

Improvements in the Determination of Decomposition Gases from 1,3,3-Trinitroazetidine and 5-Nitro-2,4-dihydro-3H-1,2,4-triazol-3-one Using Capillary Gas Chromatography–Mass Spectrometry

Weiwei Zheng, Xiaoxia Dong, Evan Rogers, Jimmie C. Oxley, and James L. Smith*

Department of Chemistry, University of Rhode Island, Kingston, RI 02881

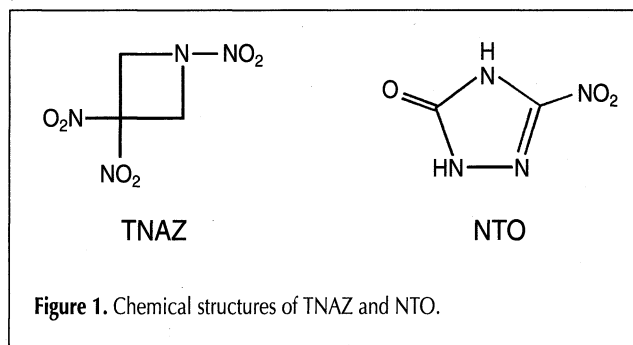
Abstract

A Chrompack PLOT fused-silica capillary column with a narrow internal diameter (0.25 mm) and PoraPLOT Q stationary phase are used for the simultaneous gas chromatographic–mass spectrometric determination of nitrogen, oxygen, carbon monoxide, carbon dioxide, nitrous oxide, nitric oxide, hydrogen cyanide, cyanogen, and water from thermal decompositions of the highly energetic materials 1,3,3-trinitroazetidine (TNAZ) and 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one. Previously this laboratory required two separate capillary columns for analyses of nitrogen, oxygen, carbon monoxide, carbon dioxide, and nitrous oxide. The detection of hydrogen cyanide and cyanogen gases as products of TNAZ thermal decomposition is verified for the first time by our laboratory using this new column.

Introduction

Highly energetic materials such as 1,3,3-trinitroazetidine (TNAZ) and 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one (NTO) (Figure 1), which decompose with the rapid liberation of heat and gas, are being considered as military explosives (1–3). The production of large amounts of gaseous products is a characteristic of explosives and other highly energetic materials. The study of thermal decomposition mechanisms requires methodologies to identify and quantify all gaseous products (4–6). Gas chromatography (GC) with thermal conductivity detection is an excellent analytical technique for the separation, identification, and quantitation of permanent gases liberated during decompositions of highly energetic materials. A Hayesep DB packed column (30 ft \times 1/8 in., 100/120 mesh) has been extremely useful for the analysis of nitrogen (N_2), oxygen (O_2), carbon monoxide (CO), nitric oxide (NO), nitrous oxide (N_2O), and water vapor (H_2O). However, this system is unable to detect small amounts of hydrogen cyanide (HCN), which we have

detected using infrared spectroscopy. This is probably because the hydrogen cyanide reacts with the stainless steel walls of the column at elevated temperatures. We are also not able to conveniently interface the Hayesep DB packed column to our mass spectrometers (MS), which are designed for capillary columns. The requirement for mass spectral detection has, until recently, necessitated the use of two different capillary columns. A Chrompack (Raritan, NJ) porous layer open-tubular (PLOT) fused-silica column with molsieve 5A stationary phase (25 m \times 0.32 mm) was used for the separation of N_2 , O_2 , and CO, and a J&W Scientific (Folsom, CA) GS-Q fused-silica column with divinylbenzene homopolymer stationary phase (30 m \times 0.32 mm) resolved CO_2 and N_2O gases. This arrangement was not wholly acceptable for two reasons. First, two MSs or frequent column switching was required in order to analyze for all the gases mentioned above. Second, the dual column arrangement was unable to detect NO, even though its presence had been confirmed with the Hayesep DB system. The acquisition of a (0.25 mm) capillary column with a narrow internal diameter from Chrompack called a PLOT fused-silica column with PoraPLOT Q stationary phase (25 m length) permitted the simultaneous determination of all the above mentioned gases. Oxygen was not observed to be a decomposition product in our studies. Its retention time, from air samples, was about 3.5 min. In addition, trace amounts of the previously unobserved decomposition gases hydrogen cyanide and cyanogen were detected.



* Author to whom correspondence should be addressed.

