Identity confirmation of drugs and explosives in ion mobility spectrometry using a secondary drift gas

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Abstract

This work demonstrated the potential of using a secondary drift gas of differing polarizability from the primary drift gas for confirmation of a positive response for drugs or explosives by ion mobility spectrometry (IMS). The gas phase mobilities of response ions for selected drugs and explosives were measured in four drift gases. The drift gases chosen for this study were air, nitrogen, carbon dioxide and nitrous oxide providing a range of polarizability and molecular weights. Four other drift gases (helium, neon, argon and sulfur hexafluoride) were also investigated but design limitations of the commercial instrument prevented their use for this application. When ion mobility was plotted against drift gas polarizability, the resulting slopes were often unique for individual ions, indicating that selectivity factors between any two analytes varied with the choice of drift gas. In some cases, drugs like THC and heroin, which are unresolved in air or nitrogen, were well resolved in carbon dioxide or nitrous oxide.
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1. Introduction

First introduced as an analytical technique in the late 1960s for the detection of trace quantities of organic vapors [1,2], ion mobility spectrometry (IMS) has developed into one of the primary analytical methods used for the detection of explosives [3–18], drugs [19–24] and chemical warfare agents [25,26]. For a more complete discussion of IMS as a detection method for explosives and drugs of abuse see reference [27].

Despite years of development, IMS instruments, when applied to real samples, still experience false positive responses [27]. A false positive response rate less than 0.05 is currently the Department of Homeland Security goal for identification of explosives (www.dhs.gov/xres/). In general false positive responses occur when a compound or mixtures of compounds ionize and drift similar to the target compound. In these cases, the instrument indicates the presence of an explosive or drug when in fact none were present. In order to ensure the absence of the target, more sophisticated analytical tests must be preformed as well as comprehensive searches of luggage or containers. Thus,

false positive responses cost both time and money. The development of simple methods that can serve as confirmatory tests for currently available commercial IMS systems would reduce the level of false positives and aid the identification of explosives, drugs and chemical warfare agents in the field. The hypothesis of this paper is that the use of an alternate drift gas, with polarizability different from that of air, may provide a simple test which can be used in the field to confirm or refute a positive response for drugs or explosives.

The use of drift gas polarizability to alter the separation of ions in an IMS was first reported in 1986 [28]. A study by Rokushika et al. using carbon dioxide and nitrogen as drift gases demonstrated that, under the normal operating conditions of an IMS, separation of reactant ion and product ion peaks were possible when carbon dioxide was used as the drift gas [28]. Prior to this investigation, the only data available in the literature for IMS studies in carbon dioxide was performed at 25 °C [29]. At this temperature all reactant ions in carbon dioxide were observed to produce essentially the same reduced mobility constant. Large clusters were formed around the core ion such that both size and shape of the ion clusters were only weakly dependent on the identity of the core ion. The conclusion from this early, low temperature, studies was that mobility of ions in carbon dioxide is largely independent of the ion species so long as the pressure

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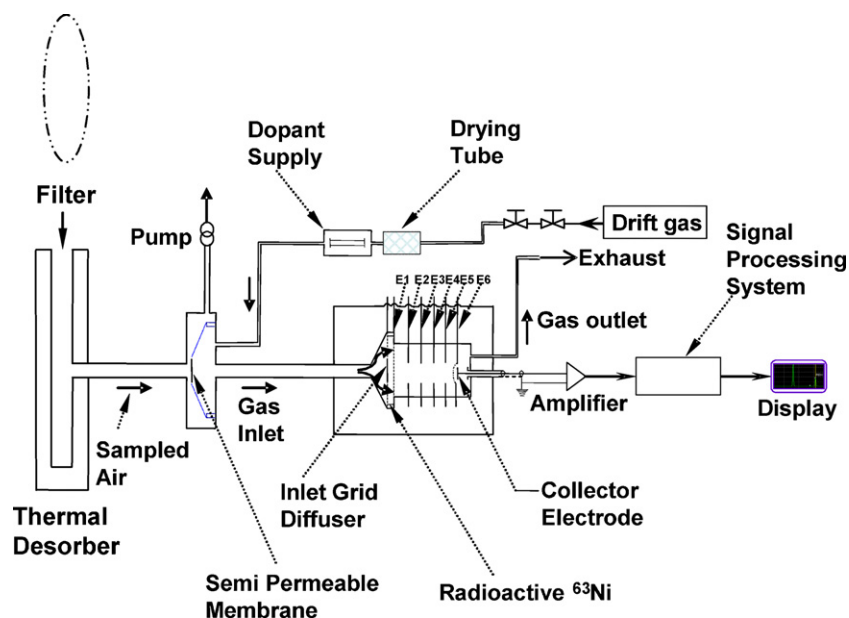*E-mail address:* hhhill@wsu.edu (H.H. Hill Jr.).

