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Perspectives

Separation of Ions from Explosives in Differential Mobility Spectrometry by Vapor-Modified Drift Gas

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Differential mobility spectrometry (DMS) of nitro-organic explosives and related compounds exhibited the expected product ions of M^- or $M\cdot NO_2^-$ from atmospheric pressure chemical ionization reactions in purified air at 100 °C. Peaks in the differential mobility spectra for these ions were confined to a narrow range of compensation voltages between -1 to $+3$ V which arose through a low dependence of mobility for the ions in electric fields at E/N values between 0 and 120 Td ($1 \text{ Td} = 10^{-17} \text{ V cm}^2$). The field dependence of ions, described as an α parameter, ranged from -0.005 to 0.02 at a separation field of 100 Td. The α parameter could be controlled through the addition of organic vapors into the drift gas and was increased to 0.08 – 0.24 with 1000 ppm of methylene chloride in the drift gas. This modification of the drift gas resulted in compensation voltages of $+3$ to $+21$ V for peaks. The improved separation of peaks was consistent with a model of ion characterization by ΔK or $K_l - K_h$, where K_l is the mobility coefficient of ions clustered with vapor neutrals during the low-field portion of the separation field waveform and K_h is for the same core ion when heated and declustered during the high-field portion of waveform.

The detection of explosives is one of the few applications where ion mobility spectrometry (IMS) is in use daily with over 10 000 mobility spectrometers in airports worldwide for screening hand-carried articles.¹ The widespread acceptance of IMS analyzers for explosives monitoring is based upon the favorable gas phase ionization chemistry for explosives at ambient pressure and the satisfactory selectivity obtained by mobility analyses.² The formation and separation of ions in IMS occur in a drift tube operated in air at ambient pressure providing practical advantages of simplicity of instrumentation and comparatively low costs of operation. This is seen in benchtop size mobility spectrometers which have been in routine use during the past decade; currently,

$\sim 10^7$ analyses for explosives are made annually with IMS instruments.³ Apart from size and cost, another advantage with this method is speed. Each measurement, including spectral interpretation and display of results, requires ~ 7 s after a sample is placed in the analyzer. Though hand-held configurations of IMS explosives analyzers are now available, unit costs, weight, and demands on power limit the possible applications for explosives detection by IMS analyzers.

The initial step in IMS response to explosives is the formation of gas phase ions from sample vapor through atmospheric pressure chemical ionization (APCI) reactions in negative polarity. This establishes the analytical strengths of this method including low detection limits and a high selectivity of response. Sample vapors are introduced into a reservoir of reagent or reactant ions, such as $O_2^-(H_2O)_n$ where $n = 1$ – 3 , and a reaction with an explosive molecule (M) yields an adduct ion, e.g., $M\cdot O_2^-(H_2O)_{n-1}$. This ion may survive intact in the drift tube only if the ion lifetimes are >1 – 10 ms as observed for some compounds including fluorophenols.⁴ More typically for explosives, ions have lifetimes below 1 ms and react further through proton abstraction, charge transfer, or fragmentation. Mobility spectra at ambient pressure and temperatures over 100 °C for explosives typically exhibit ions such as $(M - 1)^-$, M^- , and NO_2^- . Though ionization chemistry of explosives in IMS may seem more complex than electron impact methods as found in mass spectrometry, a reagent gas is added to the gas atmosphere of an IMS analyzer. Halocarbons reagent gases or dopants produce a Cl^- reactant ion, and product ions for explosives are only a single or a few product ions, usually M^- or $M\cdot Cl^-(H_2O)_n$; the dopant also provides some discrimination against common interferences. Consequently, detection limits in IMS are low and requirements for ion separation are relatively undemanding. All APCI-based reactions are dependent upon moisture, temperature, and sample vapor concentration; therefore, gas purity, moisture levels, and some aspects of sample loading must be rigorously maintained.

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In traditional mobility spectrometry, ions formed in the reaction region are extracted and injected into the drift region where separations occur through differences in drift velocities (v_d) of the ion swarms in an electric field (E) of ~ 250 V/cm. The drift velocities can be associated to molecular structure through the mobility coefficient (K , where $K = v_d/E$), and explosive ions exhibit characteristic mobilities. Thus, the selectivity of the ion chemistry noted above is supplemented with a second dimension of selectivity through ion characterization by mobility. Ionization and mobility determinations occur in the drift tube, which is, in conventional designs, an expensive component to manufacture or repair. These costs might be improved with miniaturized drift tubes, and examples of small drift tubes have been reported.^{5–7} Such small size drift tubes unfortunately often lead to degraded signal-to-noise values or losses in separation capability; moreover, conventional designs are not amenable to methods of mass production. Consequently, conventional designs with substructures of ion shutters, aperture grids, and drift rings can be seen as limiting in cost and size and an alternative approach was sought using nontraditional methods for ion characterization with asymmetric electric fields.^{8–10} A microfabricated analyzer exhibited low-ppb limits of detection for continuous vapor streams and was suitable as a gas chromatographic detector owing to fast response, low memory, and additional information orthogonal to retention time.^{11–15} This method is described as differential mobility spectrometry (DMS) and is already available commercially.¹⁶ A brief mathematical description of the method is presented below, and a comprehensive treatment can be found elsewhere.^{17,18}