Experimental

A Hewlett-Packard (Wilmington, DE) model 5890 GC equipped with an electronic pressure control system and a model 5971 electron-impact quadrupole MS was used for these studies. Manual tuning of the MS with perfluorotributylamine (PFTBA) was used to adjust relative abundances for m/z 69, m/z 100, and m/z 131 to 100, 15, and $45\% \pm 1$, respectively. The MS was run in scan mode (m/z range 15–120) with a threshold of 100 and a sampling of 4 (2.2 scans/s). Ultrapure helium was passed through moisture, hydrocarbon, and oxygen traps and was used as the carrier gas. The GC injector temperature was 100°C , and the detector–transfer line temperature was 180°C . Liquid nitrogen was used to cool the GC oven to -80°C . After 5 min, the oven temperature was increased $15^\circ\text{C}/\text{min}$ to 150°C . At the initial oven conditions (i.e., -80°C), the total flow was adjusted to 14 mL/min. The injector pressure was 0.2 psi, and the septum purge was measured to be 2.5 mL/min. Flow through the column was calculated using Hewlett-Packard software to be 1.2 mL/min (40 cm/s) at -80°C . The purge valve was initially off and turned on after 0.5 min. Because the sample was introduced before the injector, it was not possible to determine the exact split ratio. This was because the sample was split between the septum purge, the total flow vent, and the injection liner–column. We can estimate the split ratio by assuming that the splitting is proportional to the three flow rates. At the time of sample injection, these flow rates gave a split of approximately 15:1. It should be noted that systems other than Hewlett-Packard with different injector designs would not necessarily have the same split ratio.

A single calibration gas mixture from Scott Specialty Gases (Wakefield, MA) composed of 29.96 mol% N_2 , 5.04 mol% CO, 30.0 mol% CO_2 , and 25.0 mol% N_2O was used to generate standard curves for the four gases. Because fixed-volume gas sample loops were used (50, 100, 250, and 500 μL), the amounts of each gas, which were used to generate the standard curves, were reported as microliters and were computed as the product of sample loop size times mole percent of the specified gas in the calibration gas mixture.

For the studies of TNAZ and NTO, quantitation of the gases was not required. However, efficient resolution was desired for possible determinations of the isotopic distributions of nitrogen and carbon in specific gas components. Milligram amounts of TNAZ or NTO were weighed into Kimax-51 glass melting point capillary tubes (0.8–1.10 \times 100 mm) (Kimble Glass, Vineland, NJ) using a

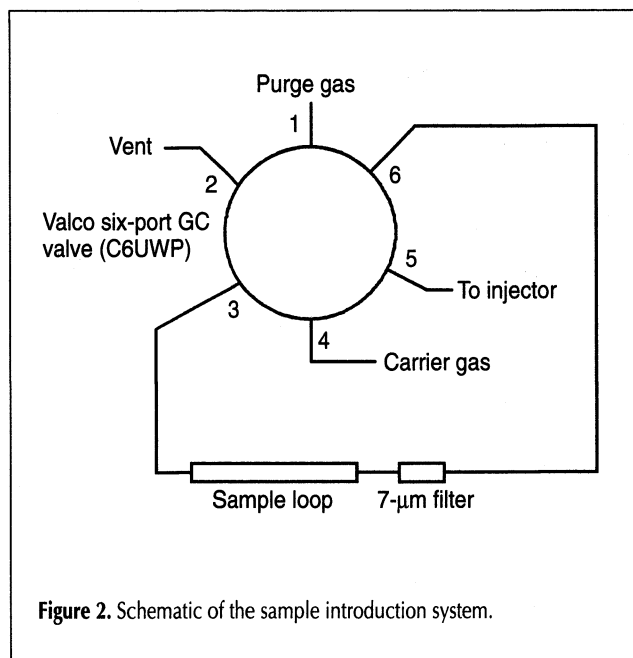


Figure 2. Schematic of the sample introduction system.

