

The synthesis of zinc picrates

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Picric acid is known to react with metals to form highly unstable metallic picrates, which are known to have been involved in serious explosive accidents. In this study, zinc picrates are synthesized from zinc powder, zinc carbonate and zinc sulfate, and the thermodynamic and explosive properties of the different compounds are examined. Differential scanning calorimetry results reveal that decomposition of zinc picrate begins at a lower temperature than picric acid. The heat of decomposition of zinc picrate was lower than that of picric acid. Zinc picrate was confirmed by thermal gravimetric analysis and Karl Fischer analysis to contain crystalline H₂O, and to dehydrate stepwise with increasing temperature. Experimental results show that the zinc picrate molecules contain approximately six molecules of crystalline H₂O. Crystalline H₂O dehydration occurred between 330 and 500 K. Zinc picrate was dehydrated by heating in a vacuum, with dehydrated zinc picrate confirmed to exhibit re-hydration properties. Activation energy of exothermic decomposition was determined to be 116.0 - 133.4 kJ·mol⁻¹ and was similar for all samples. The zinc picrate synthesized in this study had similar chemical properties independent of the synthesis method.

1. Introduction

Picric acid was used as a military explosive from World War I until the end of World War II¹⁾. At that time, picric acid was known to react with metals to form very unstable metallic picrates, with attempts made to synthesize these picrates by Lea and other authors^{2) 3)}. Examples of accidents involving metallic picrates are the detonation of metallic picrate after a metal fragment fell into burning picric acid, and picric acid that was splashed onto a metal steam pipe, producing metallic picrate that subsequently exploded when struck⁴⁾. In recent years, only a few of the studies into metallic picrates have examined chemical and pyrotechnic properties using modern analytical techniques.

Picric acid is a monovalent organic salt that dissociates into one proton and one picrate anion in H₂O solution.

When metallic cations exist in solution, the picrate anions are thought to bond ionically to the metallic cation to form a metallic picrate. One of the purposes of this study was to estimate the different properties of picrates synthesized from metal powder and picrates synthesized from metallic salt. Zinc picrates were synthesized by three methods: reaction of zinc powder with picric acid solution, reaction of zinc(II) sulfate (ZnSO₄) with barium picrate solution, and reaction of zinc(II) carbonate (ZnCO₃) with picric acid solution. A synthesis reaction is shown in Fig.1 where two picrate anions bond to a zinc cation. The products were then investigated to determine if any similar properties existed. Moreover, the amount of crystalline H₂O in metallic picrate is known to influence explosion sensitivity⁴⁾, and this is an important factor in consideration of safety. Therefore, research of crystalline H₂O in zinc picrate was performed.

2. Experimental

2.1 Synthesis of zinc picrate from zinc powder and picric acid

Picric acid obtained from Kanto Kagaku was prepared by recrystallizing from a deionized H₂O solution. Zinc powder was obtained from Wako Pure Chemical Industries, Ltd. and was used without modification.

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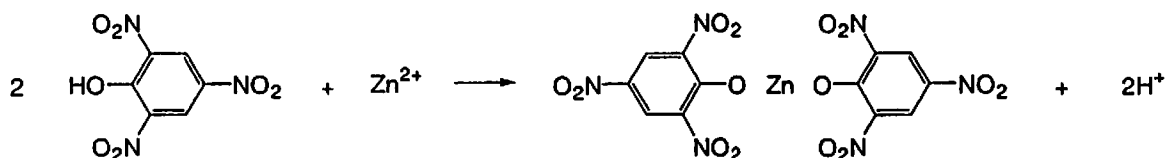


Fig.1 Zinc picrate synthesis equation.

Deionized water was used as a synthesis solvent.

Picric acid 6 g was dissolved in deionized H₂O (500 ml) to produce a saturated picric acid solution. Zinc powder (under 45 μm : 20 g) was added slowly to the saturated picric acid solution and the mixture was stirred for two hours at room temperature. As the reaction progressed the color of the solution changed from yellow to brown. The reacted solution was filtered and precipitate of the unreacted zinc powder was separated. Filtrate was heated and condensed until the quantity of the solution reached approximately 200 ml and the solution was then poured into a plastic vessel. An indistinct precipitate was confirmed in condensed solution. The solution was thus thought to contain microscopic zinc colloid. The solution was dried by draft ventilation and a brown crude crystal was obtained. This was then dissolved in about 300 ml of acetone and impurities were removed by filtration. A refined product from which insoluble impurities had been removed was obtained by drying the acetone solution. The synthesized zinc picrate was then added to dichloromethane 2000 ml to remove picric acid as a contaminant. Unreacted picric acid was extracted as a filtrate³⁾. The result of the synthesis procedure was 5.68 g of final product.