In a DMS analyzer, ions are characterized for differences in mobility between two electric fields, typically 20 and 100 Td, through a nonlinear dependence of ion mobility with electric field.¹⁹ Under normal conditions of 273.15 K and 101.325 kPa, 1 Td corresponds to $E = n_0 10^{-17} = 268.67$ V/cm, where n_0 is the Loschmidt constant. When the electric field (E/N) is below 10 Td the mobility coefficient of an ion is independent or practically independent of the electric field. As the magnitude of E/N is

increased above ~ 10 Td, the mobility coefficient becomes dependent upon field strength as shown in eq 1

$$K(E/N) = K(0)[1 + \alpha_2(E/N)^2 + \alpha_4(E/N)^4 + \dots] \quad (1)$$

where the terms are the following: $K(0)$, the mobility coefficient under zero field conditions; $\alpha_2, \alpha_4, \dots, \alpha_{2n}$, the specific coefficients of even powers of the electric field; and E/N , the field strength normalized to the gas density. The α terms are an even power series for E/N , so the absolute value for the ion velocity is independent of the electric field direction. Equation 1 can be simplified in eq 2

$$K(E/N) = K(0)[1 + \alpha(E/N)] \quad (2)$$

where $\alpha(E/N) = \alpha_2(E/N)^2 + \alpha_4(E/N)^4 + \dots$

A method of computing the α function from experimental data has been described in detail and applied to microfabricated DMS analyzers.²⁰ An alternative approach has also been suggested.²¹ Organic ions may exhibit α functions that are positive, so $K(E/N)$ increases with E/N , or negative, so $K(E/N)$ decreases with E/N .

Ions are introduced into a DMS drift tube with a flow of gas and are carried through a narrow gap between two planar electrodes as shown in Figure 1 (top frame). A high-frequency, high-voltage asymmetric waveform is applied to the electrodes resulting in an electric field, the separation field $S(t)$, that affects ion motion through different coefficients of mobility via eq 2. Ions undergo fast oscillations perpendicular to the gas flow in response to $S(t)$, and ions undergo gradual net displacement or drift toward an electrode during transport through the drift tube. The extent of displacement depends on field amplitude, field waveform, and the α function for an ion; however, an ion can be restored (i.e., compensated) to the center of the gap when a dc potential from 0 to ± 40 V is superimposed on the separation field. This second potential is called the compensation voltage and controls which ions are passed through the DMS drift tube and to a detector. A scan of the compensation voltage provides a measure of all ions in the analyzer and is termed a differential mobility spectrum (Figure 1, bottom frame). This method is now understood as a technique for ion separation based upon the ΔK of ions rather than K alone, as seen with conventional mobility spectrometers. Although methods of ion characterization using asymmetric electric fields are relatively recent developments, explosives were among the first chemicals characterized, and they exhibited attractive detection limits.^{22,23} Though microfabricated DMS analyzers are attractive owing to their small size and economies of production, preliminary results for explosives showed poor ion separation.

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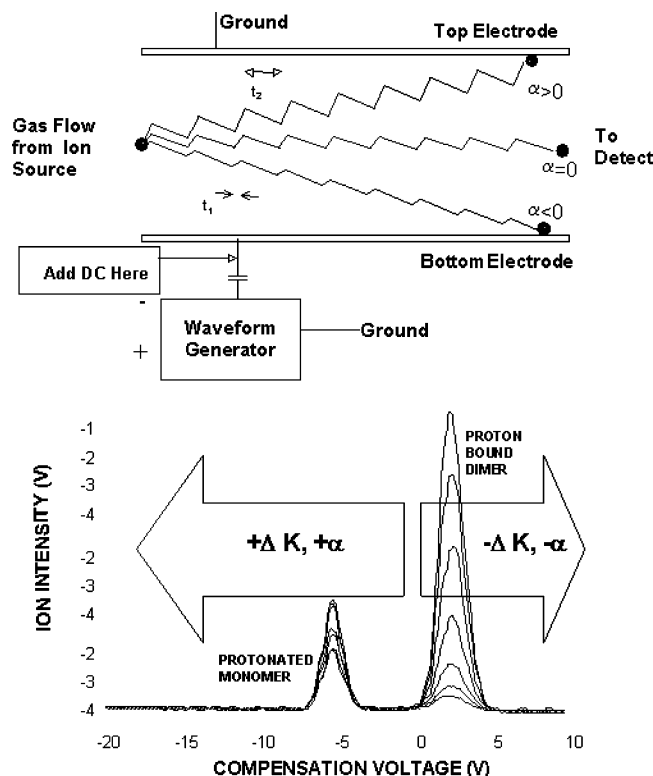


Figure 1. Schematic of a differential mobility spectrometer (top) and a differential mobility spectrum (bottom). The relationship between ΔK , α , and the compensation voltage are shown for ions with positive and negative α functions. (see eq 2).

One parameter that degrades performance of conventional IMS is moisture in the drift gas; however, this is known to improve the selectivity of the DMS analysis.²⁴ Processes responsible for positive α functions have been described as dynamic transitions of ions between declustered and clustered or short-living associations with corresponding changes in collision cross sections between two ion forms or conditions.²⁴ Moisture presumably enhanced ΔK by altering the degree of clustering for the ion under the low-field portion of the separation field. Preliminary studies with explosives demonstrated a similar effect with water and other volatile neutrals in the drift gas. Since ion separation in the DMS method is directly related to the α function of the ions, and these were affected by the drift gas composition, modification of the drift gas to alter the α function was seen as a possible method to improve the separation capability of the DMS method. The objective of these studies was to confirm this hypothesis and find the optimal conditions in terms of selectivity vis-à-vis drift gas modifiers and concentrations. Additionally, the analytical performance of microfabricated DMS drift tubes for detecting explosives was characterized.

