LA-UR -85-860

CONF-850706--8

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

LA-UR--85-860

DE85 009581

TITLE REAL TIME ANALYSIS OF PETN DETONATION PRODUCTS

AUTHOR(S) Normand C. Blais and James J. Valentini

MASTER

SUBMITTED TO Eighth Symposium (International) on Detonation
Albuquerque Convention Center
201 Marquette, NW
Albuquerque, NM 87103
Monday-Friday, July 15-19, 1985

DISCLAIMER

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

FORM NO 836 R4

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

REAL TIME ANALYSIS OF PETN DETONATION PRODUCTS

N. C. Blais and J. J. Valentini
Los Alamos National Laboratory
Chemistry Division, MS G738
Los Alamos, NM 87545

The freely expanding gases from the detonation of pentaerythritol tetranitrate (PETN) pellet were analyzed as rapidly as the molecules arrived at the mass spectrometer detector. It was found that all of the products arriving at the detector earliest, irrespective of mass, had the same velocity, 11 km s^{-1} and peaked at 5 km s^{-1}. The width of the time distributions varied from one species to another. Mass and velocity spectra of the important products were obtained and the most intense signals were found to be H_2O, CO, and CO_2, but H_2O was by far the largest. Smaller signals arising from O, HCN, HCO, and NO_2 were also found. Comparisons of the spectrum with other experiments are discussed.

INTRODUCTION

We present the results of some recent experiments which were designed to measure some of the characteristics of the immediate detonation products of explosive substances. The characteristics we report here are the mass spectrum of the gaseous products of PETN detonation and their velocity distributions. Ideally we would like to report these properties as a function of time starting with the passage of the detonation front through a particular volume of the explosive. The best that we could do here is to examine the detonation products after they had expanded to a sufficient degree that no further changes of state could occur. Our experimental conditions are such that intermolecular collisions occur only between detonation products as they expand, and this expansion occurs freely, being unimpeded by any ambient gases or surfaces before the molecular products are detected. Therefore, we cannot claim that our observed distributions are characteristic of the detonation products immediately after detonation occurs, or before expansion occurs. On the other hand our measurements are much closer to achieving that claim than the usual mass spectrometric measurements.

Several mass spectrometric measurements of detonation products and decomposition products have been reported [1-7], including those from PETN [1,4,5,7]. Most of these were made on time scales long compared to ours and with expansion constraints sufficiently restrictive that no time history of product formation could be deduced. Relatively fast measurements of decomposition products have been reported [4], but even these millisecond time scales are long compared to ours, which have resolutions in the microsecond range. Only two other groups have reported measurements on a time scale similar to ours: those of Schilf [6] and of Höh [7]. Höh has examined PETN detonation. However, no subsequent work has appeared since these reports.

As we will discuss below, our distributions in time are not characteristic of products emanating from a gaseous volume at a thermodynamically prescribed temperature. There are significant differences between our results and those of Höh. Our mass spectra are different than those reported from usual mass spectrometric measurements.

EXPERIMENTAL

The essential features of our apparatus are represented schematically in Fig. 1. Explosive pellets, in this case PETN, of from 22 to 100 mg weight were detonated in a large vacuum vessel (119 cm long x 48 cm wide x 48 cm high). The gaseous products expanded adiabatically until they arrived at the first collimating aperture, a skimmer with a 0.076 cm hole. By the time the products reached this aperture, a distance of 43 cm, the number density had decreased sufficiently that very few collisions were occurring, so that the molecular state distributions were "frozen." Almost all of the molecules that passed through this aperture reached the electron impact ionizer and 1/1000 were ionized to be mass analyzed by the quadrupole mass filter.

Before firing the pellet, the pressure in the reaction vessel was 10^{-6} Torr, which subsequently rose to a maximum of 10^{-3} Torr before diminishing. However, this pressure rise occurred only after the products had collided at least once, but probably several times, with the reaction vessel wall. By that time our measurements were completed. The three apertures through which the molecules passed to reach the detector served mostly to prevent the slow pressure rise in the reaction chamber from affecting the detector chamber. The solid angle subtended by the detector was determined by the entrance aperture of the ionizer, but all of the intervening apertures were only slightly larger than necessary to satisfy this condition. Typically, the detector chamber operated at 4 to 5 x 10^{-8} Torr and no pressure rise was observed after firing a pellet.