Fig. 1. Schematic cross-sectional view of the modified open loop IMS Itemiser unit fitted with a thermal desorber.

is greater than 100 Torr and therefore carbon dioxide was considered to be inadequate as a drift gas for IMS. With the 1986 investigation by Rokushika et al., it became clear that at higher temperatures carbon dioxide could be used as a drift gas for IMS.

In ion mobility spectrometry, the separation factor is defined as the ratio of the mobility (K_1) of the faster drifting ion (low drift time, t_{d1}) to the mobility (K_2) of the slower drifting ion (high drift time, t_{d2})

$$\alpha = \frac{K_1}{K_2} = \frac{t_{d2}}{t_{d1}}$$

The use of different drift gases to alter separation factors (α) in IMS was first demonstrated by Ashbury and Hill [30]. Using helium, argon, nitrogen and carbon dioxide, they demonstrated that separation factors could be altered by using drift gases of different polarizabilities. Matz et al. used helium, argon, nitrogen and carbon dioxide to investigate the ion mobility behavior for cocaine/metabolites, amphetamines, benzodiazepines and peptides [31]. They demonstrated that ion mobility separations of various drugs could be achieved in some drift gases which were not possible in others. Other studies used helium, the smallest and least polarizable drift gas, to derive a theoretical understanding of the interaction between an ion and a gas [32–34]. Karpas and Berant on the other hand, demonstrated that, for a homologous series of compounds, drift times in a highly polarizable gas can be predicted from those measured in a weakly polarizable drift gas [35]. Russell and co-workers, also demonstrated that the polarizability of gases for molecules from similar classes such as peptides had little effect on separation factors [36].

Thus, for small, dissimilar molecules such as drugs and explosives, it may be possible to use alternate drift gases as a rapid field confirmatory test with commercial IMS instruments, reducing the false positive response rate in the trace detection of drugs and explosives. To test this hypothesis, reduced mobilities of explosives and drugs were measured in different drift gases with a commercially available IMS instrument typical of that used in the field.

2. Experimental

2.1. Instrumentation

The IMS used in this study was a commercially available ion mobility spectrometer called "The Itemiser" (GE Security, Wilmington, MA). A schematic of the IMS as it was operated in this study is shown in Fig. 1. The IMS was modified to an open loop system for operation with the different drift gases by disconnecting the pump used to recycle the drift gas flow and connecting the gas pneumatics directly to pressurized gas tanks containing the drift gas of choice.

Eight drift gases (air, nitrogen, carbon dioxide, nitrous oxide, helium, neon, argon and sulfur hexafluoride) were investigated. Table 1 lists the molecular weight and polarizability of the drift gases studied. The drift gases were doped with low concentrations of ammonia (for drug selective detection) or methylene dichloride (for explosive selective detection).

Table 1
Molecular weight and polarizability of drift gases

Drift gas	MWt/g mol^{-1}	Polarizability (10^{-24} cm^3)[a]
Helium	4	0.21
Neon	20	0.40
Nitrogen	28	1.74
Air	28.8	1.71
Argon	40	1.64
Carbon dioxide	44	2.91
Nitrous oxide	44	3.03
Sulfur hexafluoride	146	6.54

[a] As tabulated in CRC Handbook of Chemistry and Physics, 70th ed., D.R. Lide Ed., CRC Press, Boca Raton, FL, 1989.

Sample introduction into the instrument was achieved by pipetting 1 μL sample onto sampling filters (GE Security, Wilmington, MA) made from silicone elastomeric membrane (50 μm thick × 90 mm wide). After solvent evaporation, a filter containing the know quantity of sample was inserted into the instrument's thermal desorber. Samples were introduced into the spectrometer by volatilization in a thermal desorption chamber attached to the front end of the instrument. For these investigations the desorber was operated at 220 °C. Desorbed vapors were drawn into the IMS through a semi-permeable silicone membrane (part no. PA005007, GE Security). The membrane protected the IMS tube from contamination by excluding particulate matter from the system and minimizing the amount of moisture entering the IMS tube.

Sample molecules passing through the membrane were carried into the detector by the drift gas. Contrary to most IMS instrument, in the Itemiser design the drift gas flowed in the same direction as the ions migrated. The drift gas (and the neutral analytes) flowed through an ionization chamber, 6-mm long, whose walls were lined with a 10 MBq ^{63}Ni radioactive foil, emitting low energy beta particles. As the drift gas flowed through the chamber, both positive and negative reactant ions were formed. These reactant ions then interacted with neutral sample vapors to produce compound specific product ions.

The electric field in the detector's ionization chamber was normally zero, but at 20 ms intervals, short potential pulses were applied across the chamber. A "kick-out" pulse of 0.2 ms created an electric field that forced the ions through an open grid electrode "E1" and into the ion drift region, where the ions were propelled towards the collector electrode by a constant and continuous electric field. The square-wave kick-out pulse had an amplitude of 1600 V. The ions then traveled to the collector electrode through the drift region where their arrival times were recorded.