EXPERIMENTAL SECTION

Instrumentation. Experiments were completed using two DMS analyzers designed for specific measurements. One DMS analyzer (Figure 2a) was attached to an exponential dilution flask, vapor generator, and gas chromatograph (GC), and this instrument was used for measurements of field dependence of mobility,

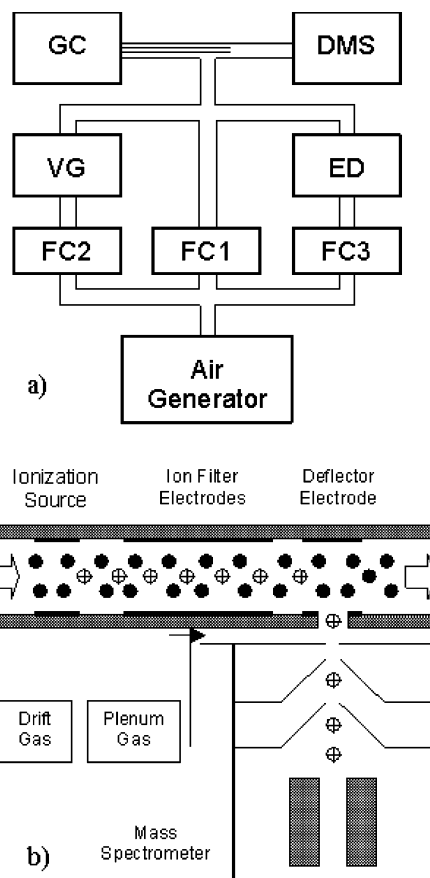


Figure 2. Schematics of two DMS analyzers (a) with a gas inlet through a gas chromatograph (GC) or an exponential dilution (ED) flask. The flow system included a vapor generator (VG), flows were controlled with digital mass flow meters (FC), and (b) a mass spectrometer as detector. The plenum gas was a stream of ultrahigh purity nitrogen gas at 100 mL/min.

for quantitative characterization of response, and for studies with modifications of the drift gas. A second DMS analyzer (Figure 2b) was interfaced to a mass spectrometer, so the core ions in the DMS spectra could be mass identified. In both instruments, the analytical parameters and components were identical and included a width of 0.5 mm between the electrodes (4×15 mm) and a 3 mCi ^{63}Ni ion source. The drift gas was air from a model 737 Addco Pure Air generator (Miami, FL) and was provided at 0.3–1 L/min and controlled with a GR series flow controller (Fathom Technologies, Round Rock, TX). The drift gas was further purified over a 5 Å molecular sieve bed (10-cm diameter \times 0.6-m long) and passed through stainless steel tubing heated to 100 °C with resistive wire. The vapor generator was used to add controlled levels of modifying vapors to the drift gas, and the exponential dilution flask was used to introduce explosive vapors at the calculated concentration into the DMS analyzer.

The DMS analyzers were operated using specialized electronics containing a separation waveform generator, a compensation voltage controller, and two $5\text{ V} \pm$ biased electrometers providing simultaneous measurements for positive and negative ion spectra. The separation waveform generator was based on a soft-switched, semiresonant circuit that incorporated a fly back transformer²⁵ and allowed variable peak-to-peak amplitudes of the asymmetric

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waveform from 200 to 1600 V without altering the waveform shape. The operating frequency of the generator was 1.3 MHz. The compensation voltage was scanned between 30 to -10 V in ~ 1 s periods through specialized Labview-based software and a model 6024E interface card from National Instruments (Austin, TX). The same software was used to digitize and store spectra for every scan. The gas chromatograph was an Agilent model 6890A modified with a μ Wave GC 3600 (ANTEK, Inc., Houston, TX). The column was a 5-m capillary column with an OV-1 bonded stationary phase. The conditions of operation included the following: initial temperature, 100°C ; initial time, 0 min; temperature ramp, $25^\circ\text{C}/\text{min}$; final temperature, 200°C ; final time, 2 min. The split ratio for the injector was 30:1, and the injector temperature was 100°C . The carrier gas was nitrogen at $0.5\text{ mL}/\text{min}$.

The mass spectrometer was one of two tandem mass spectrometers: a Sciex TAGA 6000 or a PE–Sciex API 3 (Toronto, Ontario, Canada); however, only single quadrupole scans were made in these studies. When the DMS drift tube was placed against the flange of the MS, a hole in the drift tube was aligned with the orifice in the flange of the MS (Figure 2b) allowing ion passage from the DMS to the mass spectrometer. The MS was equipped with an Apple PowerMac 7100/66 computer and API Standard Software, version 2.5.1. Details of this DMS/MS interface have been described,²⁶ and the DMS was improved with miniaturized electronics and improved mechanics of operation. In these studies, only ions of negative polarity were characterized by mass spectrometry.

Chemicals and Reagents. The following explosive compounds were obtained from Restek Corporation (Bellefonte, PA) as $1000\text{ }\mu\text{g}/\text{mL}$ solutions in acetonitrile: 4-nitrotoluene (NT); 2,6-dinitrotoluene (DNT); 2,4,6-trinitrotoluene (TNT); 4-nitrobenzene (NB); 1,3-dinitrobenzene (DNB); 1,3,5-trinitrobenzene (TNB); 1,3,5-triazine, hexahydro-1,3,5-trinitro (RDX); 1,2,3-propanetriol, trinitrate (NG); and pentaerythritol, tetranitrate (PETN). Working solutions were prepared by serial dilutions in acetonitrile with concentrations of $\sim 10\text{ }\mu\text{g}/\text{mL}$. Vapors of water, acetone, methylene chloride, and propanol were used as dopants for modifying the drift gas at vapor concentrations of 0–1000 ppm.