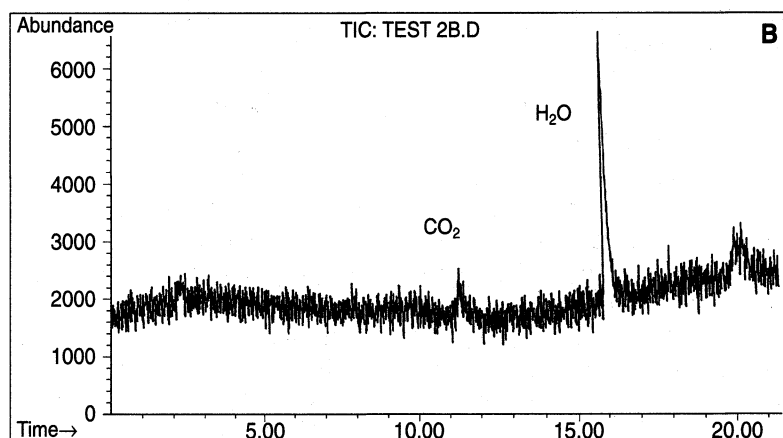
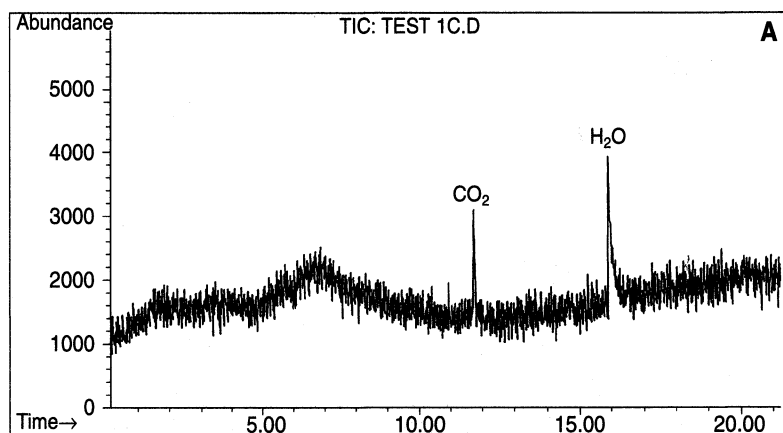
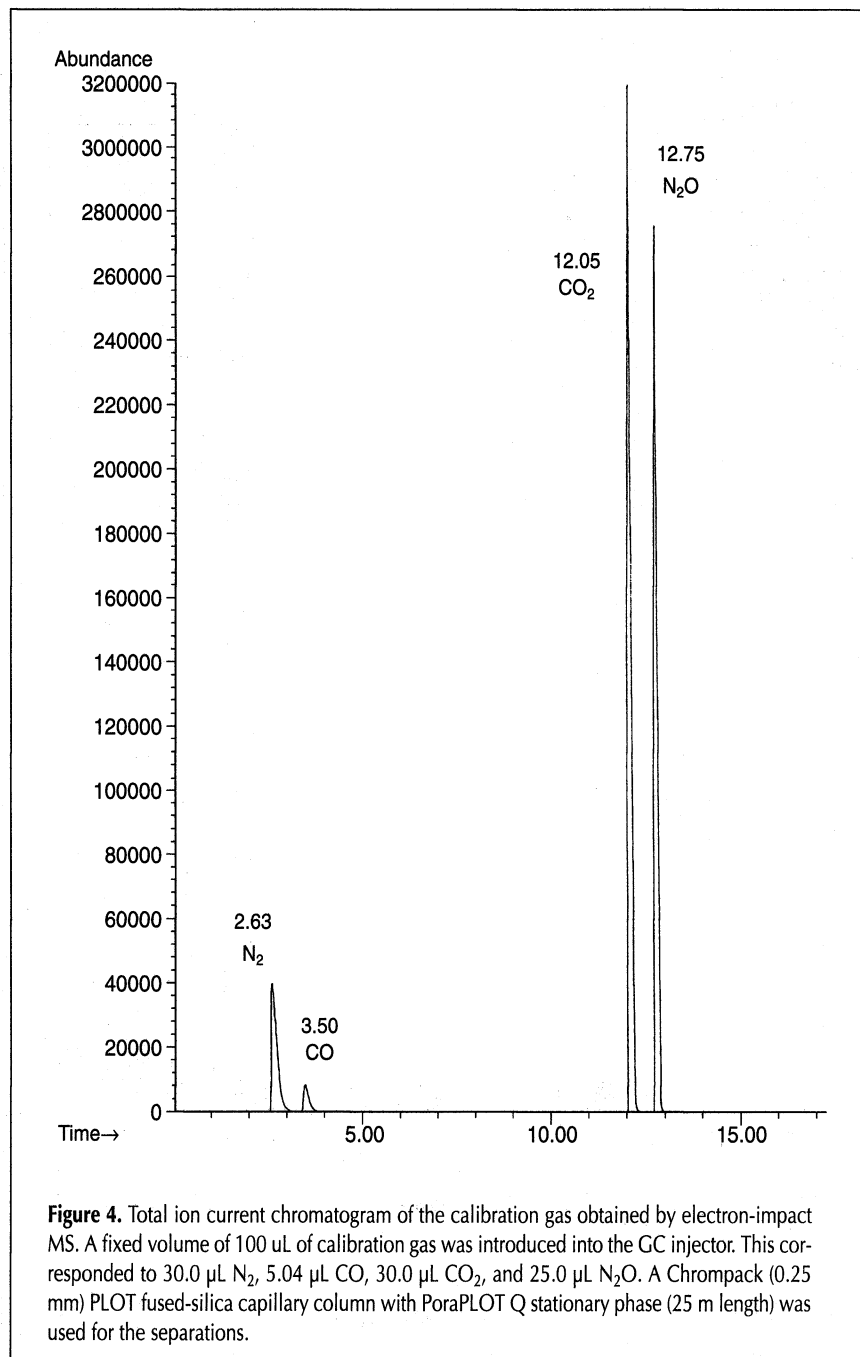


