

The synthesis of copper picrates

Makoto Matsukawa^{*}, Takehiro Matsunaga^{**}, Ken-ichi Miyamoto^{**}, Mitsuaki Iida^{**},
Masatake Yoshida^{**}, Hiroki Morinaga^{*}, and Shuzo Fujiwara^{**}

This paper reports the chemical properties of copper picrate synthesized by three different methods. Differential scanning calorimetry analysis showed that the decomposition of copper picrate starts at a lower temperature than that of picric acid, and that the heat of exothermic reaction for copper picrate was less than that for picric acid. The results of elemental and thermogravimetry analyses show that the hydrate of the copper picrate ranged from trihydrate to tetrahydrate but that it has more crystalline water at low temperature. Crystalline water dehydration occurred between 300–400 K. Copper picrate was dehydrated by heating in a vacuum and copper picrate non-hydrate confirmed to have the property of re-hydration. The copper picrate synthesized in this study had similar chemical properties for all synthesis methods.

1. Introduction

Picric acid was used as a military explosive from World War I till the end of World War II¹⁾. At that time, it was known that picric acid reacts with metals to form very unstable metallic picrates. It was known that the heavy metal salt of azide has very sensitive properties, and the heavy metal salt of picric acid has similar properties as well. Indeed, lead picrate was studied for use as a primary explosive of detonators²⁾³⁾.

In this study, copper picrates were synthesized by three methods: the reaction of copper powder with picric acid solution, the reaction of copper (II) sulfate (CuSO_4) with barium picrate solution, and the reaction of copper carbonate, [basic] (CuCO_3) with picric acid solution. These products were then investigated to determine whether they have similar properties.

2. Experiments

2. 1 Synthesis of copper picrate from copper powder and picric acid

Picric acid obtained from Kanto Kagaku was prepared

by recrystallization from a deionized H_2O solution. Copper powder was obtained from Wako Pure Chemical Industries, Ltd. and was used without modification. Deionized water was used as the synthesis solvent.

Picric acid was dissolved in H_2O (500 ml) in sufficient quantity to make a saturated picric acid solution. Copper powder (under $75\ \mu\text{m}$: 20 g) was added slowly to the saturated picric acid solution and the mixture was stirred for two hours at room temperature. The reacted solution was filtered and precipitation of unreacted copper powder separated. The filtrate was heated and condensed until the quantity of the solution reached approximately 200 ml and the solution was then poured into a plastic vat. The solution was dried by draft ventilation and a brown crystal was obtained as the product. The synthesized copper picrate was purified with dichloromethane in order to extract the contamination of unreacted picric acid in filtrate⁴⁾.

The amount of reacted product was approximately 86% of the theoretical amount.

2. 2 Synthesis of copper picrate from copper(II) sulfate and barium picrate solution

In this method, copper picrate was synthesized by way of barium picrate as an intermediate. Barium picrate was prepared from picric acid and barium carbonate in deionized H_2O ⁵⁾. An equivalent quantity of barium carbonate was used to react with the saturated solution of picric acid (500 ml). Copper (II) sulfate (CuSO_4) was

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Showa Kinzoku Kogyo Co., Ltd. Iwase 2120, Iwase, Nishi-Ibaraki
Gun, Ibaraki 309-1211, JAPAN

TEL +81-296-76-1811

FAX +81-296-76-1815

E-Mail fwkf8264@nifty.com

^{**}National Institute of Advanced Industrial Science and Technology,
1-1, Higashi Tsukuba, Ibaraki 305-8565, JAPAN

TEL +81-298-61-4785

FAX +81-298-61-4783

E-Mail t.matsunaga@aist.go.jp

added into the barium picrate solution and stirred for two hours. Barium sulfate as a precipitation by-product was filtered and separated. The filtrate was poured into a plastic vat, dried by draft ventilation, and a yellowish green crystal was obtained as the product.

The amount of product obtained was approximately 83% of the theoretical amount.