The IMS drift tube had a length of 3.9 cm, a voltage of 980 V, and a temperature of 205 ± 5 °C. The electric field established across the drift tube was 251 V cm^{-1} and the drift gas flow rate into the IMS was 900 mL min^{-1}. Pressure in the drift tube during mobility measurements varied from 698 to 703 Torr. Table 2 summarizes the operating conditions and drift gases used in these studies.

All mobility data were collected by the Itemiser's software. Under normal operating procedures an average of four scans was taken for each spectrum. Each spectrum (a combination of four scans) was displayed in near real time. The spectrum view mode was used to collect all data in this study and the software displayed 70 IMS spectrum (each a combination of four scans) on the screen over 2 s. Each IMS spectrum selected within the 70 sets can be considered to occur at a specific time within a 2 s integration/analysis time interval.

2.2. Materials and reagents

Explosive compounds studied were 2,4,6-trinitrotoluene, 2,4,6-TNT; cyclotrimethylenetrinitramine, RDX; pentaerythritol tetranirate, PETN; 1,3,5-trinitrobenzene, 1,3,5-TNB; 1,3-dinitrobenzene, 1,3-DNB; 2,3-dinitrotoluene, 2,3-DNT;

Table 2
TD-IMS operating conditions summary

Drift tube length	3.9 cm
Reaction region length	6 mm
Drift tube voltage	980 V
Kick-out pulse	0.2 ms every 20 ms interval
Electric field	251 V cm^{-1}
Drift tube temperature	205 ± 5 °C
Drift tube pressure	698–703 Torr
Desorption unit temperature	220 °C
Sample ionization	^{63}Ni foil
Sample acquisition	Surface filters or air collection
Drift gas flow	0.9 L min^{-1}
Sampling time	5 s
Analysis time	2 s
Data processing	Microsoft Excel 2003
Detection mode	Positive ion mode (NH$_3$ dopant) negative ion mode (CH$_2$Cl$_2$ dopant)
Drift gases	Helium; air; nitrogen; carbon dioxide; nitrous oxide; argon; neon; sulfur hexafluoride

2,4-dinitrotoluene, 2,4-DNT and 2,6-dinitrotoluene, 2,4-DNT. Drug compounds studied were cocaine; amphetamine, AMP; methamphetamine, METHAM; heroin; morphine, MORPH; tetrahydrocannabinol, THC; methylenedioxymethamphetamine (MDMA) and 2,4-lutidine. Chemicals chosen for these studies were obtained from Sigma Aldrich Chemical Company (St. Louis, MO). Sample solutions were prepared by dilution with methanol (HPLC grade, J.T. Baker, Phillipsburgh, NJ).

2.3. Experiments

Liquid samples of drugs and explosives were prepared at 50 μg mL^{-1} and 2,4-lutidine prepared at 93 μg mL^{-1}. One microliters sample volume corresponding to 50 ng of drug or explosive and 93 ng of 2,4-lutidine was deposited onto a clean sampling filter. All injections on filters were allowed to dry before being introduced to the instrument. The methanol solvent evaporated rapidly at room temperature leaving the analyte of interest on the surface of the filters. The filters were then placed in the detection slot of the vapor desorption unit for a sampling time of 5 s. The sampling time was the time allowed to heat the filters before desorption. Filters were cleaned by desorption in the instrument before their first use. Measurements were taken in triplicates with blank measurements taken between runs. Experiments were conducted to determine ion mobilities and evaluate mobility ratios in different drift gases for identification of explosives and drugs.

2.4. Calculations

All reduced mobility constants (K_0) were calculated from experimentally determined drift times (t_d). The reduced mobility constants were calculated with reference to TNT ion for the negative ion mode and 2,4-lutidine for the positive ion mode using Eq. (1) to correct for variations in temperature, pressure

and drift field.

$$K_{0(unknown)} = \frac{\text{drift time}_{std}}{\text{drift time}_{unknown}} \times K_{0(std)} (cm^2 V^{-1} s^{-1}) \qquad (1)$$

where $1.54 \pm 0.02\, cm^2\, V^{-1}\, s^{-1}$ was the K_0 value used for the standard TNT and $1.95 \pm 0.01\, cm^2\, V^{-1}\, s^{-1}$ was the K_0 value used for the standard 2,4-lutidine in air, respectively [37].

3. Results and discussion

3.1. Drift gases

Eight drift gases (helium, air, nitrogen, neon, argon, carbon dioxide, nitrous oxide and sulfur hexafluoride) were initially chosen for study with the IMS instrument in the positive and negative ion modes. However, instrumental limitations related to the hardware and software design were observed with helium, argon, neon and SF_6.