Several data acquisition schemes were used to accept the output signals of the Channeltron electron multiplier. Most of the data was processed by using a fast pulse preamplifier-amplifier/discriminator and a multichannel scaler (MCS) combination. Count rates of up to 5 MHz were observed, but some as

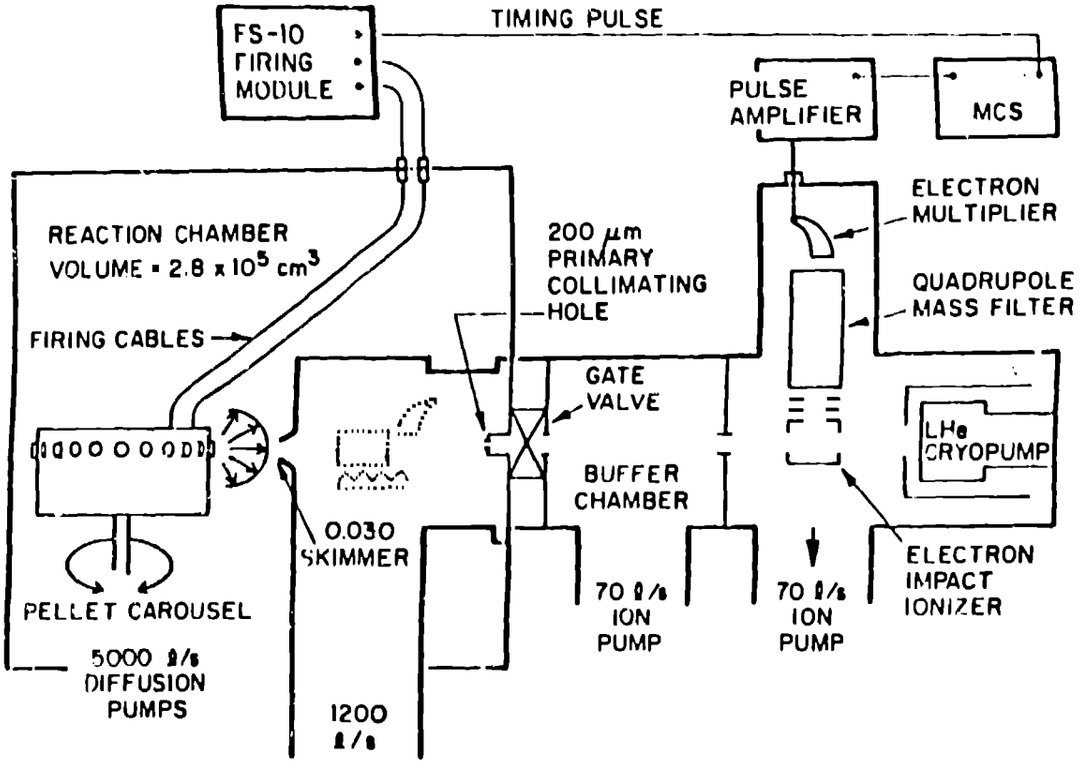

Fig. 1. Schematic of apparatus for detonation products studies. Dimensions are not to scale. Dotted section is an alternative detector placement sometimes used to check time scale of experiments.

high as 30 MHz were encountered, and special precautions were needed to prevent saturating the Channeltron. For accurate time-of-flight measurements the MCS was set at 10 μs/channel, but for quantitative pulse summation, a setting of 50 μs/channel was preferable. The flight distance from pellet to ionizer was 110 cm. At masses higher than 44 it was necessary to use an alternative data acquisition method because of radio frequency interference from the quadrupole. A storage oscilloscope with an input impedance of 100 KΩ shunted by 20 pf converted the Channeltron output to an analog signal that was photographed. Signals ranging from 2 mV to 2.0 V were obtained. Both the MCS and the oscilloscope were triggered by a voltage pulse across a 50 Ω load generated by the current induced in a one turn loop around one terminal of the firing module.

PETN pellets having a density of 1.5 to 1.6 were mounted on Capton slapper assemblies driven by flat copper bridges and detonated electrically with a 5 J pulse from an FS-10 firing module (Reynolds Industries, EBW System). Up to 30 of these were mounted on a carousel that was rotated externally to the reaction vessel. Alignment of the pellet with the detector axis was done with a grain-of-wheat light bulb-photodiode arrangement through indexing holes in the carousel. Fig. 2 is a sketch of the carousel pellet holder.