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

Zinc picrate was synthesized using barium picrate as an intermediate. Barium picrate was prepared from picric acid-saturated solution and barium carbonate, with unreacted barium carbonate separated by filtration⁶⁾. The solution was then evaporated to dryness to produce barium picrate crystals. Barium picrate 1% solution was prepared by dissolving the obtained barium picrate in deionized H₂O. Zinc (II) sulfate (ZnSO₄) was added to the barium picrate solution (500 ml) and stirred for two hours. Barium sulfate was filtered and separated as a by-product of precipitation. The filtrate was poured into a plastic vessel, dried by draft ventilation, with a yellow crystal obtained as the product. This was refined using

the method described in section 2.1. A total of 3.2g of product were obtained.

2. 3 Synthesis of zinc picrate from zinc (II) carbonate in picric acid solution

A quantity of zinc (II) carbonate corresponding to complete reaction, about 1.3 g, was added to 500 ml of picric acid solution (1%) and the mixture was stirred for two hours at room temperature. Bubbles were generated in the reacting solution, and these seemed to be carbon dioxide by-product. After reaction, the solution was filtered and unreacted zinc carbonate was separated as a residue. The filtrate was poured into a plastic vessel, dried by draft ventilation and a yellow crystal was obtained as the product. Contamination by unreacted picric acid was eliminated using the method described in section 2.1. A total of 5.48 g of product was synthesized in this way.

2. 4 Analysis Method

Differential scanning calorimetry analysis (DSC) was used to characterize the thermodynamic properties of the product. DSC measurements were conducted on a TA Instruments DSC2920. Device parameters, endothermic values and melting temperatures were calibrated with respect to fusion temperature and the endothermic heat of fusion of indium. The sample was sealed in a Au evaporated aluminum crimp cell and loaded into the apparatus, which maintains a 3 MPa nitrogen gas environment. Analysis was performed on samples weighing approximately 0.5 mg at a heating rate of 10 K·min⁻¹. The measurement range was from room temperature (about 298 K) to 823 K. Measurements were also conducted at heating rates of 1, 2, 5, 10 and 20 K/min to evaluate activation energy.

Thermal gravimetric (TG) analysis was performed to determine the crystalline water content of the products. Measurements were conducted using a TA Instruments SDT2960 simultaneous thermal gravimetry and differential thermal analysis (TG-DTA) instrument. The apparatus was flushed by Ar gas flowing at atmospheric

pressure during measurements. Sample weight was approximately 10 mg, and heating rate was $10 \text{ K}\cdot\text{min}^{-1}$.

Crystalline water content was also investigated by the Karl Fischer method using a Metrohm 758 KFD Titrino apparatus. Riedel-deHaen Hydranal Composite 5 was used with Karl Fischer reagent, and the machine was calibrated using approximately $30 \mu\text{L}$ of deionized water.

X-ray fluorescence analysis was employed to determine the metallic elements in the products. Measurements were conducted using a Shimadzu XRF-1500 wavelength dispersive x-ray fluorescence spectrometer having a LiF crystal and lattice constant ($2d$) of 4.0267 angstroms.

Molecular forms of the products were analyzed by Fourier transform infrared (FT-IR) spectroscopy by the KBr method using a Shimadzu FTIR-8200PC. The

measurement range was chosen to be between 400 and 2000 cm^{-1} to avoid influences from moisture in the air.

3. Results and discussion

3.1 Thermal analysis

The results of DSC analysis are shown in Fig. 2 and Table 1. Exothermic decomposition of zinc picrate started at $480 \text{ K} - 500 \text{ K}$, with two exothermic peaks observed at approximately 550 K and 590 K . Decomposition started at approximately 510 K , lower than the approximately 540 K for picric acid. Moreover, the exothermic heat released from zinc picrate was $3600 - 4200 \text{ J}\cdot\text{g}^{-1}$, which is less than approximate value of $5400 \text{ J}\cdot\text{g}^{-1}$ for picric acid. But, rough estimate of exothermic heat of zinc picrate ignoring zinc atomic weight, was about $4950 - 5770 \text{ J}\cdot\text{g}^{-1}$. Exothermic decomposition behaviors of all of the samples were very similar, suggesting that similar reactions occur in all of the decompositions.