Procedures. Initial Studies. In early studies by GC/DMS, stock solutions of individual explosives were characterized to determine retention times and compensation voltages for each substance. In these studies, $2\text{ }\mu\text{L}$ of the working solution was injected with a split ratio of 30, so the mass of chemical delivered to the GC column was in the subnanogram range. The injected mass was adjusted to yield a near Gaussian-shaped chromatographic peak with a width of 2–5 s. The DMS analyzer was operated continuously, and mobility spectra were obtained every second. Since the widths of individual GC peaks were $\sim 2\text{--}5$ s at baseline during an elution profile, two to five differential mobility spectra were recorded for each explosive throughout a range of concentrations. All differential mobility spectra were saved for graphic analysis made using postanalysis processing of the data.

Field Dependence. Mobility dependence on the electric field for ions of explosives was made by GC/DMS analysis of a mixture of explosives and amplitudes from 800 to 1300 V for the separation voltage. These studies allowed the dependence of the compensa-

tion voltage versus separation voltage to be determined for each peak in the differential mobility spectra. Standard procedures were used to derive the α functions.²⁰

Quantitative Response. Exponential dilution was used to generate response curves and to determine limits of detection for the explosives. In this method, a known amount of an explosive was injected into a 0.5-L heated round-bottom glass flask fitted with inlet and exhaust flows to provide calculated concentrations in the drift gas flow. The vapor concentrations of the explosives decreased exponentially according to eq 3

$$c(t) = c_0 \exp\left(-\frac{tQ}{W}\right) \quad (3)$$

where the terms are the following: c_0 , initial concentration; W , volume of the exponential dilution flask; Q , carrier gas flow rate; and t , time. The gas flow was then delivered to a DMS analyzer through heated tubing to minimize surface adsorption of the sample. The temperatures needed for explosives to obtain gas concentrations without adsorption or thermal decomposition were compound specific and ranged from 100 to 240°C .

Modification of the Drift Gas. Two experiments were used to explore the influence of the chemical modifiers in the drift gas on the field mobility dependence of the ions from the explosives. In one design, the vapor generator was used to provide a constant concentration of modifying chemical into the drift gas for GC/DMS studies. The vapor generator included a saturated vapor source, under temperature control, and a flow of purified air. Flow controllers were used to adjust the ratios of these flows, which were mixed and used as drift gas flow. In a second experiment, the effect of the concentration of the modifier chemicals was determined using exponential dilution to change the dopant concentration while the sample vapors were kept constant with a vapor generator.

Mass Identification of Ions with DMS/MS. Mass spectrometric identification of ions in differential mobility spectra was made using headspace vapors over the individual neat chemical delivered continuously to the analyzer from a hermetically sealed glass container (200 mL) at ambient temperature. Ions in the DMS were injected into the MS interface using an electric field between the interface and an electrode on the drift tube wall opposite the sampling hole (Figure 2b). A nitrogen gas curtain prevented DMS drift gas neutrals including nonionized explosive molecules from entering the MS minimizing cluster formation in the gas expansion range and preserving pumping speed of the cryogenic vacuum. All gas lines from the vapor generator to the drift tube were 80°C or more to minimize chemical losses to wall adsorption.

Data Processing. Experimental results as Labview data files were imported directly into Origin version 6.1 or into Microsoft Excel for display of the differential mobility spectra or generation of 3-D plots.

RESULTS AND DISCUSSION

Differential Mobility Spectra for Explosives and Ion Identifications. Differential mobility spectra for negative ions from nitrated aromatic compounds and explosives in purified air are shown in Figure 3a for compensation voltages from -5 to 20 V with a separation voltage (field) of 1200 V ($24\text{ kV}/\text{cm}$). All

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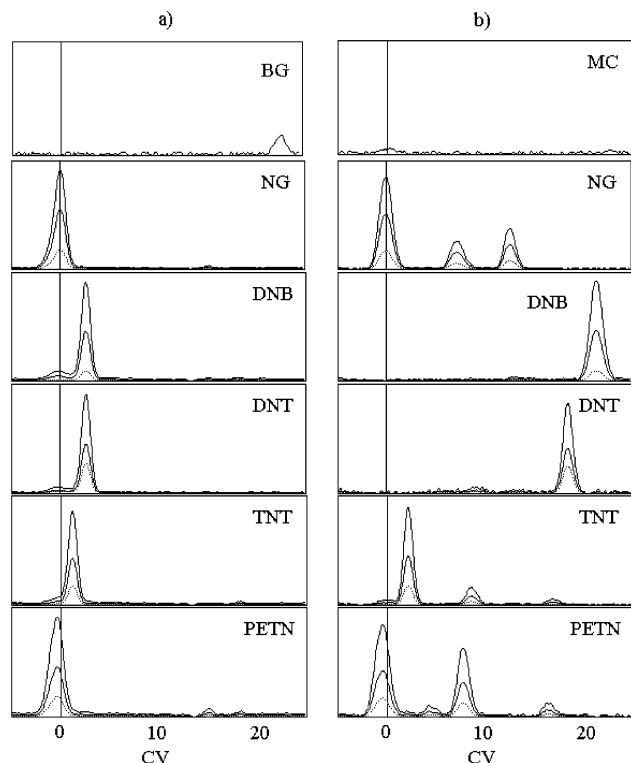


