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# Improvement of an LC/Q-TOF method for the trace analysis of peroxide-based explosives

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The peroxide-based explosives, such as TATP and HMTD contain neither nitro groups nor aromatic functionalities (Figure 1), making them difficult to detect with traditional analytical methods. These characteristics as well as their large explosive power, have led to the increasing use by terrorists and criminals over the last few decades. Since about 20 years ago, many LC/MS methods were developed based on the USEPA method 8330, which are suitable to analyze the nitro-aromatic explosives. However, due to the structure characteristics, the sensitivities of peroxide-based compounds are not as good as other explosives and the adduct ions are difficult to interpret.

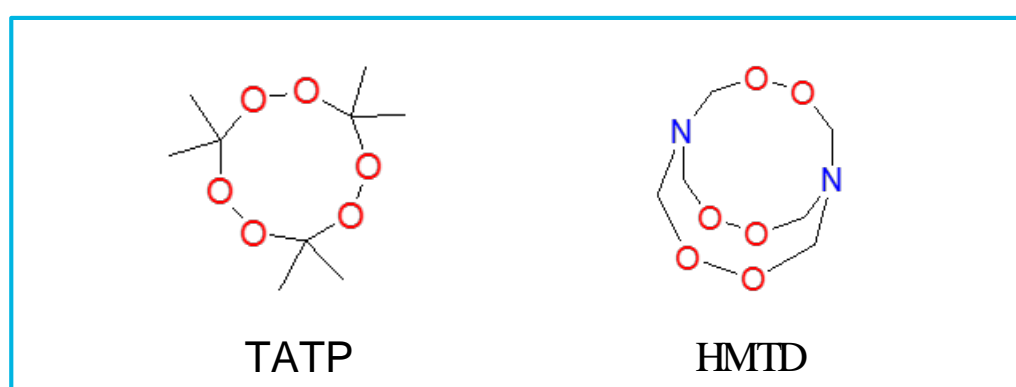


Figure 1. The Structures of peroxide-based explosives.

In this study, we improved the LC/Q-TOF method which can generate normal  $[M+H]^+$  and  $[M+NH_4]^+$  ions with a LOQ lower than 1  $\mu\text{g/L}$ .



### Sample preparation

TATP and HMTD standards dissolved in acetone separately, then progressively diluted by 50/50 (v/v) MeOH/H<sub>2</sub>O solution. Several post-explosion products were collected and dissolved in acetone.

### LC Conditions

#### 1290 Infinity II UHPLC System

Column	EC-C18 3.0X100 mm	
Mobile phase	A: ammonium aqueous with 0.5 mM ammonium fluoride; B: Methanol	
Flow rate	0.5 mL /min	
Oven Temperature	40 °C	
Injection	10 $\mu\text{L}$	
Gradient	Time	B
	0 min	30 %
	0.5 min	30 %
	2 min	65 %
	8 min	100 %

### MS Conditions

#### Agilent 6545 Q-TOF Mass Spectrometer

Ion source	APCI
Polarity	Positive
VCap	4000 V
Corona	4 $\mu\text{A}$
Dry gas temperature	275 °C
Dry gas	5 L/min (N <sub>2</sub> )
Nebulizer pressure	40 psi (N <sub>2</sub> )
Vaporizer	300 °C

### Improving LC-Q/TOF Method

Initial parameters for the MS and APCI+ ion source were chosen based on previous experimental work [1]. In methanol and water system, HMTD shows  $[M-H]^+$  ion and TATP shows a strange ion with very poor sensitivity. We tried the ammonium acetate and ammonium formate solvent as mentioned in references [2-3], HMTD showed  $[M+H]^+$  ion but LOQ is not enough. TATP generated  $[M+NH_4(OOC(CH_3)_2OOH)]^+$ , a very complex adduct ion.

Finally, we add 0.5 mM ammonium fluoride in the ammonium aqueous phase. HMTD mainly generates  $[M+H]^+$  ion, besides,  $[M-H]^+$  and  $[M+NH_4-2H]^+$  ions can also be observed. TATP forms  $[M+NH_4]^+$  ion. We can easily confirm the formulas from the normal quasi-molecular ions. As shown in Figure 2, the MFG scores are higher than 98, which mean excellent accuracy and nice isotopic pattern.