Figure 3. Typical chromatogram of a blank run (A) and a control run (B).



Mettler MT5 microbalance (Mettler Toledo, Highstown, NJ). Capillary tubes containing samples were evacuated and sealed with a miniature welding torch. Sealed samples were then immersed in a Wood's metal bath (Belmont Metals, Brooklyn, NY) at temperatures ranging from 200 to 270°C. After decomposition, one or two of the sealed capillary tubes were placed in a sample loop consisting of a 12-cm length of flexible Nalgene 870 PFA tubing ($\frac{1}{8}$ -in. i.d., $\frac{3}{16}$ -in. o.d.) (Nalgene, Rochester, NY) connected in-line with the carrier gas just before the injector. Each end of the tube was connected to a $\frac{3}{16}$ -in. $\frac{1}{8}$ -in. reducing union. The inlet side was connected to the six-port valve by means of a $\frac{1}{16}$ -in. line with a $\frac{1}{8}$ -in. brazed adapter. The outlet side was connected through a 7- μ m filter to the six-port valve using a $\frac{1}{16}$ -in. line with a $\frac{1}{8}$ -in. brazed adapter. A schematic of the sample introduction system is shown in

Figure 2. The sample loop was purged with helium prior to being switched in-line. Actual switching was done while the GC was at about 30°C; then the oven was ramped to 150°C and held for 10 min to bake the column. The oven was cooled to -80°C, and a chromatographic run was obtained without breaking the capillary tube specimens in order to check the baseline (i.e., blank run). The Nalgene 870 PFA sample loop was permeable to air. However, because it was in-line and under helium gas pressure continuously during a run, air contamination was constant and relatively low. This is evident from a typical baseline determination given in Figure 3A. The very small water and carbon dioxide peaks resulted from slight condensation at low temperature (i.e., -80°C) and eluted during the course of the run. Estimations from the permeability specifications provided by the manufacturer (Nalgene) indicated that less than 4 μ L of air was introduced into the system during the entire run (20 min). Baseline subtractions were used to correct for the continuous contributions of nitrogen and oxygen from air. Once the GC returned to -80°C, a capillary tube was broken by bending the flexible sample loop. The decomposition gases flowed into the injector and onto the column. Empty, evacuated, and sealed capillary tubes (controls) were broken into the sample introduction system and run periodically to test the integrity of the system (see Figure 3B). In addition, unheated samples were prepared and analyzed to check for possible contamination.

Results and Discussion

A total ion current chromatogram using a 100- μ L fixed volume sample loop and the standard calibration gas mixture is shown in Figure 4. Standard curves for N₂, CO, CO₂, and N₂O are given in Figure 5. In all cases, they are linear over relatively large ranges. This is evident from correlation coefficients of 0.9979, 0.9982, 0.9969, and 0.9991 for N₂, CO, CO₂, and N₂O, respectively, in Figure 5. On average, standard deviations for replicate data points ranged from about 2.5 to 3.8% of peak areas. Total ion current chromatograms of TNAZ and NTO decomposition products are given in Figure 6. They correspond to decomposition gases from 0.390 mg of TNAZ and 1.523 mg of NTO. The permanent gases of N₂, CO, CO₂, NO, N₂O, H₂O, and HCN were identified by comparison with retention times and mass spectra of authentic samples. Cyanogen was tentatively identified from its mass spectrum (molecular ion m/z