2. 3 Synthesis of copper picrate from copper (II) carbonate, [basic] in picric acid solution

A quantity of copper (II) carbonate, [basic] corresponding to the reaction was added into a picric acid solution and the mixture was stirred for two hours at room temperature. Bubbles were generated in the reacting solution which seemed to be carbon dioxide. After reaction, the mixture solution was filtrated and unreacted copper carbonate was separated as residuc. The filtrate was poured into a plastic vat, dried by draft ventilation, and a yellowish green crystal was obtained as the product. The contamination of unreacted picric acid was extracted by a method similar to that described in section 2.3.

The amount of product obtained was approximately 97% of theoretical amount.

2. 4 Analysis Method

Differential scanning calorimetry analysis (DSC): DSC measurements were obtained on a TA INSTRUMENTS DSC2920 differential scanning calorimetry apparatus. The apparatus was calibrated based on the melting point and heat of fusion of indium. The sample was sealed in an aluminum crimp cell and an atmospheric condition in the apparatus was maintained with 3 MPa pressurized nitrogen gas. The sample weight was about 1mg and the heating rate $10\text{ K}\cdot\text{min}^{-1}$.

Thermal gravity analysis (TG): The TA Instruments SDT2960 and Simultaneous TGA-DTA apparatus was used to determine the quantity of combined H_2O in the products.

The experiment was carried out under Ar gas stream. The sample weight was about 1mg and the heating rate $20\text{ K}\cdot\text{min}^{-1}$.

Elemental analysis: Elemental analyses were carried out using a Perkin Elmer 2400 Series II CHNS/O Analyzer.

X-ray fluorescence analysis: The existence of copper was determined using a Shimadzu XRF-1500 Wavelength Dispersive X-ray Fluorescence Spectrometer.

Fourier transform infrared spectroscopy analysis (FT-IR): IR spectra were obtained by a Shimadzu FTIR

-8000PC Fourier Transform Infrared Spectroscopy Apparatus. The sample was prepared by the KBr method.

3. Results and discussion

3. 1 Thermal analysis

The samples synthesized by the three methods were analyzed by DSC (see Fig. 1). The exothermic decomposition of copper picrate started at $480\text{ K} - 500\text{ K}$ and exothermic peaks were confirmed at two positions, approximately 530 K and 570 K , which are similar peaks positions with all copper picrates. This decomposition temperature was lower than that of picric acid, which was approximately 540 K . Moreover, the heat of exothermic of copper picrate was $4300\text{ J}\cdot\text{g}^{-1} - 4100\text{ J}\cdot\text{g}^{-1}$, which was less than the approximate value of $5400\text{ J}\cdot\text{g}^{-1}$ of Picric acid. There was a slight difference in the shape of exothermic decomposition curves, but the peaks appeared at a similar temperature. This suggests that similar reactions occurred in all decomposition processes. The TG-DTA analysis result was showed in Fig.2. The endothermic peak of

