# Supporting materials

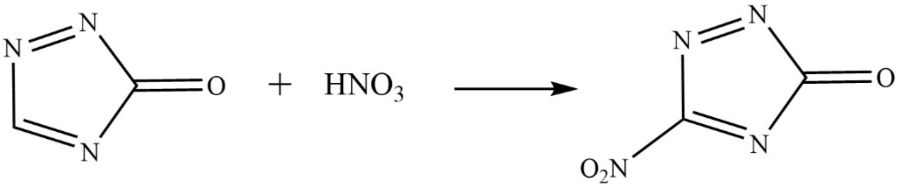
# An Ion Chromatographic Method for the Purity Analysis of the Poorly Soluble Energetic Coordination Compound Lead NTOate

**Fengyi Xia, Jiexin He, Dongxu Zhang, Ji-Min Han, Li Yang***

## 1 Reagents and Materials

3-Nitro-1,2,4-triazol-5-one (NTO) was synthesized in the laboratory following the procedure described below.

Reaction principle:



Experimental materials: 1,2,4-Triazol-5-one (TO) was purchased from Gansu Yinguang Chemical Industry Group Co., Ltd. Nitric acid ($HNO_3$) was obtained from Beijing Tongguang Fine Chemical Co., Ltd.

Preparation process: A total of 167 mL of 98% $HNO_3$ was transferred into a jacketed beaker and cooled using a circulating low-temperature water bath at 0°C. Subsequently, 67 g of TO was gradually added to the beaker while maintaining the bath temperature below 15°C. After the addition was completed, the reaction temperature was increased to 30°C and maintained for 2 h. The reaction mixture was then cooled again to 0°C, followed by filtration and washing to obtain the final NTO product.

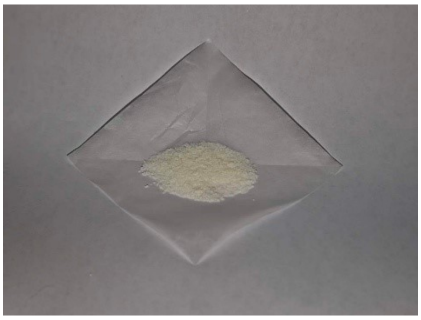


**Figure S1**. Morphology of NTO.

The obtained NTO was characterized by $^1$H NMR spectroscopy, and the results are shown in **Figure S2**. The observed signal at 12.7 ppm (–NH) is in good agreement with the values reported in the literature.

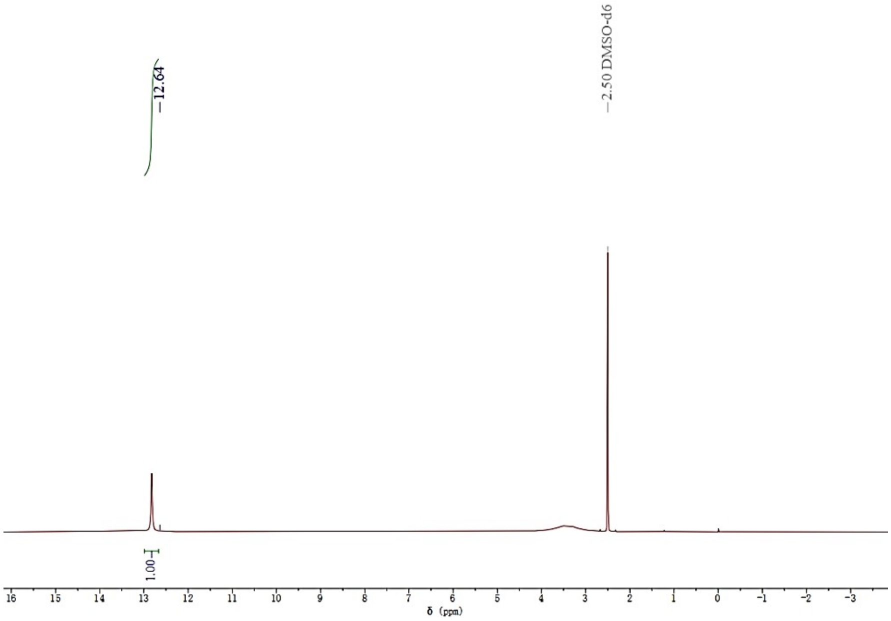


**Figure S2.** $^1$H NMR spectrum of NTO

The 3-Nitro-1,2,4-Triazole-5-One (NTO) Lead(II) Salt (lead NTOate) was synthesized in the laboratory according to the following procedure.

Reaction principle:

$2NaOH + NTO \rightarrow Na_2NTO + 2H_2O$

$$Na_2NTO + Pb(NO_3)_2 + H_2O \rightarrow NTOPb\cdot H_2O + 2NaNO_3$$

Experimental materials: Sodium hydroxide (NaOH), lead nitrate ($Pb(NO_3)_2$), absolute ethanol, and nitric acid ($HNO_3$) were purchased from Beijing Tongguang Fine Chemical Co., Ltd. 3-Nitro-1,2,4-Triazole-5-One (NTO) was self-prepared in the laboratory via the nitration of 1,2,4-triazol-5-one (TO).

Preparation process:

Step 1, preparation of 4% $Na_2NTO$ solution. A measured amount of 3-Nitro-1,2,4-Triazole-5-One (NTO) was weighed and added to an appropriate volume of 10% NaOH solution. The mixture was stirred thoroughly until the reaction was complete, and the resulting solution was set aside for later use.

Step 2, preparation of 10% $Pb(NO_3)_2$ aqueous solution. A measured amount of $Pb(NO_3)_2$ was dissolved in an appropriate volume of deionized water under stirring. The pH of the solution was adjusted to 3~4 using nitric acid, and the solution was kept for subsequent use.