RESULTS AND DATA ANALYSIS

Figure 3 is a plot of the number of counts stored in each channel of the MCS as a function of time for two mass peaks, M=12 and M=18. The dwell time was 50 μs per channel. For the M=18 distribution it was necessary to reduce the electron ionizing current by a factor of 5 to eliminate saturating the Channeltron. Figure 4 is a plot of the mass spectrum for PETN. Each mass required detonating a pellet, and the quantity plotted for each mass is directly proportional to the sum of all the counts above background from distributions of the kind shown in Fig. 3. For the more important masses, M=1, 18, 28, 30, 44, from 2 to 6 shots were averaged. The results were normalized to make the counts recorded at M=18 have a value of 100 and corrected for ionization efficiency as discussed later.

Figure 5 shows flux distributions for M=18, 28, and 44 as a function of time, velocity, and energy. These were

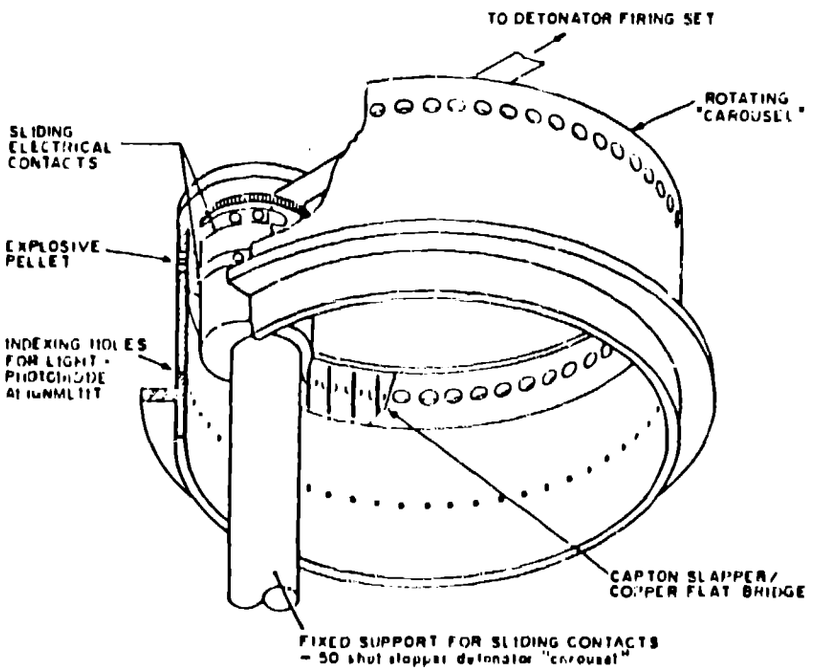

Fig. 2. Carousel on which pellets are mounted so that several detonation measurements can be made without breaking vacuum.

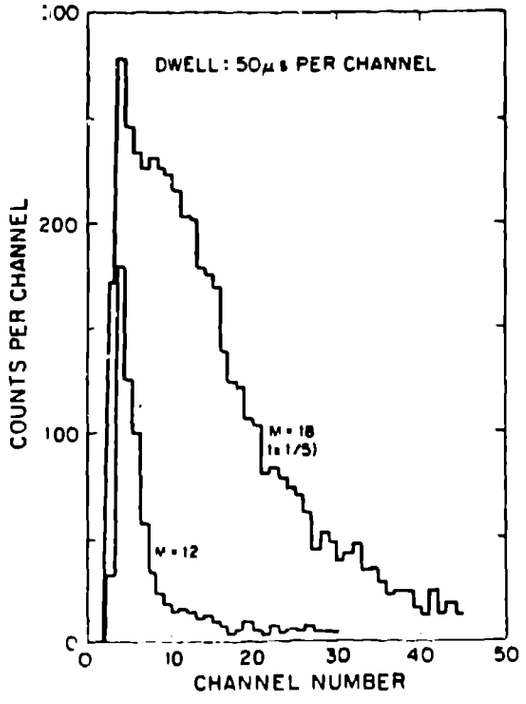

Fig. 3. A plot of raw data taken from the multichannel scaler (MCS) for two mass peaks, M=12 and M=18.

obtained from distributions of the kind shown in Fig. 3 by fitting the MCS data with cubic splines and then using the appropriate Jacobian to transform these analytical number densities to a flux distribution. The time at each channel was taken to be that at the center of the channel

$$t = (n - 1/2)\,\Delta t \quad .$$

Here n is the channel number and Δt is the dwell time of the MCS in acquiring the data. To convert to velocity, the Jacobian is proportional to the time t at each point and to convert to energy it is t^2.