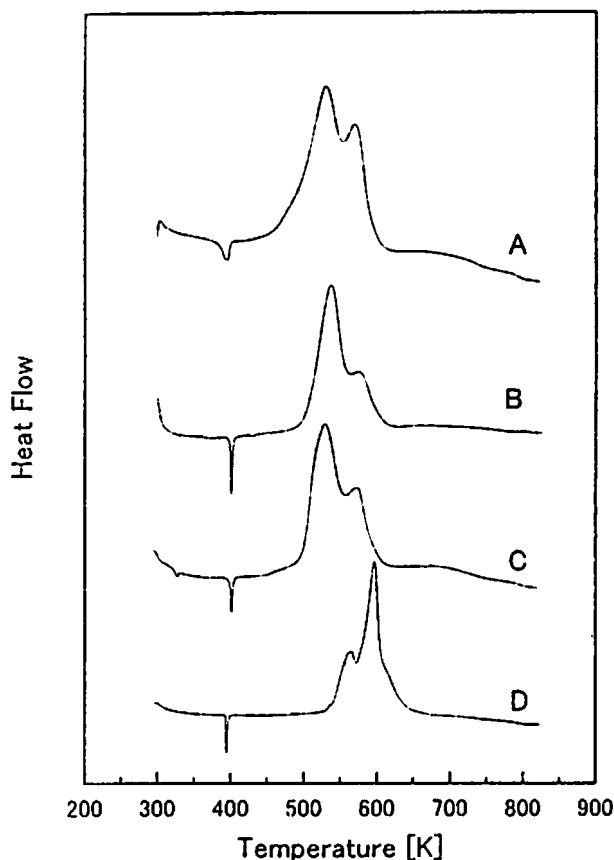


Fig.1 DSC results for copper picrates and picric acid.

A; synthesized from picric acid and copper powder, B; synthesized from barium picrate and copper sulfate, C; synthesized from Picric Acid and copper carbonate, D; picric acid (KANTO Kagaku).

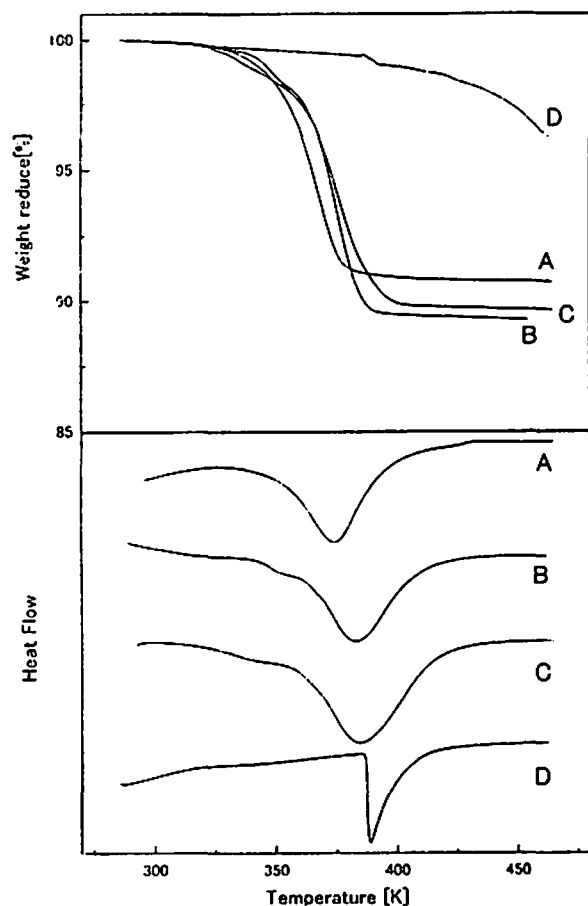


Fig.2 TG results for copper picrate at room temperature (approximately 293 K). A; synthesized from picric acid and copper powder, B; synthesized from barium picrate and copper sulfate, C; synthesized from Picric Acid and copper carbonate, D; picric acid (KANTO Kagaku)

approximately 400 K was estimated by dehydration of crystalline water. The result of TG-DTA of copper picrates showed which endothermic phenomenon occurred with weight reduction. The result of TG-DTA of picric acid showed the endothermic peak but weight reduction was unconfirmed at the same temperature. Thus, the endothermic phenomenon of copper picrate was assumed to be the dehydration of crystalline water, but the endothermic phenomenon of picric acid was indicated by the melting of picric acid crystal⁶⁾. The endothermic peak of copper picrate appeared at a different temperature between the DSC result and TG-DTA result, to DSC measurement by crimped cell and under 3Mpa pressure, but TG-DTA measurement by open cell and at atmospheric pressure.

