

Accuracy in Trace Analysis

Table 3. VG 9000 analysis of BCR high purity aluminum

Element	Conc. ppm (ion beam ratio)	RSD %
Mg	0.800 ^a	10
	.792 ^b	8.5
Si	.755	6.3
	.766	2.5
Ca	.126	19
	.149	15.4
Ti	.272	11.8
	.243	14.4
V	.048	6.3
	.047	6.4
Cr	.010	20
	.011	20
Mn	.036	8.3
	.038	7.8
Fe	.497	10
	.519	5.6
Ni	.042	26
	.054	14.8
Cu	.130	42
	.128	27.3
Zn	.017	23.5
	.019	10.5
Pb	.017	11.8
	.017	11.8
Th	.007	14.2
	.006	14.6
U	.005	20
	.005	20

^a Upper level figures are internal measurements (same sample).
^b Lower level figures are external measurements (different samples).

References

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Studies of Limit of Detection on 2,4,6-Trinitrotoluene (TNT) by Mass Spectrometry

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Various ionization methods including positive chemical ionization (PCI), negative chemical ionization (NCI) and electron impact (EI) were used to study the mass spectra of TNT. Methane, isobutane and ammonia were used as the CI reagent gases. The mass spectrometric quantitation in this study was performed by selected ion monitoring (SIM), with sample introduction via a short capillary column and a solids probe. The best TNT detection limit (ca. 0.020 ng) was obtained with the NCI-SIM technique with isobutane as a reagent gas.

Introduction

The trace analysis of explosives is of importance in forensic science and analytical problems encountered in this field involve the detection of nanogram quantities of explosives in extracts obtained from post-explosion residues [1]. The identification of an explosive residue usually involves extracting the debris with acetone or methanol, then separating the extract by chromatographic methods coupled with a detection technique. Single ion monitoring (SIM) by combined gas chromatography-mass spectrometry is the most promising technique to determine a trace amount of an explosive in an unknown mixture.

The mass spectra of a series of explosives have been reported [2-3]. This report describes the investigation of the limit of detection (LOD) of TNT by gas chromatography-mass spectrometry.

Experimental

All mass spectra were generated with a Finnigan Model 4023 combined gas chromatograph/mass spectrometer (GC/MS) equipped with a dual

CI/EI source. Ultra-high purity methane, isobutane and ammonia (Matheson, Morrow, GA) were used as CI reagent gases.

A 1000 ppm solution was prepared by dissolving purified TNT in acetone, then diluted to different desired concentrations as standard sample solutions. TNT was eluted on a two-meter-long fused silica capillary column (Supelcowax 10) using a helium carrier at 8 psig head pressure. The GC temperature was programmed from 80–250 °C at 30 °C/min. Triplicate 1.0 μ L injections of each sample were made.

To operate the solid-probe, the temperature was kept at 40 °C for 2 minutes then heated to 60 °C directly. Triplicate 1.0 μ L samples of a series of standard solutions were injected into separate 5 μ L glass vials, allowed to air dry, and then introduced into the ion source via the solid-probe.

The selected ions monitored in different modes and the optimized quantitation conditions are listed in table 1. The quantification signal was obtained by the GC peak area, which was the integrated ion current during elution of TNT.

Table 1. Comparison of different methods with short capillary column GC/MS and solids probe for determination of TNT (Source temperature: EI at 250 °C, CI at 150 °C)

Technique	Reagent gas		Ion monitored (m/z)	LOD (ng)	
	Type	Pressure (torr)		GS/MS	Solid-probe
EI			210	38	75
PCI	CH ₄	1.0	228	8.3	21
NCI	CH ₄	1.0	227	0.27	
PCI	<i>i</i> -C ₄ H ₁₀	1.0	228	5.8	9.8
NCI	<i>i</i> -C ₄ H ₁₀	1.0	227	0.02	
PCI	NH ₃	1.2	168	12	35
NCI	NH ₃	1.2	227	1.3	

Results

For the quantitative studies, the limit of detection (LOD) was calculated as the amount of sample necessary to give a signal-to-noise (S/N) ratio of 3. Based on the results of a series of standard TNT solutions, the calibration curves were constructed. From these calibration curves the limit of detection for EI, PCI and NCI with CH₄, *i*-C₄H₁₀ and NH₃ as reagent gases were calculated and are tabulated in table 1. The relative standard deviations of integrated signals for the triplicate analyses having S/N ratio greater than 3 ranged from 5% to 25%

for the PCI technique and 2% to 17% for NCI.