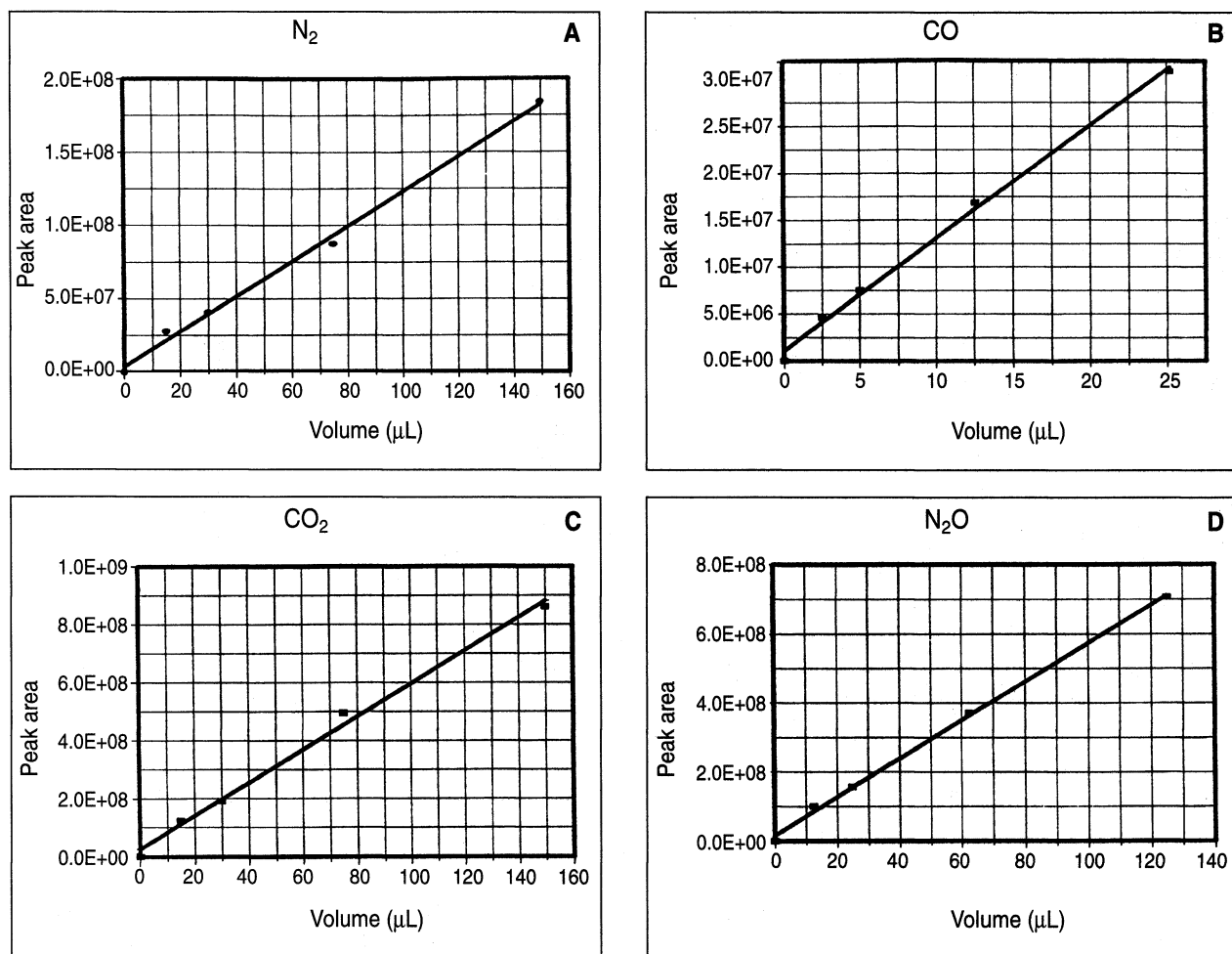


Figure 5. Standard curves for N₂ (A), CO (B), CO₂ (C), and N₂O (D) gases.

52). The prominent NO peak, associated with the decompositions of both TNAZ and NTO samples, was consistent with previous studies using the Hayesep DB system. It was not possible to detect NO with the dual capillary column system.

Conclusion

The Chrompack narrow-internal-diameter (0.25 mm) PLOT fused silica capillary column (25 m length) with PorapLOT Q stationary phase has dramatically improved our analytical capabilities for compositional analyses of decomposition gases. An important benefit to our laboratory is the replacement of a dual column method, which was unable to detect NO gas, with a single column method.