3. 2 Molecule form of copper picrate

The result of X-ray fluorescence analysis shows the products from each synthesis method had characteristic X

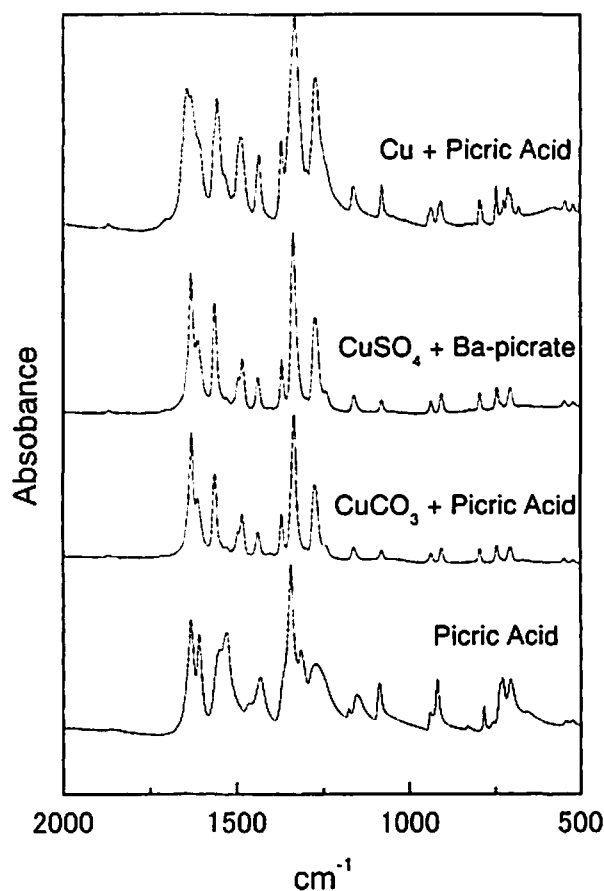


Fig.3 FT-IR spectra of copper picrates and Picric Acid.

rays, which showed the existence of a copper element in each product. A barium element was not detected in the sample synthesized from barium picrate and copper sulfate.

Adsorption of 1270cm^{-1} of FT-IR showed stretch bonding between a phenyl group and an oxygen atom (see Fig. 3). Furthermore, approximately 1330 cm^{-1} and 1560 cm^{-1} absorptions exhibit N-O stretch bonding. The peak at 1315 cm^{-1} , which appeared as a result of picric acid, disappeared as a result of copper picrate, which indicated O-H stretch bonding of the phenol group. The results of FT-IR by copper picrate and picric acid were very similar to each other. Therefore, the copper picrate was estimated to be similar in molecular form to picric acid.

Table 1 shows the results of elemental analysis; however, the results of the elemental ratio of oxygen and copper were calculated based on the result of carbon and hydrogen quantity, and the quantity of crystalline H_2O was calculated based on the result of hydrogen and carbon quantity ratio. The results of species and numbers of element were estimated for molecules of two piece picrate anion. Therefore, copper picrate had the form of a copper cation with two molecules of picrate anions, which was the same result for all synthesis-method samples.

Table 1 Elemental analysis result of copper picrate

Element	Atomic Weight*	Picric Acid + Copper powder			Barium picrate + CuSO ₄			Picric Acid + CuCO ₃		
		results** (wt.%)	element ratio***	theoretical weight ratio**** (wt.%)	results** (wt.%)	element ratio***	theoretical weight ratio**** (wt.%)	results** (wt.%)	element ratio***	theoretical weight ratio**** (wt.%)
C	12.01	24.99	12	25.12	23.58	12	24.73	24.71	12	25.12
H	1.01	1.76	10	1.76	1.84	11	1.91	1.67	10	1.76
N	14.01	13.72	6	14.65	13.30	6	14.42	14.08	6	14.65
O*****	16.00	47.21	17	47.40	45.83	17.5	48.04	46.15	17	47.40
Cu*****	63.54	11.02	1	11.07	10.40	1	10.90	10.89	1	11.07
Combined H ₂ O*****		3			3.5			3		