DISCUSSION

The most prominent feature of the mass spectrum in Fig. 4 is that at mass 18, H_2O^+. Our best estimate is that it is about a factor of 5 larger than that at M=28, the next largest unrelated feature. Mass 17 is consistent with the dissociative ionization of H_2O to OH^+, and therefore there is very little NH_3^+ in the spectrum. The peak at M=15 is probably CH_3^+, so that at most only 3% of the M=16 can arise from CH_4^+.

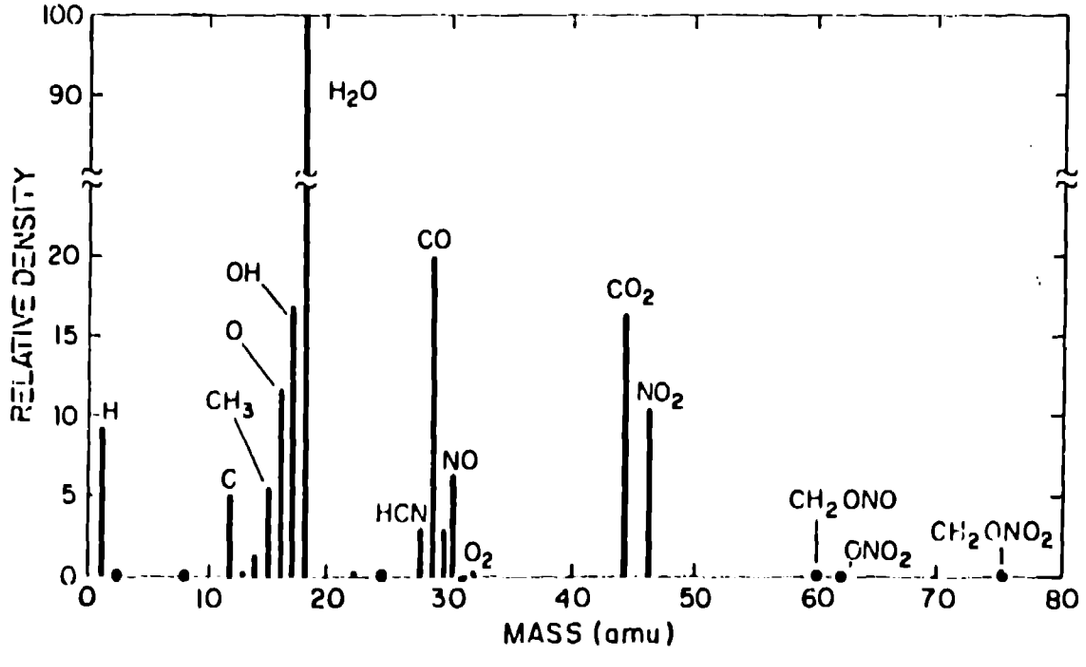

Fig. 4. Mass spectrum of PETN detonations. Intensities were obtained by summing all recorded counts of data such as in Fig. 3 and correcting for ionization efficiencies. Circles are masses for which no measurable signals were observed.