Interestingly, we can see a subsidiary peak (Figure 2b EIC) for TATP in our experiment as the literature reports [4], which suggested the second peak due to the second conformer and may serve as an added confirmation the TATP is present.

### Quantification

Our improved LC/Q-TOF method is also good at quantification. Figure 3 shows the external calibration curves for HMTD and TATP. The LOQ for both compounds is lower than 1 ug/L. From 1 to 1000 ug/L, linear calibration curves were employed with  $R^2 > 0.99$  and accuracy 90~110 %.

The method is sensitive enough for real sample detections. When we test the post-explosion products which were collected and dissolved in acetone, the main challenge is that the signal of background contaminants is very high. Although the contaminant is separated from our target compounds, care must be taken to not contaminate the analytical system.

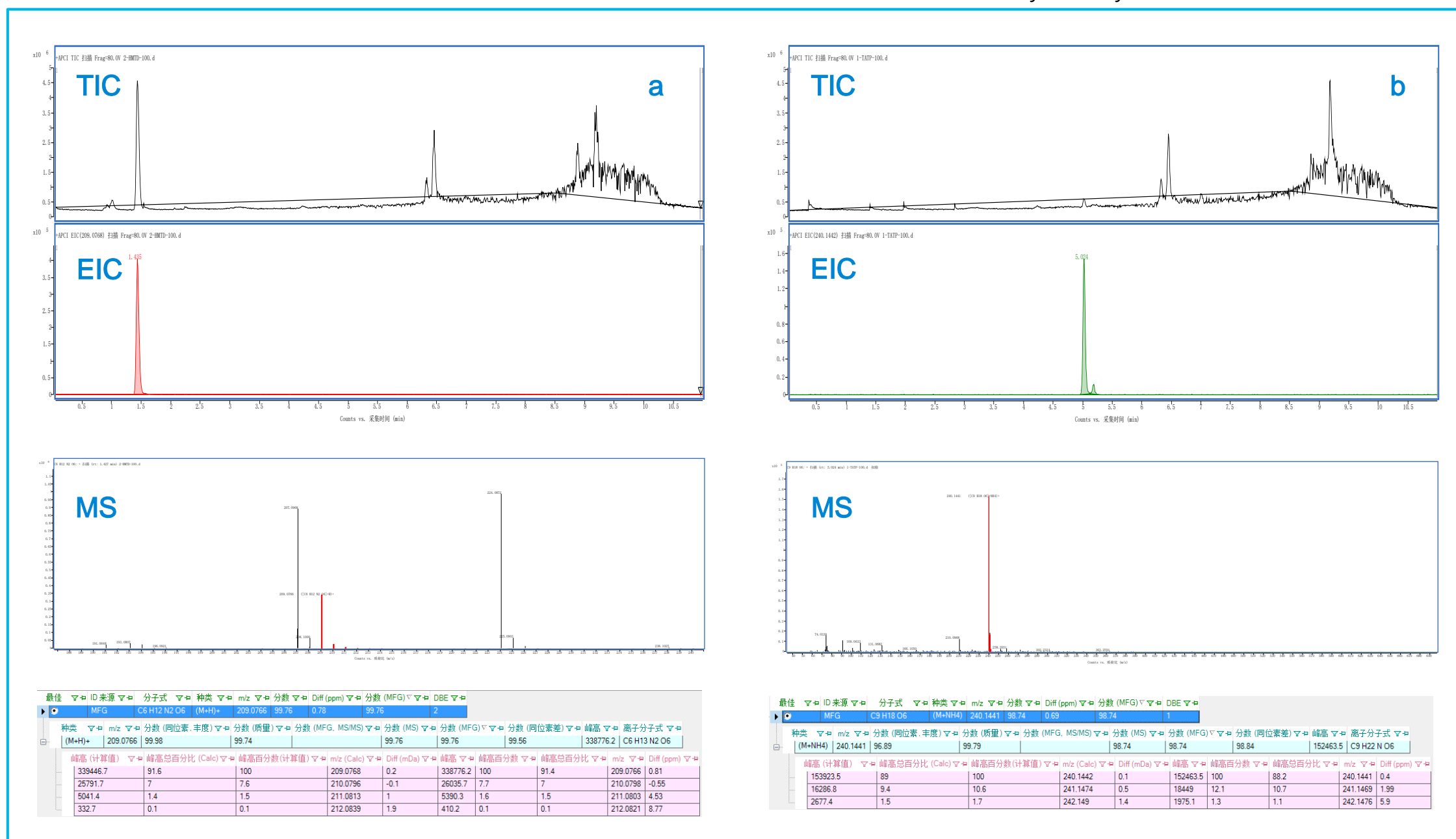


Figure 2. The typical TIC, EIC and MS spectra of a) HMTD and b) TATP.

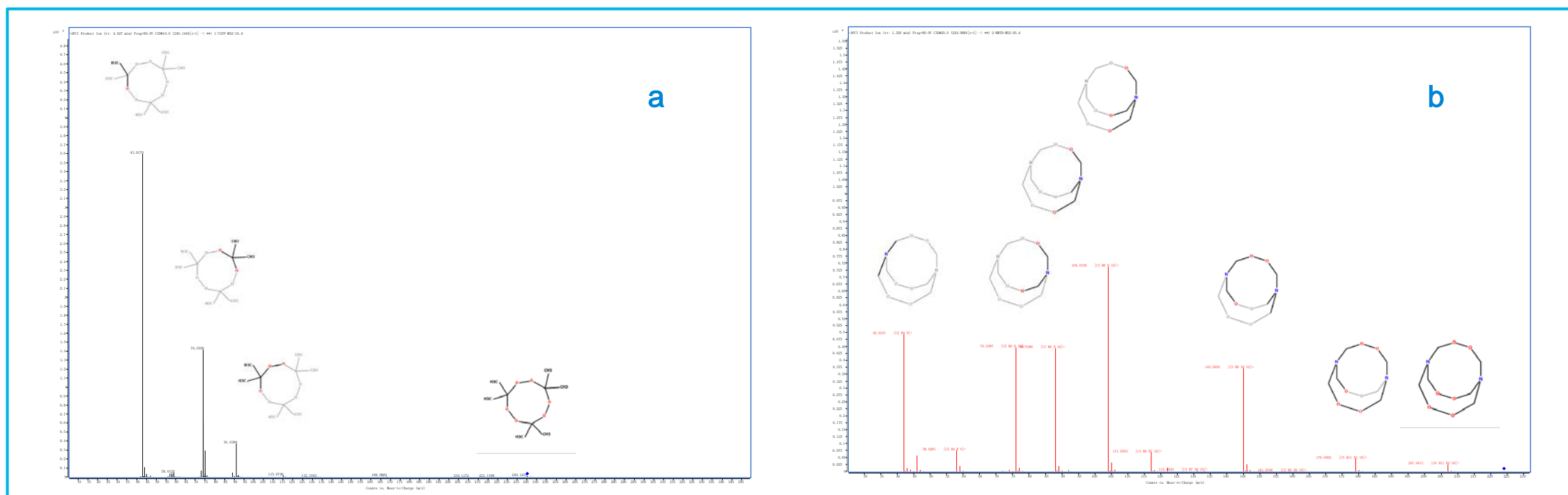


Figure 4. The MS/MS spectra of a) TATP and b) HMTD, which can be interpreted automatically by MSC software.

### Identification

Accurate mass measurement and fragment information provided by Q-TOF greatly increases the confidence of identification. With the help of MSC software, tandem mass spectrum can be interpreted corresponding to the structures of TATP and HMTD (Figure 4).