With argon and neon, a high current was observed for the background. Fig. 2 is an example response from background spectra with argon as drift gas. The high current background that occurred when using argon or neon was contributed by "penning ionization" [38]. Upon collisions with beta particles, argon and neon form neutral metastables which can be carried through the ion gates and into the drift region of the spectrometer with the carrier gas flow. Ionization in the drift region can occur through the "penning ionization" process as shown below.

$$Ar^* + Ar \rightarrow Ar + Ar^+ + e$$

$$Ne^* + Ne \rightarrow Ne + Ne^+ + e$$

Because the drift gas flow of the Itemiser is concurrent with ion flow, the metastable gas was swept into the drift region of the Itemiser and ions formed in the drift region through the penning ionization process created high background current and noise which interfered with the spectrum.
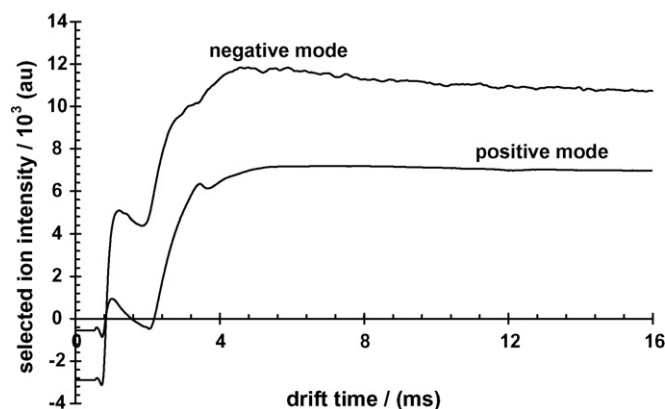

Fig. 2. Ion mobility spectra illustrating the limitations of the instrumentation design when using argon as drift gas.

With helium drift gas, ions drifted too fast to be recognized by the system's computer. Thus, helium was eliminated from the studies. The problem associated with SF_6 was that the software could not display spectra beyond 16.5 ms. Because, SF_6 had the highest polarizability of the drift gases investigated, ion drifts were too slow to be recorded by the instrument's software. Although the reactant ion peak (RIP) was measurable in SF_6, product ion peaks occurred after the instrument's drift time cut off. These limitations in instrument and software design reduced the drift gases available for this investigation to air, nitrogen, carbon dioxide and nitrous oxide.

3.2. Reduced mobilities in alternate drift gases

3.2.1. Reactant ions

Due to the high proton affinity of ammonia and the high electron affinity of methylene chloride, which were used as dopants in this study, background spectra of ammonium ion (NH_4^+) for the positive ion mode and chloride ion (Cl^-) in the negative ion

Table 3
Database of reduced mobility values for drugs and explosives in different drift gases obtained from IMS

Compound	MWt/g mol^{-1}	K_0 (Air)[a] [lit K_0]	K_0 (N$_2$)[a] [lit K_0]	K_0 (CO$_2$)[a]	K_0 (N$_2$O)[a]
Cl$^-$	35.5	3.05 [3.06]	3.02 [3.01]	1.34	1.37
1,3-DNB	168	1.71	1.71	0.98	1.02
2,3-DNT	182	1.66	1.63	0.97	1.00
2,4-DNT	182	1.68 [1.67]	1.67 [1.61]	1.00	1.02
2,6-DNT	182	1.67 [1.65]	1.66 [1.61]	1.00	1.02
1,3,5-TNB	213	1.69	1.70	1.01	1.03
RDX	222	1.47 [1.44]	1.47 [1.49]	0.94	0.95
TNT	227	1.54 [1.53]	1.54	0.96	0.96
PETN	316	2.53 [2.51]	2.53 [2.51]	1.33	1.33
NH$_4^+$	18	2.98	2.96	1.46	1.44
AMP	135	1.66 [1.68]	1.67 [1.67]	1.02	1.00
METHAM	149	1.63 [1.63]	1.64 [1.64]	1.03	1.00
MDMA	193	1.47 [1.47]	1.47	0.94	0.92
Morphine	285	1.23 [1.19]	1.23 [1.21]	0.85	0.83
Cocaine	303	1.17 [1.17]	1.18 [1.16]	0.80	0.78
THC	314	1.06 [1.06]	1.06 [1.04]	0.75	0.74
Heroin	369	1.06 [1.04]	1.06 [1.09]	0.79	0.77
2,4-Lutidine	107	1.95 [1.95]	1.95 [1.95]	1.20	1.18

[a] K_0 values are in cm^2 V^{-1} s^{-1}.

mode were observed. The product ions reported in this study resulted from the ion-molecular gas phase reaction of these reactant ions with the neutral vapors of the drugs and explosives introduced into the IMS. Table 3 lists molecular weights of the drugs and explosives investigated along with the K_0 values of their product ions. For many of these drugs and explosives, reduced mobilities in these alternate drift gases have not been previously reported.