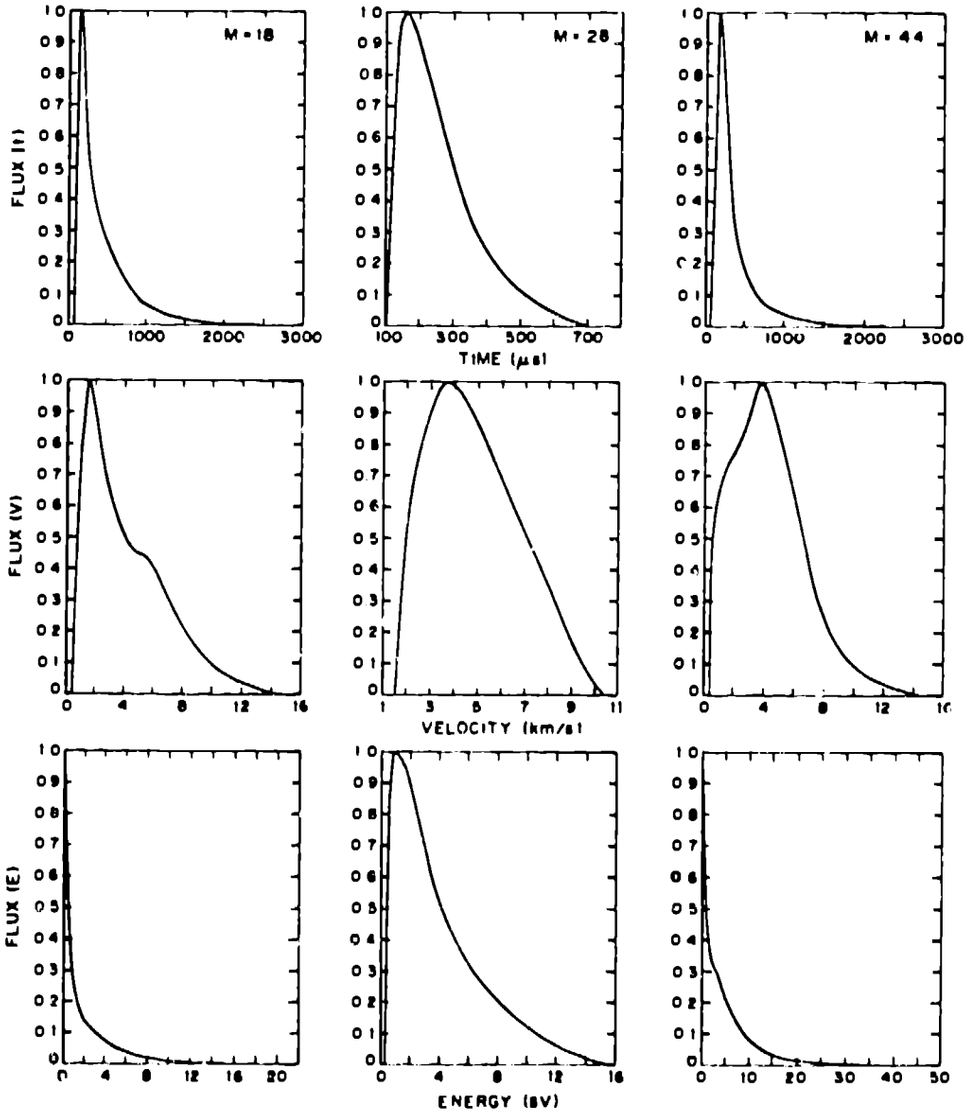

Fig. 5. Flux distributions for masses 18, 28, and 44 plotted as a function of time, velocity, and energy.

M=16 is then O^+, but it must be noticed that O_2^+ is very small. Mass 44 is clearly CO_2^+ since the expected peak at M=22, CO_2^{++}, has the correct magnitude. Most likely mass 28 is predominantly CO^+. We cannot determine if the mass peaks at m=1, 12, 14 are fragmentation ions from larger parent molecules. We observe evidence for the presence of HCN, HCO, but the mass 30 peak is probably fragmentation from NO_2, the parent being clearly evident at mass 46. There are no signals at masses 2, 8, 24 (C_2^+) with significant intensity above the background or electrical noise.

The intensities in Fig. 4 have been corrected approximately for the ionization efficiency of the species. The stable molecules, H_2O, CO, CO_2, NO_2 were corrected by using published tables of relative sensitivities [8] at electron impact energies of 70 eV. Our electron energy was actually 100 eV, but the relative intensities should be about the same. We corrected the ion signals at M=1, 12, 15 as though they were fragments from CH_4. For other masses, such as M=16 or 29, for which the species is too uncertain or for which no sensitivities were available, we left uncorrected .

This spectrum is in sharp contrast to the mass spectrum of confined or unconfined detonations of PETN [1] using steady state analysis methods. To the level of accuracy appropriate to these experiments, both the confined and the unconfined detonations have similar product spectra, with most of the products appearing at M=18, 28 and 44. Each of these has about the same fractional molecular yield, 3.4 to 3.7 molecules per molecule of PETN. The strength of our mass 18 product is not consistent with this pattern of yield. The faster time resolved mass spectra obtained from fracturing studies [4] reveal the presence of radicals, such as CH_3 at mass 15, that are present in our spectrum but which are understandably absent in the equilibrium analysis. But for the fracturing experiments also, the peak at M=18 (H_2O) has a conspicuously lower relative intensity than our results indicate. Fracturing PETN also produces some high mass products, namely M=60 and 76, attributed to CH_2ONO and CH_2ONO_2. As the fracturing becomes more energetic, only the M=60 persists. Our experiments indicated the trace presence of M=60, M=62 (ONO_2) and M=76 but in such small amounts that a quantitative estimate is impractical to make. Höh [7], on the other hand, reports a spectrum with many features in common with ours, but the most prominent feature is mass 28. In contrast to our results, mass 28 is larger than the mass 18 by a factor of 3 and larger than mass 44 by a factor of 7. So while the presence of radicals is corroborated in both free expansion experiments, the quantitative details of the spectrum differ considerably.