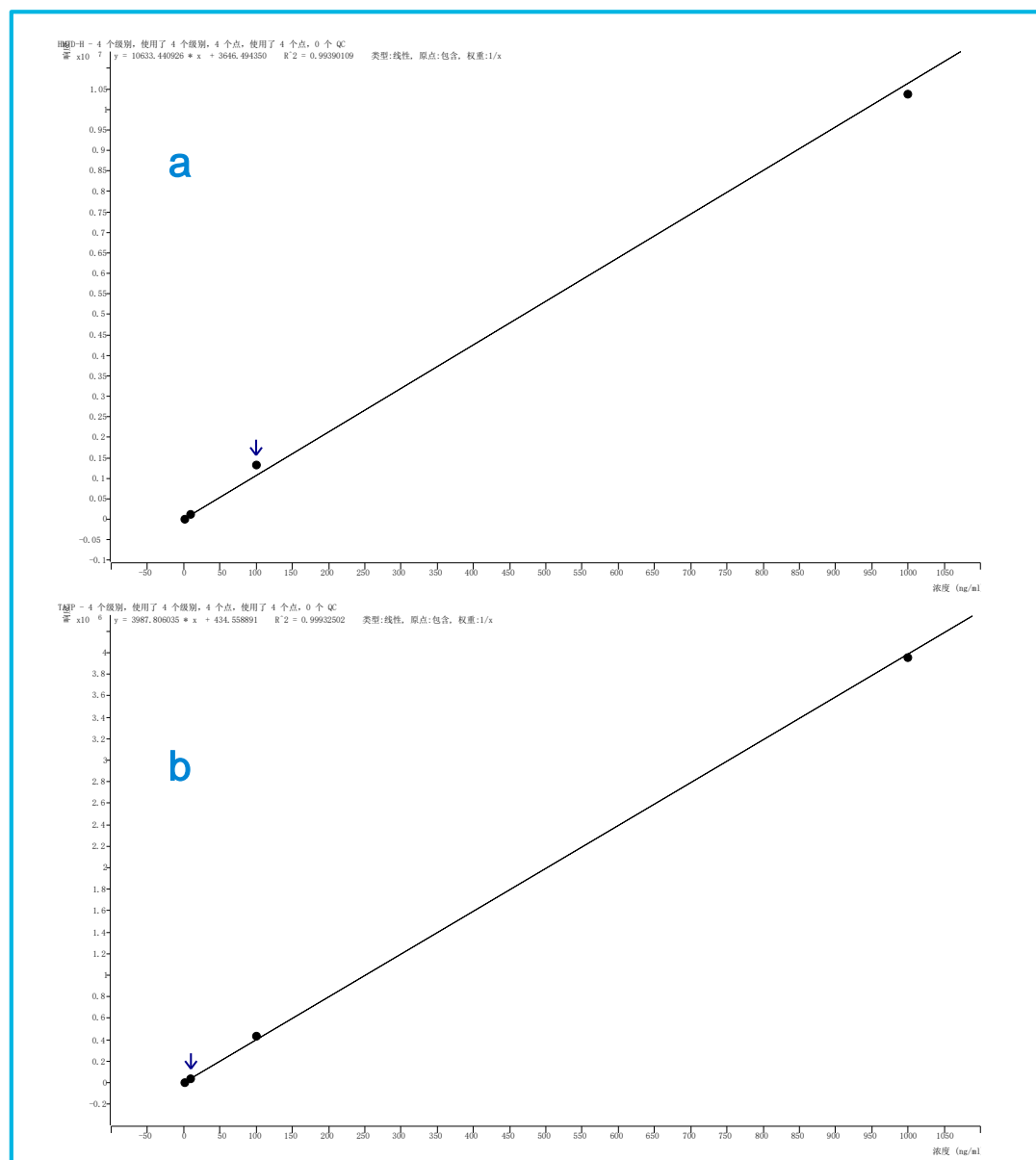


Figure 3. The external calibration curves for a) HMTD and b) TATP.

### Conclusions

- The improved LC/Q-TOF method with reasonable adduct ions and good sensitivity which is suitable for qualitative and quantitative analysis of TATP and HMTD.
- With the help of software, isotopic pattern and the fragment information can be interpreted corresponding to the structures, which increases the confidence of identification to the peroxide-based explosives.

### References

- [1] Agilent application 5989-2449.
- [2] Schulte-Ladbeck R, Vogel M, Karst U. *Anal Bioanal Chem*, **386**: 559–565.
- [3] DeTata D, Collins P, McKinley A. *Forensic Sci Int*, **233**: 63–74.
- [4] Widmer L, Watson S, Schlatter K, Crowson A. *Analyst*, **127**: 1627–1632.