3.2.2. Product ions from drugs

2,4-Lutidine with a known reduced mobility of $1.95 \pm 0.01 \, cm^2 \, V^{-1} \, s^{-1}$ in air was used as the daily standard to insure that the IMS unit was responding properly. Despite numerous IMS investigations with 2,4-lutidine, its K_0 values in carbon dioxide and nitrous oxide had not been reported previously. They were determined to be 1.20 ± 0.02 and $1.18 \pm 0.01 \, cm^2 \, V^{-1} \, s^{-1}$, respectively.

The differences in K_0 values for a specific drug in different drift gases can be attributed to the difference in polarizability of the drift gases and thus the differences in interactions between the analytes and the drift gasses. As expected, mobility decreased as drift gas polarizability and mass of the ion increased. Increase in drift gas polarizability has the effect of greater interaction between the drift gas and the established electric field across the drift tube. This effect will result in ions drifting slowly in the IMS drift tube, accounting for a decreased reduced mobility value. On the other hand, as the size of the ion increases, the collision cross-section and thus the ionic radii of the ions increases, resulting in a decreased reduced mobility value.

Fig. 3 shows positive mode IMS spectra of amphetamine (AMP) and methamphetamine (METHAM) in the four drift gases studied. The ammonium reactant ion peak migrated in air and nitrogen with a time of 3.09 ± 0.01 and 3.12 ± 0.01 ms, respectively. In carbon dioxide and nitrous oxide the RIP had much longer migration times of 6.32 ± 0.02 and 6.41 ± 0.03 ms, respectively. Similarly, the response ions of both AMP and METHAM migrated with much longer times in the more

Fig. 3. Ion mobility spectra for AMP and METHAM in different drift gases: air, nitrogen, carbon dioxide and nitrous oxide. The spectra demonstrated that as the polarizability of the drift gas increases, mobility decreases. Furthermore the arrival times of the pair of compounds were inverted as drift gas changes from low to high polarizability.
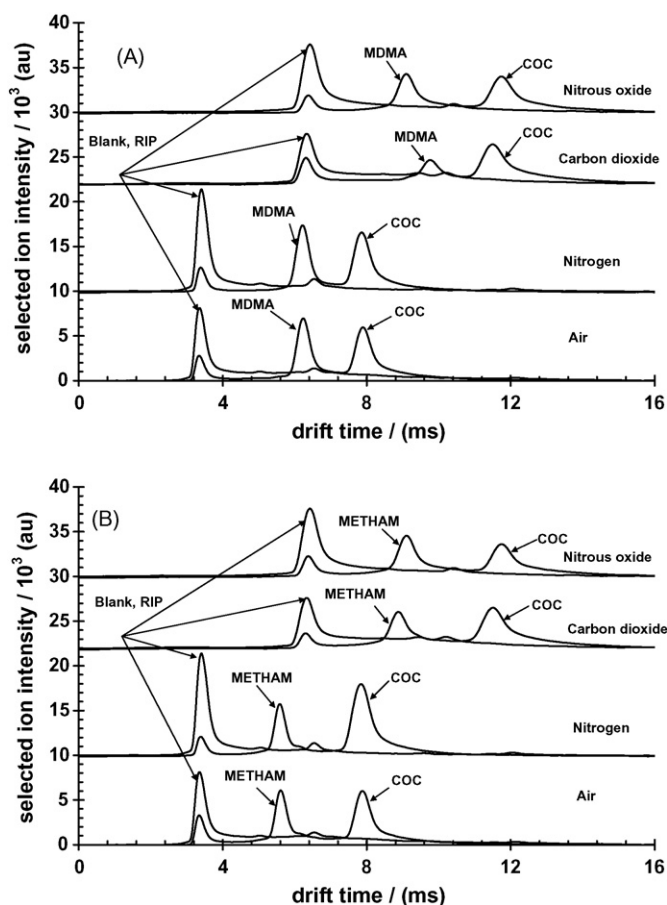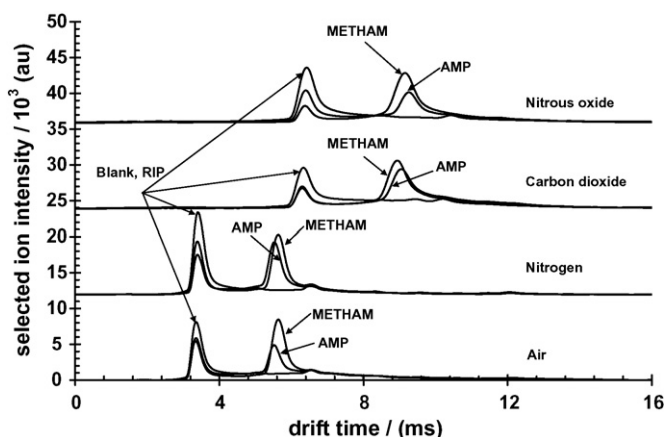

Fig. 4. Ion mobility spectra of (A) MDMA and cocaine mixtures and (B) METHAM and cocaine mixtures. The results demonstrated the pattern of responses obtained for drug mixtures in different drift gases: air, nitrogen, carbon dioxide and nitrous oxide.