* Quotation from NIST Standard Reference Database 69 (2001)

** Analysis results (included the quantity of combined H₂O molecules)

*** Calculate base: C=12

**** Theoretical weight ratio were calculated by based on element ratio

***** Oxygen and copper element ratio were calculated by based on result of carbon and hydrogen quantity

***** The quantity of combined H₂O was calculated by based on result of hydrogen quantity

3. 3 Crystalline water in copper picrate

TG-DTA analysis results are shown in Fig. 2 and Table 2. Weight reduction occurred gradually from about 300 K, and ended at about 420 K. The weight of the sample from picric acid and copper powder was reduced by 9.17%, that of the sample of copper (II) sulfate and barium picrate as well as that of the sample of copper (II) carbonate were each reduced by 10.3% and 10.5%. This reduction was 3–4 molecules as H₂O. Therefore, these samples were estimated to be trihydrate - tetrahydrate. The results from element analysis are similar to those of TG-DTA. For the above reason, each copper picrate was estimated to have 3–4 molecules of crystalline water (see Table 1).

The quantity of crystalline water at low temperature

was analyzed by copper picrate maintained in humid air at low temperature (approximately 270 K), and that of the obtained sample was analyzed by thermal gravity analysis whose result was deca-hydrate that was seven molecules more than the result of the sample in room temperature (Fig.4). According to literature^{7,8)}, copper picrate obtained by cooling of the hot solution had about 10 molecules of H₂O. Because of this, copper picrate was deca-hydrate at low temperature.

In the above results, the quantity of crystalline water differed slightly under the same analytical conditions with each method of synthesis. This, it was surmised, was because the crystalline waters in copper picrate were in the metastable phase at room atmosphere. Thus, few molecules of crystalline waters were considered easily

Table 2 Result of TG analysis for copper picrate at room temperature (approximately 293 K) and low temperature (273 K–276 K)

		Copper powder + Picric Acid	CuSO ₄ + Barium picrate	CuCO ₃ + Picric Acid
Crystal in room temperature (approximately 293K)	Weight reduction	9.17%	10.54%	10.36%
	H ₂ O molecule	2.92	3.41	3.34
Crystal in low temperature (273K–276K)	Weight reduction	24.83%	25.07%	26.39%
	H ₂ O molecule	9.56	9.68	10.37

dehydrated at room atmosphere. Room atmospheric conditions were estimated to be dissimilar when samples were measured.

3. 4 Dehydrate of crystalline water

Copper picrate was dehydrated under the conditions described below, in a vacuum chamber, and the property of dehydration was confirmed.

- 1) Room temperature (approximately 293 K), 12 hours, vacuum (under 133 Pa)

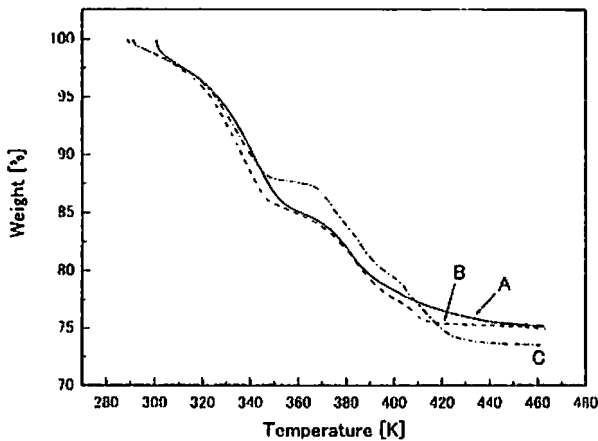


Fig.4 TG results for copper picrate at low temperature (approximately 273 K–276 K). A; synthesized from picric acid and copper powder, B; synthesized from barium picrate and copper sulfate, C; synthesized from Picric Acid and copper carbonate