Figure 3. Differential mobility spectra of the explosives in pure air (left frame) and 1000 ppm of methylene chloride in air (right frame). Explosives are from top: background spectrum; 1,2,3-propanetriol, trinitrate (NG); 2,6-dinitrotoluene (DNT); 1,3-dinitrobenzene (DNB); 2,4,6-trinitrotoluene (TNT); pentaerythritol, tetranitrate (PETN). Volt-axe axis may be multiplied by -1 for comparison to Figure 1.

spectra exhibited an intense peak within a comparatively narrow range for compensation voltages from -1 to $+3$ V (fields of 20–60 V/cm). The absence of peaks between compensation voltages of 5–20 V suggested that little fragmentation of the product ions had occurred apart from a barely discernible peak for nitroglycerin (at 14 V compensation voltage) and peaks of low intensity for PETN (also at 14 V). This demonstrated an insensitivity to fragmentation of the product ions in a strong electric field; previously, little fragmentation was observed for explosive product ions formed through ionization in air at ambient pressure in the comparatively low field of traditional mobility spectrometers.² Product ion peaks in DMS spectra, as seen in Figure 3, suggest that the product ion intensity was concentration dependent but that ion identity, seen in the compensation voltage, was independent of concentration.

Another feature of the spectra shown in Figure 3a is the low or negligible intensity for the reactant ion peak at a compensation voltage of ~ 22 V. A peak for $\text{O}_2^-(\text{H}_2\text{O})_n$, the reactant ion in negative polarity with clean air, was observed at separation fields from 14 kV/cm to 20 kV/cm. The relative and absolute intensity of the reactant ion peak changed as the separation field was increased. For example, compensation voltages for peaks of TNT, and the reactant ion peak, at various $S(t)$ were 0 V, 5.9 V at 14 kV/cm; 0.5 V, 10.5 V at 18 kV/cm; and 0.8 V, 14.5 V at 20 kV/cm. The intensity of the reactant ion peak declined with these $S(t)$ values 2, 1.5, and 0.2 V respectively. This constitutes a type of low-mass bias in the current microfabricated DMS analyzer, and a reactant ion peak could be detected in Figure 3a when

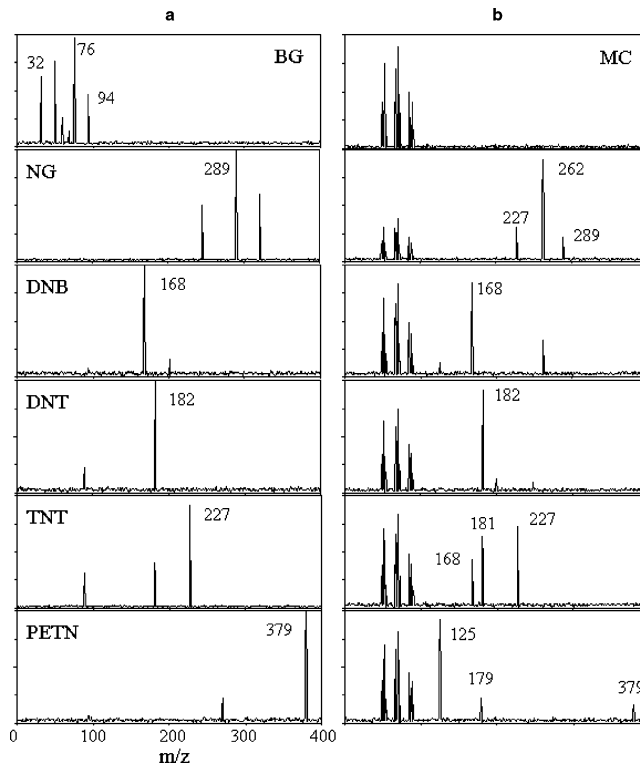


Figure 4. Mass spectra of the explosives in pure air (left frame) and 1000 ppm of methylene chloride in air (right frame). A background spectrum is shown in the top frame. Below the background spectrum are nitroglycerin (NG), 1,2,3-propanetriol, trinitrate; dinitrotoluene (DNT); 1,3-dinitrobenzene (DNB); 2,4,6-trinitrotoluene (TNT); and pentaerythritol, tetranitrate (PETN).

amplification was increased; the peak appeared at a compensation voltage of 22 V. A background spectrum without explosive vapor showed no detectable peaks apart from the reactant ion at an $S(t)$ of 20 kV/cm and below. No peaks were detected in the background spectra at an $S(t)$ of 24 kV/cm.