polarizable drift gases. The product ion for AMP migrated at 5.55 ± 0.01, 5.53 ± 0.01, 9.08 ± 0.01 and 9.27 ± 0.01 ms in air, nitrogen, carbon dioxide and nitrous oxide, respectively. On the other hand, the product ion of METHAM migrated at 5.66 ± 0.01, 5.63 ± 0.01, 8.97 ± 0.01 and 9.19 ± 0.01 ms in air, nitrogen, carbon dioxide and nitrous oxide, respectively. Note that in air AMP had a faster drift time than METHAM while in carbon dioxide it had a slower drift time, demonstrating that these two drugs exhibited different interactions with low and high polarizable drift gases.

Fig. 4(a and b) provides other example spectra of drug mixtures using MDMA:Cocaine and METHAM:Cocaine. As with the AMP and METHAM examples above an increase in drift gas polarizability increased migration times. Reduced mobilities for these drugs in the different gases are given in Table 3. As shown previously, the mobilities of each of these drugs changed as a function of drift gas polarizability.

3.2.3. Product ions from explosives

In the negative mode with CH_2Cl_2 as the dopant gas, TNT was used as the mobility standard and its K_0 values in both carbon dioxide and nitrous oxide were reported for the first time as 0.96 ± 0.01 and $0.96 \pm 0.01 \, cm^2 \, V^{-1} \, s^{-1}$, respectively.
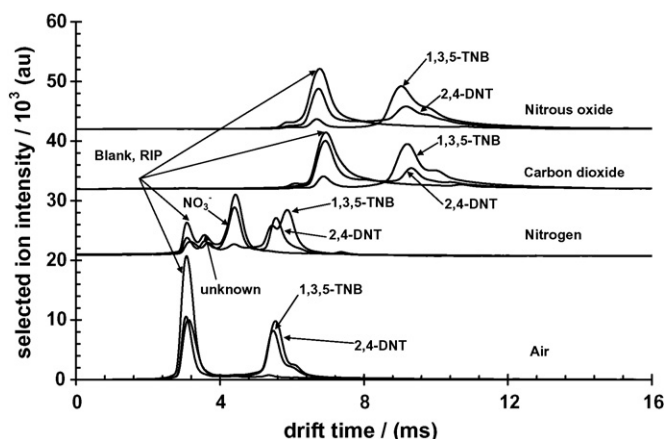
Fig. 5. Ion mobility spectra for 1,3,5-trinitro benzene (1,3,5-TNB) and 2,4-dinitro toluene (2,4-DNT) in different drift gases: air, nitrogen, carbon dioxide and nitrous oxide. The spectra demonstrated that as the polarizability of the drift gas increases, mobility decreases. Furthermore the arrival times of the pair of compounds switches as drift gas changes from low to high polarizability.

Fig. 5 shows examples of negative ion mobility spectral overlays of a background, 1,3,5-trinitro benzene (1,3,5-TNB) and 2,4-dinitro toluene in the different drift gases. When operating in the negative mode, the reactant ion peak is the Cl^- ion. Drift times for the reactant ion peak were 3.05 ± 0.02, 3.08 ± 0.01, 6.92 ± 0.01 and 6.77 ± 0.03 ms in air, nitrogen, carbon dioxide and nitrous oxide, respectively. These drift times produced the following respective reduced mobility values: 3.05 ± 0.03, 3.01 ± 0.02, 1.34 ± 0.01 and 1.37 ± 0.01 cm^2 V^{-1} s^{-1}. These values compared well with those reduced mobility values reported previously in the literature for chloride ion in air and nitrogen of 3.06 ± 0.02 and 3.01 ± 0.01 cm^2 V^{-1} s^{-1}, respectively [37]. The mobilities of Cl^- ion in drift gases of carbon dioxide and nitrous oxide have not previously been reported in the literature. In these studies they were measured to be 1.34 ± 0.02 cm^2 V^{-1} s^{-1} in carbon dioxide and 1.37 ± 0.01 cm^2 V^{-1} s^{-1} for nitrous oxide, respectively. Similar to Cl^- ion, the response ions of both 1,3,5-TNB and 2,4-DNT migrated with much longer times in the more polarizable drift gases. The product ion for 1,3-TNB migrated at 5.49 ± 0.02, 5.45 ± 0.02, 9.22 ± 0.02 and 9.03 ± 0.02 ms in air, nitrogen, carbon dioxide and nitrous oxide, respectively. On the other hand, the product ion of 2,4-DNT migrated at 5.54 ± 0.01, 5.56 ± 0.01, 9.32 ± 0.01 and 9.11 ± 0.01 ms in air, nitrogen, carbon dioxide and nitrous oxide, respectively. As with the case of the drugs AMP and METHAM, 1,3,5-DNB had a faster drift time than 2,4-DNT in air while in carbon dioxide 1,3,5-DNB had a slower drift time than 2,4-DNT.