TG-DTA analysis results are shown in Fig. 3. Immediately after synthesis of the crystals, crystalline water properties can possibly be changed by refinement. Thus, the synthesized sample, which dissolved in deionized H_2O , was recrystallized and dried in vacuum at 298 K for 24 hours. Results of TG-DTA of zinc picrates revealed that endothermic phenomenon accompanied weight reduction. The weight reduction occurred gradually from approximately 330 K , and ended at around $470 \text{ K} - 500 \text{ K}$. TG-DTA results for picric acid exhibited an endothermic peak at 390 K , whereas weight reduction started at above 430 K . Thus, weight reduction could not be confirmed at the same temperature as the endothermic peak. The endothermic phenomenon observed in picric acid indicated melting of picric acid crystal, whereas the weight reduction at approximately 430 K was thought to be either decomposition and/or evaporation of the picric acid^[1].

The endothermic phenomenon observed in zinc picrate was assumed to be dehydration of crystalline water. The

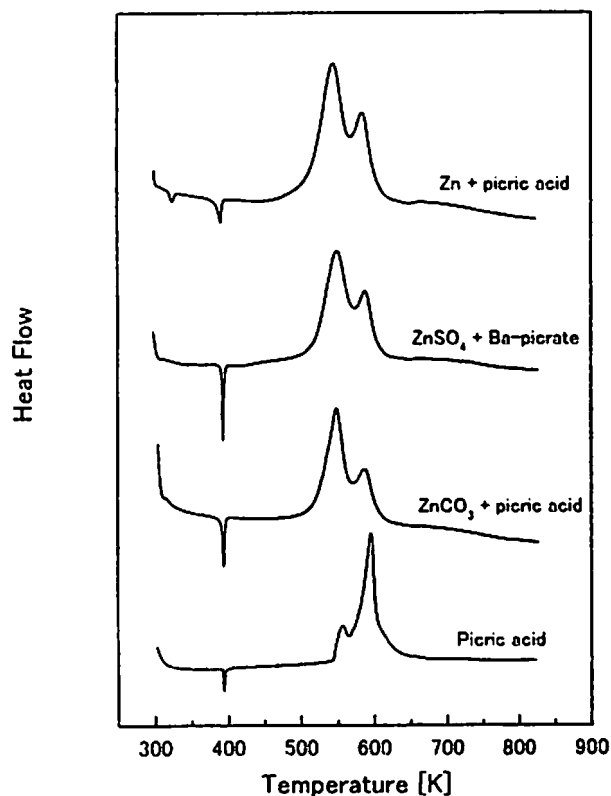


Fig.2 DSC results for zinc picrates and picric acid.

Table 1 DSC and TG results for zinc picrate.

		Zinc powder + Picric Acid	ZnSO ₄ + Barium picrate	ZnCO ₃ + Picric Acid
DSC	Exothermic peaks	545 K, 584 K	549 K, 588 K	548 K, 587 K
	Exothermic heat	$3633 \text{ J}\cdot\text{g}^{-1}$	$4236 \text{ J}\cdot\text{g}^{-1}$	$3867 \text{ J}\cdot\text{g}^{-1}$
TG	Weight reduction	17.9 %	17.4 %	17.0 %
	H ₂ O molecules	6.3	6.1	5.9