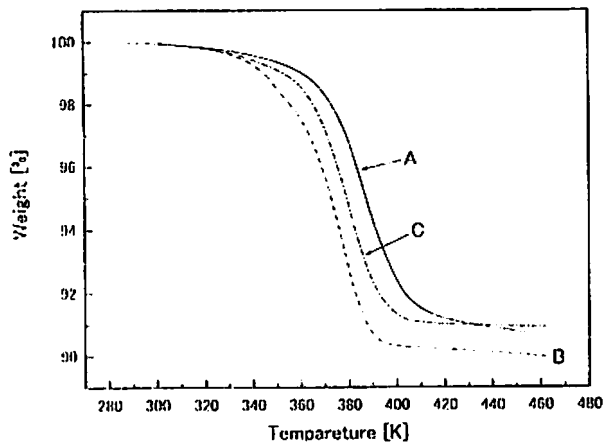


Fig.5 TG results for copper picrate after vacuum (under 133 Pa) by room temperature (approximately 293 K) 12 h. A; synthesized from picric acid and copper powder, B; synthesized from barium picrate and copper sulfate, C; synthesized from Picric Acid and copper carbonate

- 2) 393 K, 4 hours, vacuum (under 133 Pa)
- 3) 473 K, 1 hour, vacuum (under 133 Pa)

The results of TG for the above dehydrated condition samples are shown in Figs.5, 6, and 7 and in Table 3. The result of dehydration by condition 1) is an estimated similar weight reduction for the sample before dehydration, approximately tri-hydrate, and this sample was not confirmed to dehydrate. The samples dehydrated from condition 2) and 3) were confirmed to be almost dehydrated.

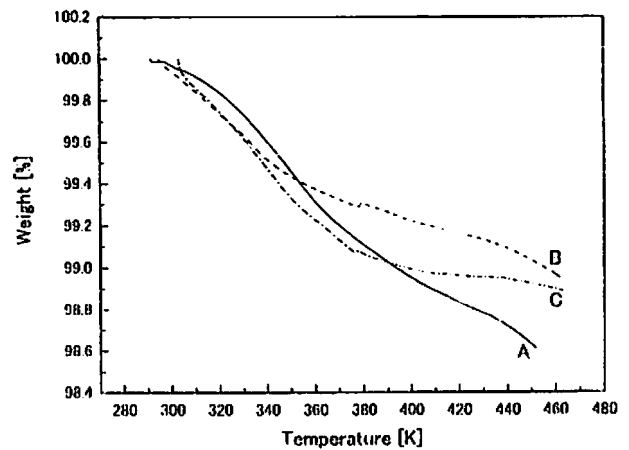


Fig.6 TG results for copper picrate after vacuum (under 133 Pa) by 393 K, 4 h. A; synthesized from picric acid and copper powder, B; synthesized from barium picrate and copper sulfate, C; synthesized from Picric Acid and copper carbonate.

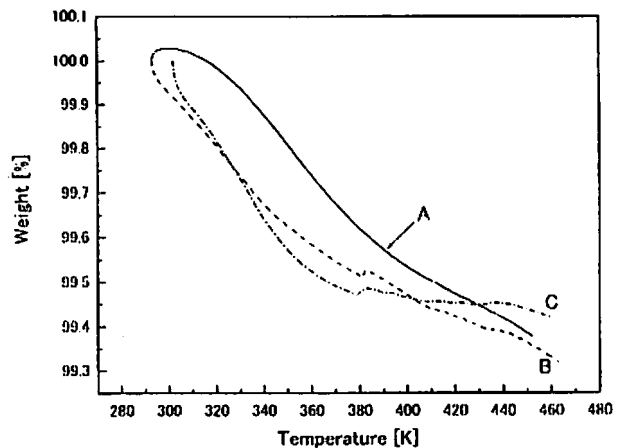


Fig.7 TG results for copper picrate after vacuum (under 133 Pa) by 473 K, 1 h. A; synthesized from picric acid and copper powder, B; synthesized from barium picrate and copper sulfate, C; synthesized from Picric Acid and copper carbonate.