Similarly to the positive mode data, the mobility of product ions decreased as the polarizability of the drift gases increased. With the negative ion studies, however, some deviations were observed with respect to the mass of an explosive ion and the expected K_0 value. For example the highest mass of explosives studied was that for PETN with molecular weight of 316 g mol^{-1}. PETN however showed the highest K_0 value for all explosives studied. The response ion for PETN was identified by drift time to be that of NO_2^- ion. In this investigation,

the thermal desorber was operated at $220\,^\circ$C using the drugs mode desorber rather than at $180\,^\circ$C normally used for explosive detection. Thus, the NO_2^- ion may have resulted from thermal decomposition of PETN.

The chloride ion, as well as the product ions of 1,3-DNB, 2,3-DNT, 2,4-DNT, 2,6-DNT,1,3,5-TNB and RDX were all found to drift slower in carbon dioxide than in nitrous oxide while the product ions of 2,4,6-TNT and PETN produced similar drift times in carbon dioxide to those in nitrous oxide (see Table 3).

3.3. Relative mobilities of ions in different drift gases

While it is clear from the previous discussion that ion mobility values of a given analyte ion will decrease with increasing mass and polarizability of the drift gas, it also appears that these increases may not be proportional for all ions. If they were proportional, as determined by Russell and co-workers [36] and Karpas and Berant [35] for ions of similar structure, then alternate drift gases would be of little use for effecting novel separations or for use as a confirmatory test in the field. One easy way to determine the proportionality of mobilities in various drift gases is to plot mobility with respect to drift gas polarizability. Plots of reduced mobility versus drift gas polarizability were linear with correlation coefficients ≥ 0.99. The linear regression data summarized from these plots are shown in Table 4. The slopes of these plots provide information on proportionality. If the slopes are the same, then the mobilities are proportional with polarizability and no separation or identification advantages exists with changes in drift gases. As can be clearly seen from the table, the slopes for some compounds vary significantly while others are similar.

The smaller, more compact ions such as Cl^-, NH_4^+ and NO_2^- (the product ion from PETN) where the charge density is

Table 4
Linear regression data for plots of reduced mobility vs. polarizability of four drift gases (air, nitrogen, carbon dioxide & nitrous oxide) obtained from explosive and drug ions

Compound	MWt/g mol^{-1}	Reduced mobility		
		$(-)$ Slope	Intercept	R^2
Cl^-	35.5	1.36 ± 0.03	5.33 ± 0.40	0.99
1,3-DNB	168	0.57 ± 0.02	2.68 ± 0.30	0.99
2,3-DNT	182	0.53 ± 0.01	2.55 ± 0.21	0.99
2,4-DNT	182	0.53 ± 0.01	2.59 ± 0.22	0.99
2,6-DNT	182	0.53 ± 0.01	2.58 ± 0.24	0.99
1,3,5-TNB	213	0.54 ± 0.03	2.63 ± 0.41	0.99
RDX	222	0.42 ± 0.01	2.19 ± 0.21	0.99
TNT	227	0.46 ± 0.01	2.31 ± 0.32	1.00
PETN	316	0.96 ± 0.02	4.18 ± 0.41	0.99
NH_4^+	18	1.22 ± 0.02	5.07 ± 0.13	1.00
AMP	135	0.53 ± 0.02	2.58 ± 0.21	1.00
METHAM	149	0.49 ± 0.02	2.49 ± 0.10	1.00
MDMA	193	0.44 ± 0.02	2.23 ± 0.10	1.00
Morphine	285	0.31 ± 0.03	1.77 ± 0.20	1.00
Cocaine	303	0.31 ± 0.01	1.70 ± 0.10	1.00
THC	314	0.25 ± 0.01	1.50 ± 0.20	1.00
Heroin	369	0.22 ± 0.02	1.44 ± 0.10	1.00
2,4-Lutidine	107	0.61 ± 0.01	2.99 ± 0.10	1.00

Table 5
Relative mobility ratios for drugs

Compound	K_0 (Air)/K_0 (Air)	K_0 (N$_2$)/K_0 (Air)	K_0 (CO$_2$)/K_0 (Air)	K_0 (N$_2$O)/K_0 (Air)
NH$_4^+$	1.00 ± 0.01	0.99 ± 0.01	0.49 ± 0.01	0.48 ± 0.01
2,4-Lutidine	1.00 ± 0.01	1.00 ± 0.01	0.62 ± 0.01	0.61 ± 0.01
AMP	1.00 ± 0.01	1.01 ± 0.01	0.61 ± 0.01	0.60 ± 0.01
METHAMP	1.00 ± 0.01	1.01 ± 0.01	0.63 ± 0.01	0.61 ± 0.01
MDMA	1.00 ± 0.01	1.00 ± 0.01	0.64 ± 0.01	0.63 ± 0.01
Morphine	1.00 ± 0.01	1.00 ± 0.01	0.69 ± 0.01	0.67 ± 0.01
Cocaine	1.00 ± 0.01	1.01 ± 0.01	0.68 ± 0.01	0.67 ± 0.01
THC	1.00 ± 0.01	1.00 ± 0.01	0.71 ± 0.01	0.70 ± 0.01
Heroin	1.00 ± 0.01	1.00 ± 0.01	0.75 ± 0.01	0.73 ± 0.01