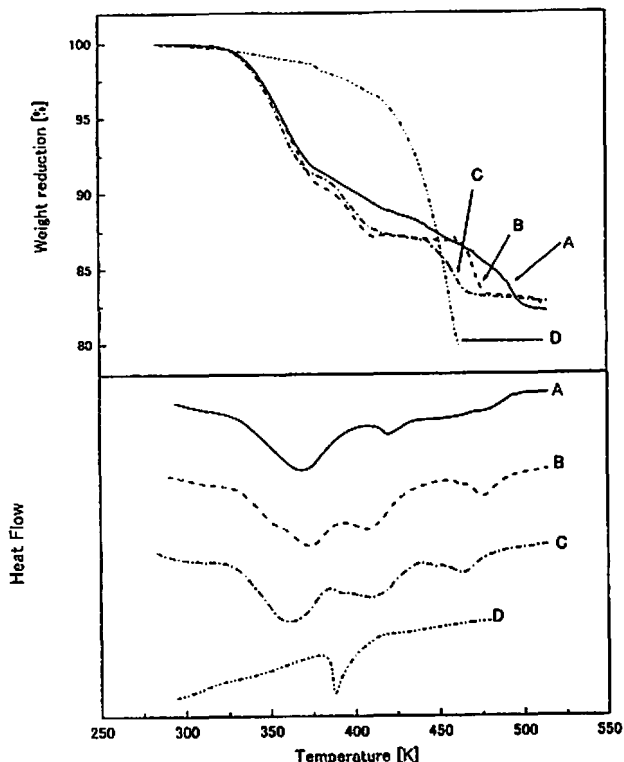


Fig.3 TG results for zinc picrate at room temperature (approximately 293 K).
 A) Synthesized from picric acid and zinc powder, B) synthesized from barium picrate and zinc sulfate, C) synthesized from picric acid and zinc carbonate, and D) picric acid (KANTO Kagaku).

endothermic peak in zinc picrate appeared at different temperatures in DSC and TG-DTA results. The reason was the different sample conditions, as the sample was in a crimped cell and under 3 MPa pressure in DSC measurements, but in an open cell and at atmospheric pressure in TG-DTA measurements.

3. 2 Molecular form of zinc picrate

The result of X-ray fluorescence analysis, obtained by LiF spectrum crystal, revealed that the products from each synthesis method had reflection patterns at 37.5 degrees and 41.8 degrees, as shown in Fig. 4. These are the characteristic X ray patterns of zinc, and are caused by the presence of zinc in each product. Reflections at approximately 18 degrees were caused by rhodium being used as the X-ray tube filament, while reflections at approximately 86 degrees were due to the influence of titanium from the sample holder. Barium was not detected in the sample synthesized from barium picrate and zinc sulfate.

Adsorption of 1270 cm^{-1} in the FT-IR results, shown in Fig. 5, indicate bond stretching between a phenyl group

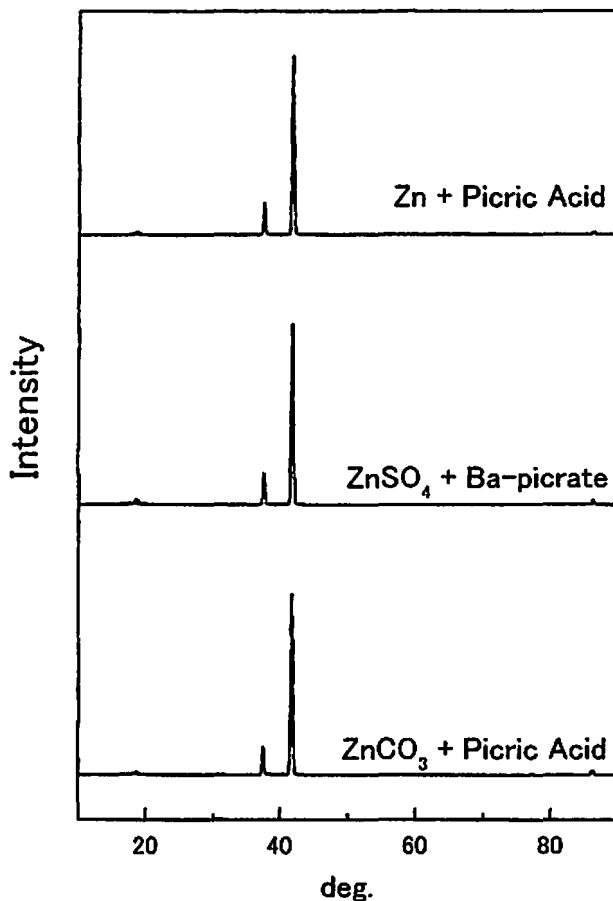


Fig.4 X-ray fluorescence results.