From table 1 and figure 1, it was found, as reported [4], that except for NH₃–NCI, the LOD by CI is at least one order lower than that by EI. Regardless of reagent gas used, the ion currents under electron capture conditions in the negative mode exceeds that in the positive ion mode by one or two orders of magnitude. The most sensitive result, an LOD of 0.020 ng was obtained in *i*-C₄H₁₀–NCI mode as shown in figure 1. Perhaps the energy transfer with isobutane is much less than with methane, and thus causes less fragmentation of the TNT molecular ion (M^+) which was selected as the monitored ion.

The results of quantification of TNT in standards with a solids probe are shown in table 1. The LOD of both PCI and EI modes are at the same levels. In the NCI technique we always obtained a false signal at the same retention time as TNT. Therefore, the LOD of this technique cannot be defined. All the calibration curves were nonlinear as shown in figure 2. The lower response (i.e., sensitivity) at low amounts injected may be due to adsorption in the entire system, including the glassware and syringe.

Conclusion

For the determination of TNT at trace levels, mass spectrometry has been shown to offer several advantages over other techniques. Comparing various MS monitoring modes with different reagent gases, the best monitoring mode for determination of TNT was shown to be isobutane negative chemical ionization with selected ion monitoring of the M^+ of TNT at m/z 227. In a standard solution, the best TNT detection limit obtained with a short capillary column GC/NCI-SIM was 0.020 ng. Therefore, this NCI-SIM technique with its high sensitivity made it the preferred method for post-explosion residue analysis.

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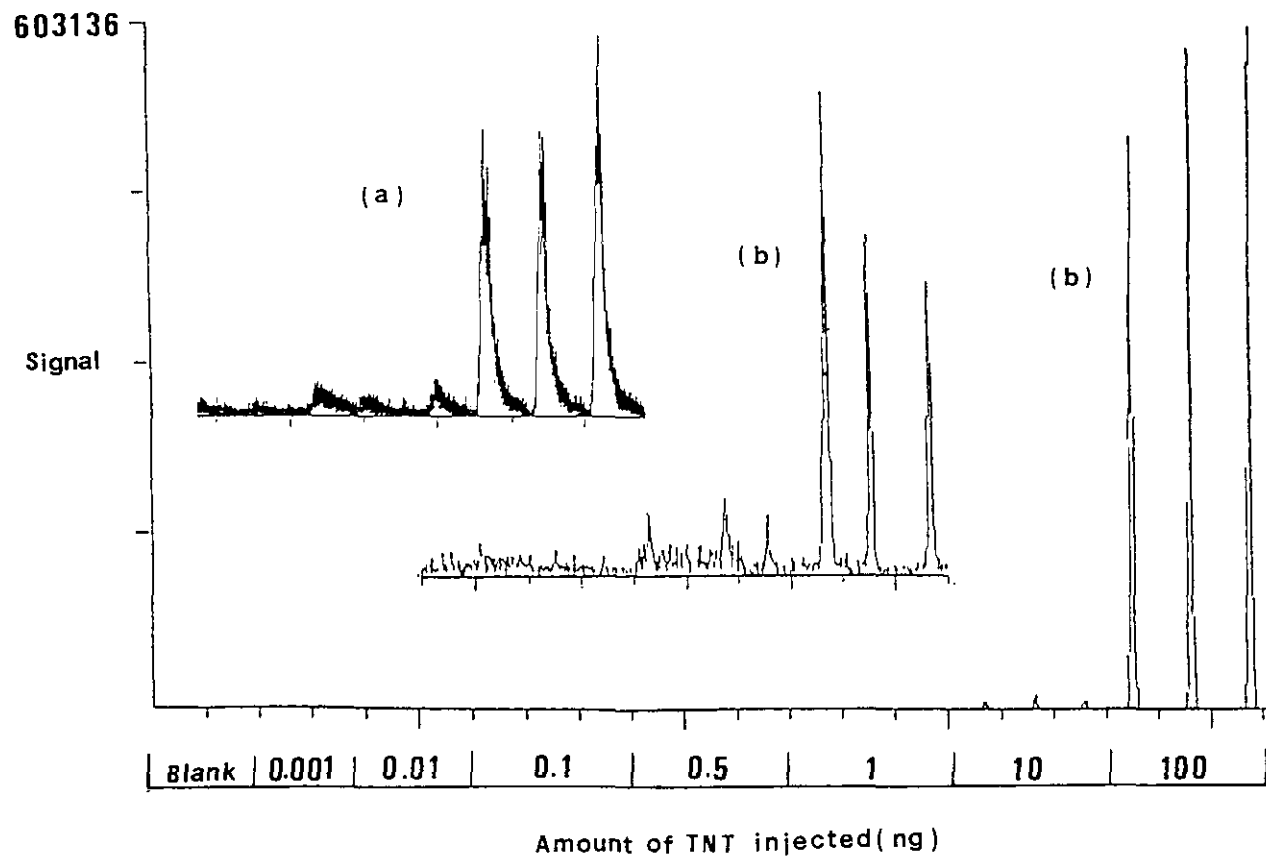