The mass spectrum for negative reactant ions in air drift gas (Figure 4a, top scan) showed peaks at m/z 32, 50, and 68 which were O_2^- , $\text{O}_2^-(\text{H}_2\text{O})$, and $\text{O}_2^-(\text{H}_2\text{O})_2$, respectively. The abundance of ions decreased in the order $\text{O}_2^-(\text{H}_2\text{O})_2 > \text{O}_2^-(\text{H}_2\text{O}) > \text{O}_2^-$, however, ion transport through the interface region precludes efforts to describe an accurate quantitative distributions of the ions. Other ions also were seen at low abundance and included m/z 94, 76, and 60, which were $\text{CO}_2^+\text{O}_2^-\text{H}_2\text{O}$, $\text{CO}_2^+\text{O}_2^-$, and CO_3^- , respectively. All these ions were unresolved, appearing as a single negative ion peak, in the differential mobility spectrum. When chemical was added to the DMS/MS apparatus, the intensity of these ions decreased and other ions, the product ions, appeared. Mass spectra for the explosives are shown in Figure 4a (bottom five frames) and ions were identified for each explosive as the following: nitroglycerin, m/z 227 (M^-) and m/z 289 ($\text{M} + 62$, or $\text{M}\cdot\text{NO}_3^-$); DNB, m/z 168 (M^-); DNT, m/z 182 (M^-); TNT, m/z 227 (M^-); and PETN, m/z 379 ($\text{M} + 63$ or $\text{M}\cdot\text{HNO}_3$). These mass spectra showed little fragmentation of the explosives to small ions and were consistent with differential mobility spectra, which exhibited a simple profile for product ions. The ion most commonly observed was M^- (DNB, DNT, and TNT) which is produced by hydride abstraction reactions from $\text{M}\cdot\text{O}_2^-(\text{H}_2\text{O})_n$; however, no measurable amounts of $\text{M}\cdot\text{O}_2^-(\text{H}_2\text{O})_n$ were found

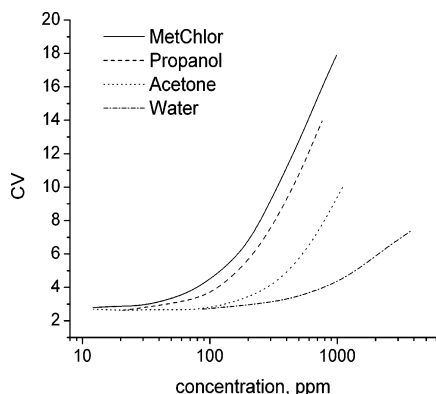


Figure 5. Compensation voltage vs solvent concentration for 2,6-DNT at 50 ppb in air at 150 °C and an $S(t)$ of 20 kV/cm. Dopant gases are identified as labels.

at the limits of detection. Low voltage differences were used on the lenses in the MS interface to minimize any ion decomposition in the transition between ambient pressure and high voltage. Nonetheless, negative findings in DMS/MS cannot preclude the existence of $M \cdot O_2^-$ rather than M^- in the DMS analyzer since the reaction of $M \cdot O_2^-(H_2O)_n$ to M^- should be facile. Ions were observed in PETN and nitroglycerin that were formed from fragmentation reactions and then an association between these fragment ions and other explosive neutrals.

α Functions and Gas Composition. The separation of ions in DMS arises through differences in mobilities at upper and lower values of the $S(t)$. This is understood to occur through the declustering of ions during the upper value for $S(t)$ and the formation of cluster ions during the lower field portion of $S(t)$. This model was formed from studies with moisture and organophosphorus compounds and could be associated with collision frequencies between ions and water molecules to form water clusters during the 120 ps lower field period.^{24–26} At the upper field the ions are desolvated providing a difference in the mobility constant with decreased collision area. In Figure 5, the influence of various dopants on the compensation voltage for DNT is shown, and the effects from a solute in the supporting atmosphere had a dramatic affect with DNT and other explosives. Interestingly, individual solvents affected the compensation voltage in characteristic ways given that the core ion should be the same regardless of the solvent added to the drift gas.

In Figure 6a, α function plots or plots of α versus E/N are shown for explosives at 0.1 ppm moisture in air at 150 °C. The α

Table 1. α Parameters for Explosives at 110 Td

	$\alpha \times 100$	compensation voltage V	molar mass
nitrobenzene	3.20	4.69	123
dinitrobenzene	2.63	3.83	168
trinitrobenzene	1.16	1.89	213
nitrotoluene	2.82	2.85	137
dinitrotoluene	2.76	2.83	182
trinitrotoluene	1.24	1.25	227
RDX	0.387	0.17	222
nitroglycerin	-0.260	-0.53	227
PETN	-0.599	-1.07	316

plots show the field dependence of an ion and reflect possible ion separations through differences in mobility at high and low fields. The difference of α was only -0.005 to 0.02 as shown in Table 1. This is smaller by a factor of 2 than the values obtained for ketones from acetone to octanone, where α values were 0.05 – 0.1 . Fragment ions for DNT and DNB with light mass show a profile slightly exaggerated versus the other ions with comparatively high molar mass. The results are normal and suggest an ion dependence on electric field found with larger ions. The results suggest that the best ion separation will occur with E/N values of ~ 120 Td. This corresponds to an electric field of 24 kV/cm at 660 Torr ambient pressure in Las Cruces, NM.

Enhanced Separation in Differential Mobility Spectrometry by Addition of Modifiers to the Drift Gas. Methylene chloride was added to the drift gas since the plot in Figure 5 suggested a dramatic change in α functions as shown in Figure 6b and because methylene chloride was expected to give Cl^- as a reactant ion, the ion commonly used in commercial IMS explosives detectors. Differential mobility spectra for explosives with methylene chloride in the gas flow are shown in Figure 3b and may be directly compared to the plots shown in Figure 3a. The differential mobility spectra were obtained under conditions identical to those used earlier only with the addition of methylene chloride at 1000 ppm in air, calibrated against results from the exponential dilution flask studies. Changes in the vapor concentration of the explosives, when the dopant concentration was constant, cause no change in the compensation voltage of the ions or patterns of the DMS spectra.