Step 3, synthesis of NTO Lead(II) Salt. The $Pb(NO_3)_2$ aqueous solution was used as the base solution and placed in a reactor equipped with a stirrer. The solution was heated in a 60°C water bath under continuous stirring. The $Na_2NTO$ solution was then slowly added dropwise into the reactor over approximately 40 min. After the addition was complete, the reaction mixture was maintained at 60°C for an additional 10 min. Heating was then stopped, and the system was cooled to below 35°C before discharging. The resulting precipitate was filtered, washed with deionized water 2~3 times and absolute ethanol 1~2 times, and then air-dried in a cool, shaded place to obtain the final lead NTOate product.

**Figure S3.** Morphology of lead NTOate.

The obtained lead NTOate was characterized by FT-IR spectroscopy, and the results are shown in **Figure S4.**

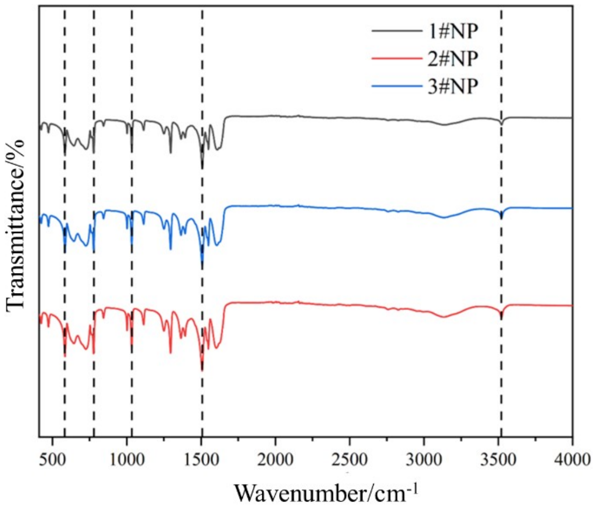


**Figure S4**. FT-IR spectrum of the lead NTOate sample.

From the FT-IR spectral features, it can be observed that the characteristic absorption bands of the lead NTOate sample in the nitro group region (1550 cm$^{-1}$ and 1300 cm$^{-1}$) and the carbonyl region (~1680 cm$^{-1}$) are generally consistent. In addition, a broad absorption band appears around 3400 cm$^{-1}$, indicating the presence of crystallization water.

All reagents were of analytical grade unless otherwise stated. Acetic acid

(⩾99.7%), $Na_2CO_3$ (⩾99.9%), $NaHCO_3$ (⩾99.9%), and NaOH (⩾99.8%) were purchased from Beijing Tongguang Fine Chemicals Co., Ltd. Ultrapure water (18.2 MΩ·cm) was prepared using a CSR-1-10 purification system. Ion chromatography (IC) was performed on a Metrohm 792 Basic IC system equipped with a conductivity detector and a chemical suppressor.

## 2 Experimental Procedures

### 2.1 Preparation of Standard and Sample Solutions

Lead NTOate standard samples were purified by recrystallization prior to analysis. Approximately 0.5 mL of 5% acetic acid was added to dissociate the NP salts, yielding a stock standard solution with a concentration of 2000 mg/L. The stock solution was subsequently serially diluted to prepare a series of working standard solutions with concentrations of 0.5, 1.0, 2.0, 5.0, 20.0, 50.0, and 100.0 mg/L, which were used for the construction of calibration curves and for the evaluation of analytical parameters, including the limit of detection and precision. Lead NTOate samples were likewise dissolved using approximately 0.5 mL of 5% acetic acid to obtain solutions at the corresponding concentrations. Prior to IC analysis, all solutions were filtered through a 0.22 μm microporous membrane to remove particulate matter and prevent clogging of the chromatographic column.

### 2.2 Ion Chromatography Conditions

Column：HR AC-15（250 mm×4.6 mm）；Eluent：4 mM $Na_2CO_3$+1.8 mM $NaHCO_3$；Flow rate：0.7 $mL\cdot min^{-1}$；Column temperature：25°C；Injection volume：25 μL；Regenerant：50 $mmol\cdot L^{-1}$ $H_2SO_4$；Rinse solution：ultrapure water。

## 3 Analytical Method Validation

**Table S1. summary of method validation results**

| Parameter | Result | Description |
|---|---|---|
| Calibration range | 0.5~100 $mg \cdot L^{-1}$ | The linear relationship is good within three orders of magnitude |
| Regression equation | $Y=0.0152X+0.00415$ | |
| $R^2$ | 0.9996 | exhibited an excellent linear correlation |
| LOD | 0.1 $mg \cdot L^{-1}$ | S/N=3 |
| LDQ | 0.3 $mg \cdot L^{-1}$ | S/N=10 |
| Recovery | 99.78~100.74% | exhibited high accuracy |
| Precision | <0.4% | n=3 |
| Repeatability (RSD) | 0.45~0.72% | six parallel measurements |

## 4 Comparison with EDTA Titration Method

The purity of the NP salt determined by EDTA titration was 98.3%, while the purity obtained by the IC method was 97.74%, which was slightly lower than that determined by the titration method. The results obtained by the two methods were generally consistent, indicating the reliability of the IC method for evaluating lead NTOate purity. The slight difference may be attributed to the fact that EDTA titration determines the total Pb content, which may include contributions from other lead-containing species present in the sample. In contrast, the IC method directly quantifies the $NTO^{2-}$ anion and can effectively eliminate interference from other Pb-containing impurities. Moreover, compared with EDTA titration, which requires masking agents and strict pH control, the IC method provides a simpler and more efficient approach for purity assessment.