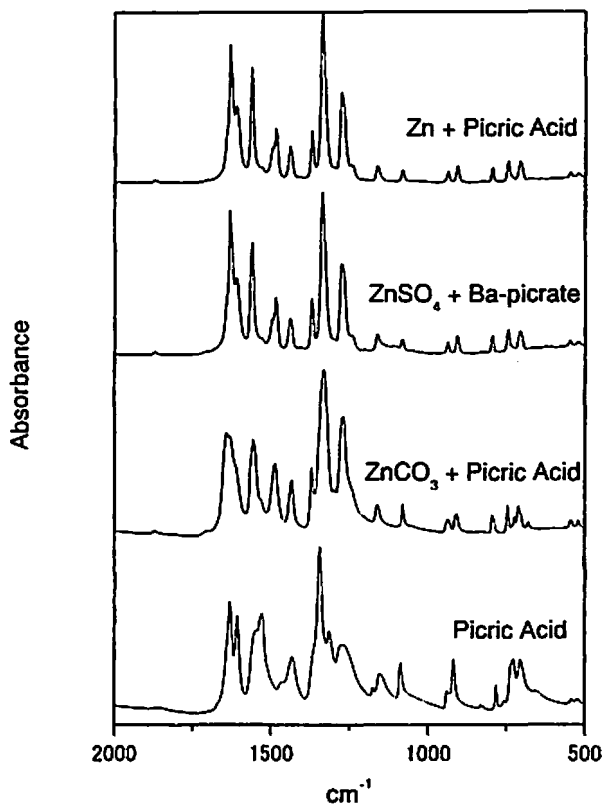


Fig.5 FT-IR spectra of zinc picrates and picric acid.

Table 2 Karl Fischer analysis results for zinc picrate.

		Zinc powder + Picric Acid	ZnSO ₄ + Barium picrate	ZnCO ₃ + Picric Acid
Karl Fischer analysis	H ₂ O content	16.1 %	17.5 %	17.0 %
	H ₂ O molecules	5.6	6.2	5.9

and an oxygen atom. Furthermore, absorptions at approximately 1330 cm⁻¹ and 1560 cm⁻¹ suggest N-O bond stretching. The peak at 1315 cm⁻¹, which appeared to be caused by picric acid, disappeared in zinc picrate, indicating O-H bond stretching of the phenol group. The results of FT-IR of zinc picrate and picric acid were very similar, and zinc picrate was therefore estimated to be similar in molecular form to picric acid. Similar results have been obtained in previous studies^(8,9) of iron picrate and copper picrate.

3.3 Crystalline water in zinc picrate

Crystalline H₂O amounts results are shown in Table 1. The weight of the sample from picric acid and zinc powder was reduced by 17.9 %, that of the sample of zinc (II) sulfate and barium picrate was reduced by 17.4 %, and that of the sample of zinc (II) carbonate and picric acid was reduced by 17.0 %. These reductions correspond to about 6 molecules of H₂O. These samples were thus estimated to be hexahydrate from results of TG-DTA.

Karl Fischer analysis results are shown in Table 2. H₂O content of the sample prepared from picric acid and zinc powder was 16.1 %, that of the sample of zinc (II) sulfate and barium picrate was 17.5 %, and that of the sample of zinc (II) carbonate and picric acid was 17.0 %. These amounts correspond to about 6 molecules of H₂O. Thus, these samples were estimated to be hexahydrate from results of Karl Fischer analysis.

The result of crystalline water content analysis for the sample synthesized from picric acid and zinc powder, exhibited disagreements between the results of thermal

gravimetric analysis and Karl Fischer analysis. This suggests that the measurements from thermal gravimetric analysis were not only measuring the dehydration of crystalline water. Weight reduction, apart from dehydration, was thought to have possibly been due to detachment of solvate, which is thought to have been generated by refinement by acetone, decomposition of sample and so on. The sample that was synthesized from picric acid and zinc powder exhibited an obviously different outer appearance to the other samples. The reason for this was thought to be microscopic impurities, such as unreacted materials, which were not removed by refining but remained in the molecular structure.

In the results shown in Tables 1 and 2, the quantity of crystalline water differed slightly under the same analytical conditions for each synthesis method. From observation of TG curves, weight reduction of samples prepared from barium picrate + zinc sulfate and picric acid + zinc carbonate exhibited clear steps, but weight reduction of the sample prepared from picric acid and zinc powder exhibited a smooth step. Thus, the difference in crystalline H₂O adsorption conditions was surmised to be partly due to differences in synthesis methods. The existence of microscopic impurities at molecular level and/or solvate, as mentioned earlier, was thought to have changed crystalline H₂O conditions.