The addition of the dopant caused complete replacement of the reactant ions by $Cl^-(H_2O)_n$ in the mass spectra (Figure 4b, top scan). Moreover, the chloride ion caused the formation of $M \cdot Cl^-(H_2O)_n$ for NG replacing $M \cdot NO_2^-$ as the primary ion, as

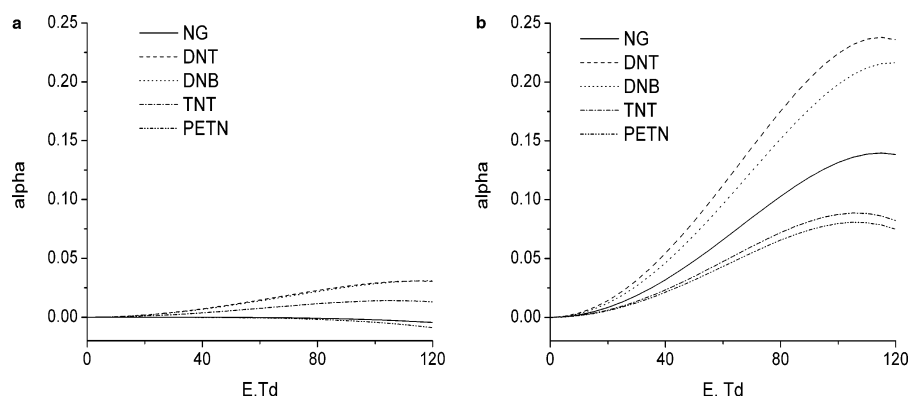


Figure 6. α functions²⁰ of the explosives ions in pure air (left) and a 1000 ppm mixture of methylene chloride/air (right).

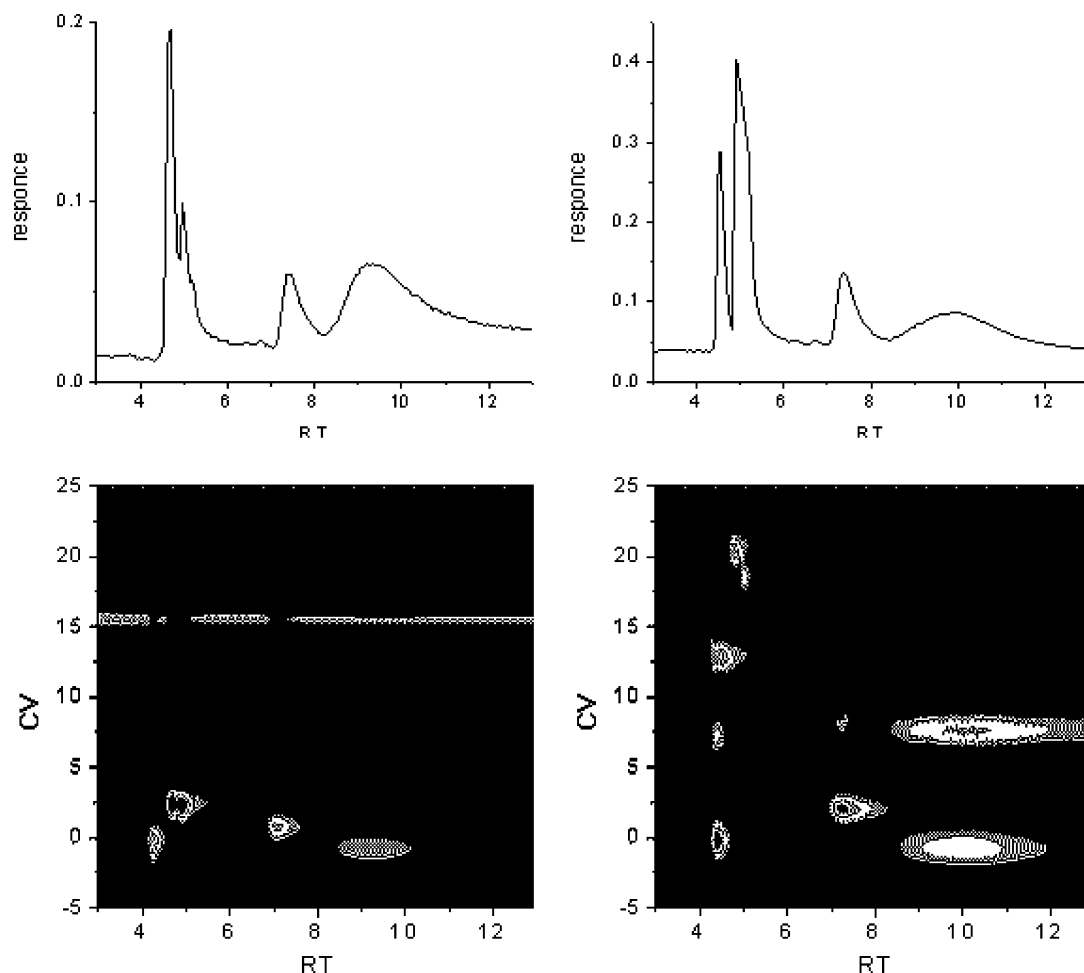


Figure 7. GC/DMS analysis of the explosives mixture syringe injection of 2 μ L with a concentration of NG of 0.078 mg/mL at 4.2 min; DNB of 0.156 mg/mL at 4.7 min; DNT of 0.047 mg/mL at 4.8 min; TNT of 0.047 mg/mL at 7.2 min; PETN of 0.125 mg/mL at 10 min. GC parameters: $T = 50\text{--}210\text{ }^{\circ}\text{C}$; split ratio = 30; injection = 2 μ L. DMS parameters: SV = 1050 V; drift gas flow rate = 0.5 L/min; concentration of MC = 1000 ppm. Top frames: integrated GC profile. Bottom frames: 2-D map of the GC/DMS analysis. Left frames for pure air as DMS drift gas. Right frames for methylene chloride/air mixture as DMS drift gas. Voltage axis may be multiplied by -1 for comparison to Figure 1.

