in organic phase and it was produced barium hydroxide crystalline, combining hydroxide ion at the cathode, which was produced as the result of electrolysis of water. The other hand, it was also discovered that solid barium hydroxide could not be obtained by the electrolysis of the aqueous solution of barium salt unless the solution at the cathode was concentrated by evaporation.

barium hydroxide produced most effectively when aqueous solution of barium acetate was, nitrate and chloride following in the order. Furthermore, generally alcohols were good solvent for the extractive electrolysis such as isobutylalcohol, isoamylalcohol and hexylalcohol.

The identification of the product to be barium hydroxide was performed by X-ray analysis and differential thermal analysis (DTA) and the composition was determined by titration analysis using Mg-EDTA and eriochrom black T. The result showed that the product was  $\text{Ba}(\text{OH})_2 \cdot X\text{H}_2\text{O}$  and "X" was between 6 and 7, lower than 8.

### 概 要

バリウム塩水溶液を疎水性有機溶媒と接触させ、陽極を水溶液中に陰極を有機溶媒中に浸し、定電流またわ定電圧で抽出的に電解した。

バリウムイオンは電氣的に有機相に抽出され、水の電解の結果陰極で生成した水酸イオンと結合して水酸化バリウムとなり直接固体として折出した。他方水溶液の普通の電解では、陰極液を蒸発濃縮しなければ固体として水酸化バリウムを得ることはできなかった。

抽出電解において酢酸塩を用いたときが最もよく水酸化バリウムが折出した。また溶媒ではイソブチルアルコールが最も都合のよい溶媒であった。

また生成物は水酸化バリウムで水和数は8よりちいさく、6と7の間であった。