Figure 1. Quantitation of TNT by short capillary column a) $\text{NCI}(i\text{-C}_4\text{H}_{10})\text{-SIM}(227)$, b) $\text{NCI}(\text{CH}_2)\text{-SIM}(227)$.

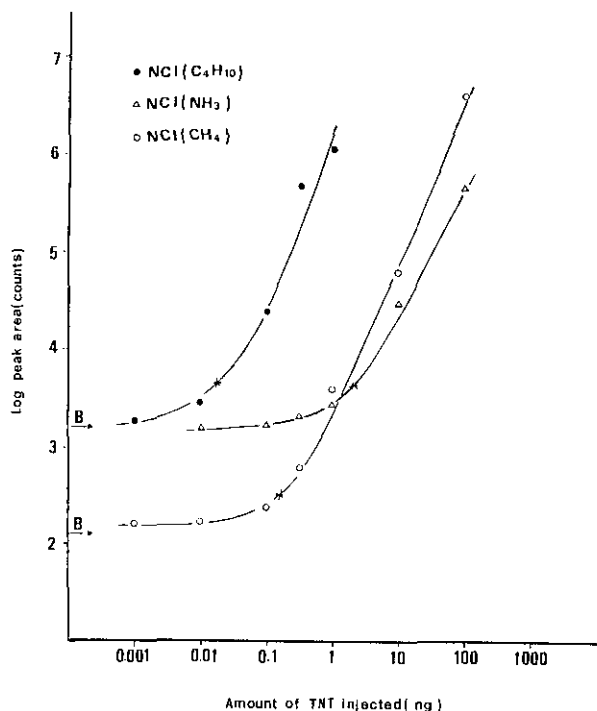


Figure 2. Calibration curves for the short capillary column NCI(*i*-C₄H₁₀)-SIM(227), NCI(CH₄)-SIM(227) and NCI(NH₃)-SIM(227) quantitation of TNT.

B denotes the response of the acetone blank.

* indicates the LOD.

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Absolute Cross-Section Measurements in XQQ Instruments: The NBS Round Robin

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Triple-quadrupole (QQQ) tandem mass spectrometry (MS/MS) is used for the analysis of multi-component mixtures [1]. The analysis makes use of the collisionally activated dissociation (CAD) of "parent" ions. A "parent" ion may be a molecular radical cation, a protonated molecule, or a "progeny" fragment ion (daughter, granddaughter, etc., produced by the CAD of a larger precursor parent ion). A "parent" ion selected by the first quadrupole (Q1) interacts with a target gas within the second quadrupole (Q2). Q2 channels undissociated "parent" ions and "progeny" fragment ions into the third quadrupole (Q3) for mass analysis. The instrument thus produces a CAD spectrum of each initially selected "parent" ion.

But XQQ instruments (QQQ, BEQQ, etc.) are complex ion-optical devices [2-8]. So the choice of parameter settings and/or of instrument design can provide a distorted view of the molecular dynamics of the CAD process (e.g., if there are scattering losses due to poor ion containment within Q2, fringing fields between Q2/Q3, etc. [2-8]). So one observes instrument-dependent CAD spectra.

The key MS/MS parameters are:

- 1) the "target thickness"=(actual path length traversed by the ion in its complex oscillatory trajectory through the gas target)×(effective number density of the CAD target gas);

- 2) the type of target gas (influences the extent of energy transfer);

- 3) the center-of-mass interaction energy, E_{cm} ;

- 4) the energy level of the analyzing quadrupole Q3 relative to that of Q2;

- 5) the Mathieu parameter q_2 (rf voltage of Q2) and restrictive interquadrupole apertures of diameter $< 1.4 r_0$; and

- 6) differences in mass-dependent conversion gain of ion detectors.

For any one molecule, these key MS/MS parameters can cause the relative intensities among its var-