seen in the mass spectra. Other weakly held associations between M and Cl^- would be expected for these explosives but would not be directly observed with ion dissociations in the DMS/MS interface. The mass spectrum for PETN was largely comprised of fragment ions and was consistent with peaks near 12 V in the DMS spectra. Fragments in the mass spectrum supported fragmentation in the differential mobility spectrum. Those explosives with ions that were dramatically affected in compensation voltage by the addition of methylene chloride in the drift gas showed little if any discernible differences in mass spectra compared to an undoped condition. Consequently, the interpretation is that the ion was not fragmented but was present as two species in the DMS analyzer and was an associated ion at low field or a declustered ion at high field as shown in eq 4



Consequently, the differences in mobility (ΔK) between the declustered and cluster ions should be high, and a large compensation voltage would be needed to bring the ion to a stable

passage. This is the only possible interpretation mindful that the ions are not being fragmented by the addition of methylene chloride into the supporting atmosphere. The adduct ion with chloride would not be expected in the mass spectra owing to declustering of the ion during passage from ambient pressure to high vacuum. This specific example of vapor modifiers in the drift gas of a differential mobility spectrometer may represent general possibilities for improved ion separation.

GC/DMS Characterization of Mixtures of Explosive. The combination of gas chromatography with DMS is understood to have value in several facets. The preseparation step adds retention information to compensation voltage for enhanced specificity, and the introduction of constituents as single constituents or an elution peak with a few compounds increases the reliability of the APCI reactions. Results from GC/DMS determinations of explosives in a mixture are shown in Figure 7a where only air is used as the gas. There is chemical resolution in the chromatographic retention axis but limited separation in the compensation voltage or ΔK axis. The addition of methylene chloride at 1000 ppm in the drift gas can be seen in the topographic plot as seen earlier in the DMS spectra as shown in Figure 3b, where the ΔK axis is enhanced and the overall analytical specificity is improved.

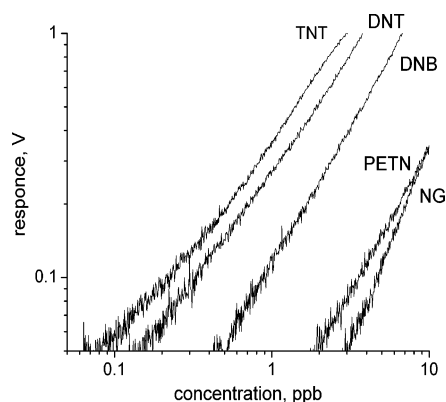


Figure 8. Response curves of the DMS analyzer for explosives in a continuous vapor stream.

Quantitative Response. Response curves for the nitrobenzenes and nitrotoluenes are shown in Figure 8 for the monitoring of a continuous vapor stream of chemical in air. The plots extend from 100 to 0.1 ppb where a systematic error was anticipated from vapor losses to surface adsorption at such low concentrations. This may be evident in the slight differences of slope between 0.1 and 1 ppb versus 1 to 100 ppb. At the high concentrations, the curves begin to flatten owing to saturation of the ion source region, a complication in all uses of gas phase ion chemistry with sources at ambient pressure. Results for detection limits for some explosives with a microfabricated DMS analyzer are given in Table 2. These levels are suggestive of suitable analytical performance for a trace explosives detector.

CONCLUSION

The separation of ions in differential mobility spectrometry can be controlled by modifying the drift gas with a small amount of some solvents and has been applied for the determination of

Table 2. Limits of Detection for Explosives in a Microfabricated Drift Tube for Differential Mobility Spectrometry

name	LOD (S/N = 2) ppb
2,4,6-trinitrotoluene (TNT)	0.08
1,3,5-trinitrobenzene (TNB)	0.1
2,6-dinitrotoluene (DNT)	0.15
1,3-dinitrobenzene (DNB)	0.5
1,3,5-triazine, hexahydro-1,3,5-trinitro (RDX)	0.5
pentaerythritol, tetranitrate (PETN)	2
4-nitrobenzene (NB)	2
4-nitrotoluene (NT)	2
1,2,3-propanetriol, trinitrate (NG)	3
1,2-ethanediol, dinitrate	8

explosives with a microfabricated drift tube. An addition of 1000 ppm of methylene chloride into the purified air drift gas increased the dependence of the ion mobility upon the electric field for explosive ions by 3 to 6 times. This caused increases in the compensation voltages for ions of explosives. A practical consequence of this is a corresponding increase in the analytical space of the DMS spectra. These findings have demonstrated the suitability of microfabricated drift tubes with DMS for detecting explosive ions in scrubbed air at low-ppb levels and response times of ~ 1 s. The changes in selectivity make this measurement method a possible technology for the detection of explosives. The DMS/MS studies demonstrate that the core ion is not being altered, and the observed dependence of mobility upon electric field may be explained in terms of the dynamic cluster-decluster model.

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