3.4 Yield

Table 3 shows the synthesis yields of zinc picrate. Crystalline H₂O was calculated by use of the Karl Fischer method in Table 2.

Table 3 Calculation results of yield (based on crystalline H₂O amount).

	Molecule weight as anhydrate	Crystalline water molecules*	Product amount[g]	Yield[%]
Zinc powder + Picric Acid	522.67	5.6	5.68	70.0
ZnSO ₄ + Barium picrate		6.2	3.2	67.3
ZnCO ₃ + Picric Acid		5.9	5.48	79.8

*Crystalline H₂O value was obtained from Table 2, Karl Fischer method.

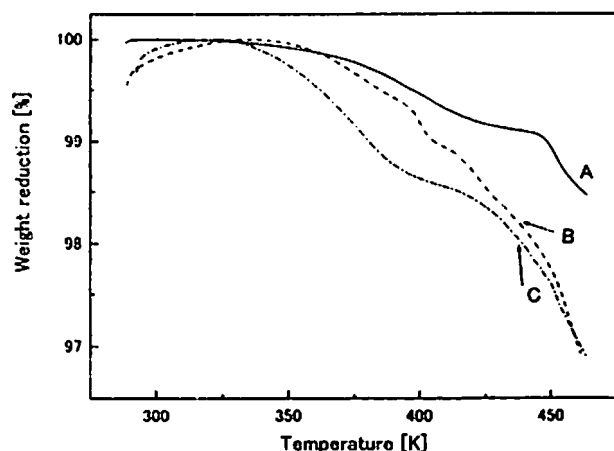


Fig.6 TG results for zinc picrate after drying in vacuum (under 133 Pa) at 393 K for four hours.

A) Synthesized from picric acid and zinc powder, B) synthesized from barium picrate and zinc sulfate, and C) synthesized from Picric Acid and zinc carbonate.

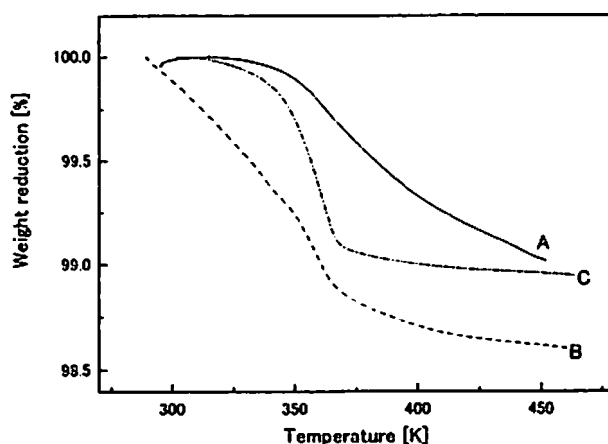


Fig.7 TG results for zinc picrate drying in vacuum (under 133 Pa) at 473 K for one hour.

A) Synthesized from picric acid and zinc powder, B) synthesized from barium picrate and zinc sulfate, and C) synthesized from picric acid and zinc carbonate.

The result shows that the sample, which synthesized from picric acid and zinc carbonate, was of highest yield, but the sample, which synthesized from barium picrate and zinc sulfate, of lowest one.

3. 5 Dehydrate of crystalline water

Zinc picrate was dehydrated under the conditions described below in a vacuum chamber, and dehydration properties were confirmed. The same parameters were used as in previous studies that analyzed iron picrate and copper picrate⁹¹⁾.

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

The results of TG for samples dehydrated using the parameters above are shown in Figs. 6 and 7, and Table 4. The samples were confirmed to be almost completely dehydrated.

Similar results were obtained in studies of iron picrate and copper picrate⁹¹⁾, which were almost dehydrated by drying using the same parameters.

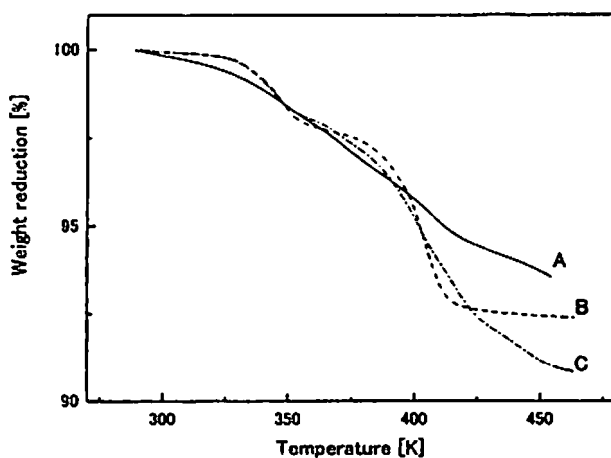


Fig.8 TG results for zinc picrate after re-hydration in a water desiccator for four hours.