Clearly the mass balance of all of these spectra must add up to that of the explosive, and the steady state mass spectra have been shown to do that. Our measurements are too quantitatively uncertain to allow such an analysis, especially since the time dependence must also be included in such an analysis.

Examinations of the plots of the kind shown in Fig. 3 or those of Fig. 5 show that the initial arrival time of all of the masses, has close to a common value, and that the most probable arrival time for all of the distributions also show that same trend. Typically the initial time is about 100 μs and the most probable 215 μs. These correspond to velocities of 11 km/s and 5 km/s (no corrections have been made for the uncertain ion flight time, but this correction is small). Of course, after transforming to velocity coordinates, the most probable flux velocity is not the same as the velocity corresponding to the peak of the arrival time. The most probable velocity becomes 4 km/s.

The uniformity of the early arrival times, or alternatively of the higher velocities irrespective of mass, clearly indicates that these molecules did not originate from a gas that could be characterized by a temperature distribution. This feature is reminiscent of a hydrodynamic expansion of a gas at very high Mach numbers with very little viscous slippage between the constituent masses. Using mass 28 as an example, the peak velocity would be appropriate to a temperature of 15000 K, while the spread in velocity for our observed distribution is 4000 K. However, as we see in Fig. 3, the width of the distribution depends on the mass of the ion observed. If the mass 12 signal is C^+ from the dissociative ionization of a heavier parent mass, such as CH_3, one would not expect the widths to differ significantly from other masses. Perhaps mass 12 comes from unreacted C as a product.

Transforming to energy coordinates is easily done, as we show in Fig. 5, but the shape of the curves is more questionable. This is because of the broad time distributions and the large effect of the t^2 Jacobian. Even small waviness in the time distribution arising from the spline fitting procedure produces spurious bumps in the distribution. Where the energy distribution peaks is also very difficult to determine. Nonetheless, we see that there are a considerable number of products with energies in the elecron volt region.

The velocities we obtain are about half of those obtained by Höh, et al. [7] and our early arrival times are more uniform than theirs. Nonetheless, it is clear that for both experiments the distributions have a considerable mass flow velocity superimposed on the thermal kinetic energy distributions. It is tempting to speculate that our early arriving molecules are products that emanate from a thin layer near the closest surface of the PETN pellet. These are moving the fastest after the pellet detonates and are moving in the direction of the detector. Since most of our products have about the same mass and not very different collision cross sections, they become uniformly accelerated from behind by the remainder of the expanding products.

ACKNOWLEDGMENTS

We wish to thank F. Archuleta and A. Garcia for their enthusiasm and diligence in assembling the apparatus.

REFERENCES

1. D. L. Ornellas, "Calorimetric determinations of the heat and products of detonation for explosives: October 1961 to April 1982," UCRL-52821 (1982).

2. V. Krishna Mohan and Tong B. Tang, "Flow and explosive decomposition of thermally unstable solids: A study with time-resolved mass spectrometry," Phys. and Chem. of Solids (to be published).

3. N. C. Paul, "Mass spectrometric analysis of complex gas mixtures," U.S. Nat. Tech. Inform. Serv., AD Rep. No. 737402. Available from Govt. Rep. Announce. (U.S.) 1972, 72, 71-2.

4. H. M. Hauser, J. E. Field and V. Krishna Mohan, "Fracture induced decomposition of a brittle high explosive: pentaerythritol tetranitrate," Chem. Phys. Lett. 99, 66 (1983).

5. G. D. Miller, L. D. Laws and R. H. Dinegar, "Kinetics of the thermal decomposition of solid PETN," Nineteenth Symposium (Int.) on Combustion, p.701 (1982).

6. N. Schilf and H. Trinks, "Four-channel magnetic mass spectrometer for dynamic measurements of fast reactions," Int. J. Mass Spectrom. Ion Phys. 37, 123 (1981).

7. A. Höh and F. Aulinger, "Mass spectrometric and time-of-flight analysis of gaseous detonation products in high vacuum," Dyn. Mass Spectrom. 5, 165 (1977).

8. A. Cornu and R. Massot, "Compilation of Mass Spectral Data," 2nd edition, VI (Heyden & Son, 1975).