This system was able to simultaneously detect N₂, CO, CO₂, NO, N₂O, H₂O, HCN, and cyanogen. Cyanogen and HCN had not previously been observed during TNAZ decompositions. HCN was also detected as a product of NTO decomposition for

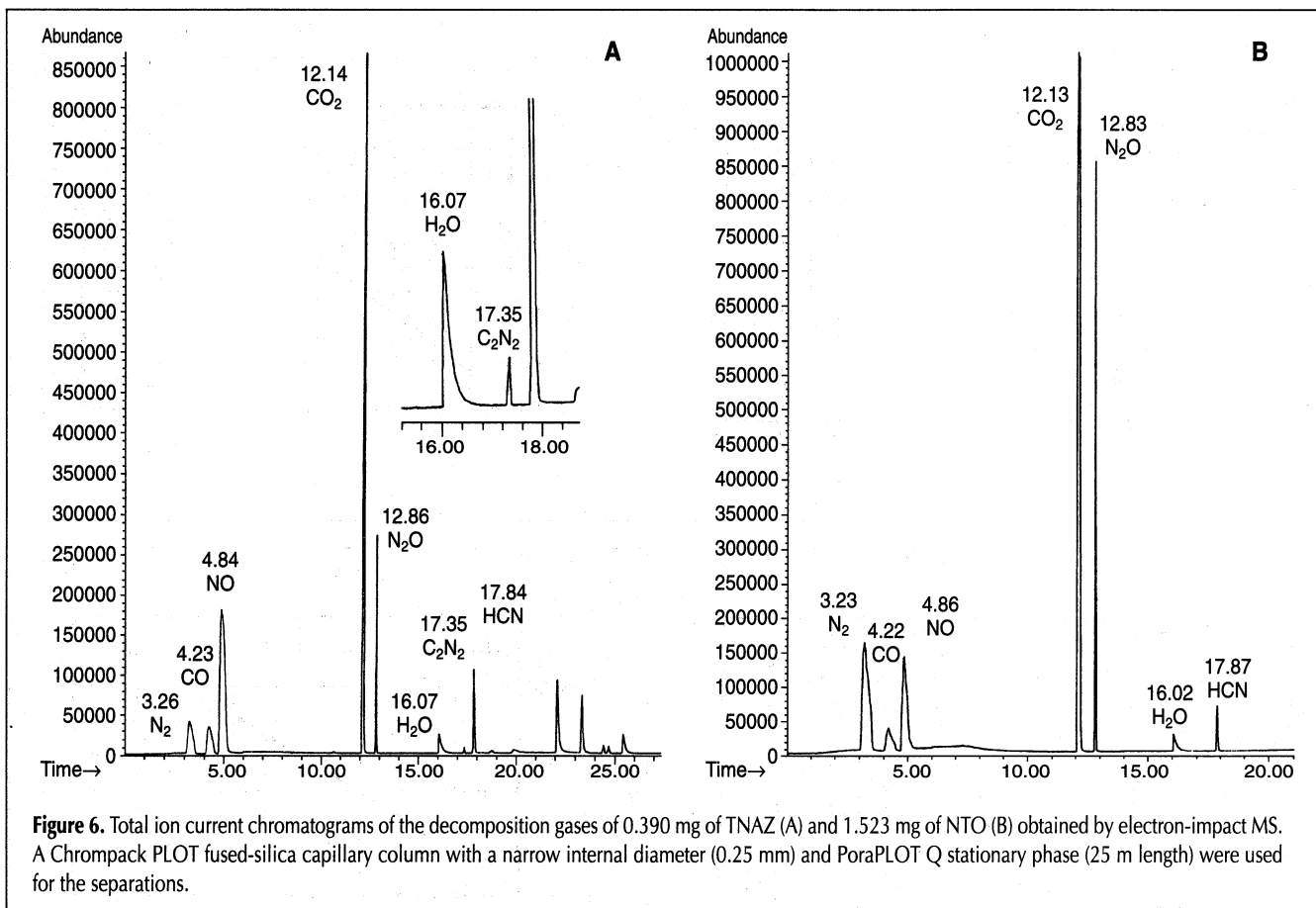
the first time. Cyanogen, HCN, and NO gases were not seen using the dual capillary column configuration.

Acknowledgment

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