Table 3 Result of TG analysis for copper picrate after dehydration (see text 3.4 1) – 3))

		Copper powder + Picric Acid	CuSO ₄ + Barium picrate	CuCO ₃ + Picric Acid
Vacuum at room temperature	Weight reduction	9.11 %	10.05 %	9.08 %
	H ₂ O molecule	2.90	3.23	2.89
Vacuum at 393K, 4h.	Weight reduction	1.39 %	1.06 %	1.11 %
	H ₂ O molecule	0.41	0.31	0.32
Vacuum at 473K, 1h.	Weight reduction	0.62 %	0.68 %	0.58 %
	H ₂ O molecule	0.18	0.20	0.17

3. 5 Re-hydration of crystalline water

Copper picrate dehydrated as described in 3.4 3), was used for a re-hydration property test. A dehydrated sample was kept in water desiccator at room temperature (approximately 293 K) for four hours, then analyzed by TG analysis (Fig. 8). The result was a confirmed weight reduction of 10 – 15 % which corresponds to 3 – 5 molecules of H₂O. This result suggests the possibility of re-hydration. Copper picrate had 3 – 5 molecules of H₂O as re-hydrated H₂O molecules.

4. Conclusions

From the experimental and analytical results, the following conclusions can be drawn:

- (1) The result of X-ray fluorescence proved the existence of a copper element in synthesized products, and FT-IR results indicated products with similar molecular form to picric acid. These results were the same regardless of the method of synthesis. As a conclusion, it is shown that copper picrate was synthesized.
- (2) The results of TG-DTA analysis and elemental analysis showed the products were trihydrate to tetrahydrate. Further, the sample at low temperature was decahydrate.
- (3) Crystalline water of copper picrate was dehydrated at over 393 K, for 4 hours and under vacuum (under 133 Pa), and dehydrated copper picrate had the property of re-hydration.
- (4) This study indicates that copper picrate was synthesized from the picric acid solution and copper powder. The products of different methods of synthesis were different in appearance, but their chemical properties

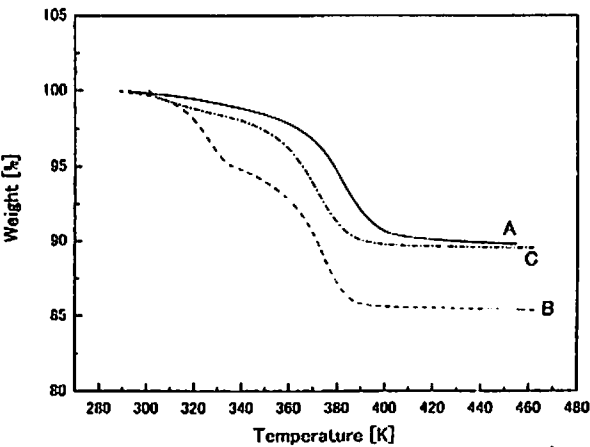


Fig.8 TG results for copper picrate after re-hydration. A; synthesized from picric acid and copper powder, B; synthesized from barium picrate and copper sulfate, C; synthesized from Picric Acid and copper carbonate.

were similar. Consequently, it was proved that copper picrate was synthesized not only by the reaction of other picrates (ex. barium picrate) or picric acid with copper salt, but also by the reaction of a picric acid solution with copper powder reaction.

References

- 1) U.S.ARMY ARRADCOM, ENCYCLOPEDIA OF EXPLOSIVES AND RELATED ITEMS, 8, 285 (1978)
- 2) S. Kinoshita and S. Nakahara, J. Ind. Explos. Soc., Japan, 17, 202 (1956)
- 3) K. Okumura, K. hasue and K. Okazaki, J. Ind. Explos. Soc., Japan, 36, 326 (1975)
- 4) K. Nakagawa, K. Amita, and H. Mizuno, Bull. Chem.