A) Synthesized from picric acid and zinc powder, B) synthesized from barium picrate and zinc sulfate, and C) synthesized from picric acid and zinc carbonate.

3. 6 Re-hydration of crystalline water

Zinc picrate dehydrated by aforementioned condition 3.4 2) was used for a re-hydration property test. A dehydrated sample was placed in a water desiccator at

Table 4 Results of TG analysis of zinc picrate after dehydration.

		Zinc powder + Picric Acid	ZnSO ₄ + Barium picrate	ZnCO ₃ + Picric Acid
Vacuum at 393 K, 4 h.	Weight reduction	1.3 %	2.6 %	2.8 %
	H ₂ O molecules	0.4	0.8	0.8
Vacuum at 473 K, 1 h.	Weight reduction	0.9 %	1.4 %	1.1 %
	H ₂ O molecules	0.3	0.4	0.3

Table 5 Results of TG analysis of zinc picrate after re-hydrating for four hours in a water desiccator.

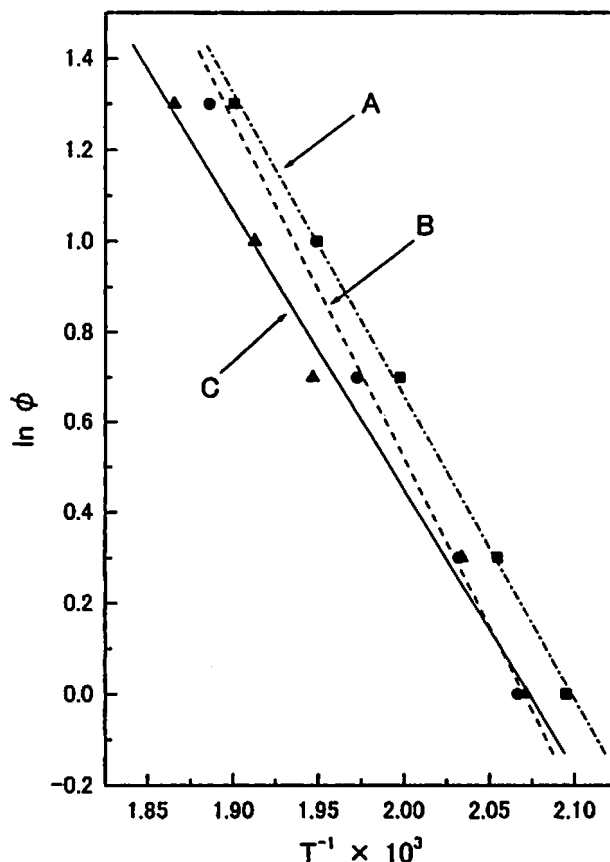
		Zinc powder + Picric Acid	ZnSO ₄ + Barium picrate	ZnCO ₃ + Picric Acid
H ₂ O desiccator for 4 h.	Weight reduction	9.7 %	7.6 %	9.2 %
	H ₂ O molecules	3.1	2.4	2.9

room temperature (approximately 293 K) for four hours, and then analyzed by TG analysis, with the results shown Fig. 8 and Table 5. A weight reduction of 7.6–9.7 %, corresponding to 2–3 molecules of H₂O, was confirmed by these results suggesting possible re-hydration. Zinc picrate contained 2–3 molecules of H₂O as re-hydrated H₂O molecules from wet air.

These results show that zinc picrate re-adsorbed crystalline water after dehydration, but the quantity of re-adsorbed water was less than samples dried at 25 deg. in vacuum after recrystallization from H₂O. In addition, the form of weight reduction curves for samples after re-adsorption of crystalline water (Fig. 8) differed from those of samples before dehydration (Fig. 3), suggesting that crystalline water conditions were differ between samples before dehydration and samples after re-adsorption of crystalline water. The study of Takahashi⁽¹⁰⁾ confirmed that different weight reduction curves were obtained for samples after rehydration of crystalline water and samples before dehydration. This suggests that rehydrated water molecules adsorb onto different positions to the original positions prior to dehydration.

From measurement results of Fig. 3, zinc picrate synthesized by the different methods appear to have different forms, indicating that the zinc picrate had different weight reduction phenomenon, and as the results in Table 4 show, the crystalline water amount differs between the samples before and after re-hydration. These phenomena suggest that the crystalline water does not have a fixed position, and adsorption positions were influenced by external factors and hydration history. Thus, differences in crystalline water contents between the different synthesis methods were thought to be due to differences in the adsorption conditions of the crystalline water.

Furthermore, zinc picrate crystal was dried at 298 K in a vacuum when performing thermal gravimetric analysis measurements, under which conditions the crystal was transparent before drying, but devitrified after drying. This may be similar to crystalline copper sulfate hydrate, which is known to devitrify to lose crystallinity by


Fig.9 Ozawa's plots of decomposition start temperature of zinc picrates.

- A) Synthesized from picric acid and zinc powder, B) synthesized from barium picrate and zinc sulfate, and C) synthesized from picric acid and zinc carbonate

dehydration using heat. Zinc picrate was also confirmed to devitrify by heat. Thus, all samples, which were dehydrated by vacuum and were devitrified, were concluded to contain hexahydrate, but zinc picrate, which was not dried in vacuum, was supposed to have the potential to hold more crystalline water molecules, a few of which one able to easily dehydrate at room temperature.

3. 7 Activation energy of exothermal decomposition

The activation energy of zinc picrate synthesized by each synthesis method was obtained by the Ozawa method⁽¹¹⁾.

Table 6 Results of temperature of start of decomposition (T_0) and activation energy of exothermic decomposition.

Heating rate	Zinc powder + Picric Acid	ZnSO ₄ + Barium picrate	ZnCO ₃ + Picric Acid
1 K·min ⁻¹	477.3 K	483.9 K	482.8 K
2 K·min ⁻¹	483.2 K	492.1 K	491.7 K
5 K·min ⁻¹	496.4 K	507.0 K	513.7 K
10 K·min ⁻¹	513.0 K	513.2 K	522.9 K
20 K·min ⁻¹	526.2 K	530.2 K	536.1 K
Activation energy	121.4 kJ·mol ⁻¹	133.4 kJ·mol ⁻¹	116.0 kJ·mol ⁻¹

The DSC results measured at 1 K·min⁻¹, 2 K·min⁻¹, 5 K·min⁻¹, 10 K·min⁻¹, 20 K·min⁻¹, and the temperature decomposition started (T_0) obtained from the exothermic curve of decomposition were extrapolated to give the baseline. T_0 was plotted at each heating rate, and this was analyzed using Ozawa's equation, as shown in Fig. 9 and Table 6. The activation energy of zinc picrates was thus found to be between 116.0 kJ·mol⁻¹ and 133.4 kJ·mol⁻¹, with the results for each sample approximately the same. This suggests that the exothermic peak is caused by the same reaction in all of the samples.

4. Conclusions

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

- (1) The results of X-ray fluorescence analysis proved the existence of zinc in synthesized products, and FT-IR analysis results suggested products having a molecular form similar to picric acid. These results were the same regardless of synthesis method. Zinc picrate was thus shown to have been synthesized.
- (2) The results of thermal gravimetric analysis showed that dehydration of crystalline water occurred step-by-step at 330–500 K. Furthermore, the results of thermal gravimetric analysis and Karl Fischer analysis indicated that the samples contained hexahydrate.
- (3) Crystalline water of zinc picrate was dehydrated at 393 K for four hours in a vacuum (under 133 Pa), or at 473 K for an hour in a vacuum (under 133 Pa), and the resulting dehydrated zinc picrate was able to be re-hydrated. The number of re-hydrated H₂O molecules was less than the number of dehydrated molecules.
- (4) The activation energy of the decomposition reaction

of zinc picrate was estimated to be between 116.0–133.4 kJ·mol⁻¹.

- (5) This study indicates that zinc picrate can be synthesized not only from other picrates (ex. barium picrate) or picric acid and zinc salt, but also from reaction of picric acid solution and zinc powder. Products of different synthesis methods appeared to be different, but the chemical properties were similar.

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