high, produced the larger slopes of 1.36, 1.22 and 0.96, respectively. Larger product ions, where the charge density is relatively low, produced the smaller slopes (0.22 for heroin) and were less affected by the polarizability of the drift gas. Thus, it would seem that ions with high charge density are capable of more efficiently polarizing gases with high polarizability than are ions with a lower charge density.

Table 4 provides a wealth of information with respect to the separation and identification of ions by the use of alternate drift gases. In summary, there are three conditions of interest:

(1) When both the slope and intercept of reduced mobility versus polarizability plots are the same, no separation or qualitative information is possible by varying the drift gas. Compounds which fall into this category include the dinitrotoluenes. They all have slopes of 0.53 and intercepts of 2.55–2.59.
(2) When the slope is the same but the intercepts are different, ions can be separated by IMS in all gases but no qualitative information is obtained by varying the drift gas. An example of this class would be morphine and cocaine. Both have slopes of 0.31 but they have intercepts of 1.77 and 1.70, respectively. These drugs can be separated in all drift gases but varying the drift gas does not provide additional information on their identity.
(3) The third case is where ions have a different slope. In this case, ions can potentially be separated in one gas but not in another and changes in drift gas provide additional qualitative information. Compounds which fall into this classification include heroin and cocaine where the slopes are 0.22 and 0.31, respectively. Other examples of this class

of compounds include DNT and RDX with slopes of 0.53 and 0.42; DNT and TNT with slopes of 0.53 and 0.46 and TNT and PETN with slopes of 0.46 and 0.96.

Changes in relative mobilities of ions in one drift gas relative to another allow the use of alternate drift gases for compound confirmation. Tables 5 and 6 provide mobility ratios relative to air for the drugs and explosives tested in this study. For example, the ratio of the reduced mobilities of the product ion for cocaine in carbon dioxide to that in air was determined to be 0.68 ± 0.01 and that for amphetamine was found to be 0.61 ± 0.01. Thus, by comparing the two drugs in the two different gases, addition qualitative information can be obtained. If an ion mobility peak has the same mobility as amphetamine in air and the same relative mobility as amphetamine in carbon dioxide then the probability that the ion producing this peak was the product ion for the drug amphetamine is higher than if only the mobility peak in air is used as the qualifying data.

Even when relative mobilities are similar such as the case with amphetamine and methamphetamine clear destitutions can be made in the spectrum. For example, the carbon dioxide/air relative mobilities of amphetamine and methamphetamine were found to be 0.61 ± 0.01 and 0.63 ± 0.01, from the spectra shown in Fig. 3. It was clear that the compounds reversed elution patterns from gases of high to low polarizability. In air the amphetamine eluted before the methamphetamine while in carbon dioxide it eluted after the methamphetamine.

While the example of amphetamine and methamphetamine is one in which the relative mobilities are similar, the example of THC and Heroin provide a clear example of the effect of alternate drift gas on relative mobilities. The carbon dioxide/air

Table 6
Relative mobility ratios for explosives

| Compound	K_0 (Air)/K_0 (Air)	K_0 (N$_2$)/K_0 (Air)	K_0 (CO$_2$)/K_0 (Air)	K_0 (N$_2$O)/K_0 (Air)
Cl$^-$	1.00 ± 0.01	0.99 ± 0.01	0.44 ± 0.01	0.45 ± 0.01
1,3-DNB	1.00 ± 0.02	1.00 ± 0.02	0.57 ± 0.02	0.60 ± 0.02
2,3-DNT	1.00 ± 0.02	0.98 ± 0.02	0.58 ± 0.02	0.60 ± 0.02
2,4-DNT	1.00 ± 0.01	0.99 ± 0.01	0.60 ± 0.01	0.61 ± 0.01
2,6-DNT	1.00 ± 0.01	0.99 ± 0.01	0.60 ± 0.01	0.61 ± 0.01
1,3,5-TNB	1.00 ± 0.02	1.01 ± 0.02	0.60 ± 0.02	0.61 ± 0.02
RDX	1.00 ± 0.01	1.00 ± 0.01	0.64 ± 0.01	0.65 ± 0.01
TNT	1.00 ± 0.01	1.02 ± 0.01	0.64 ± 0.01	0.64 ± 0.01
PETN	1.00 ± 0.02	1.00 ± 0.02	0.53 ± 0.02	0.53 ± 0.02
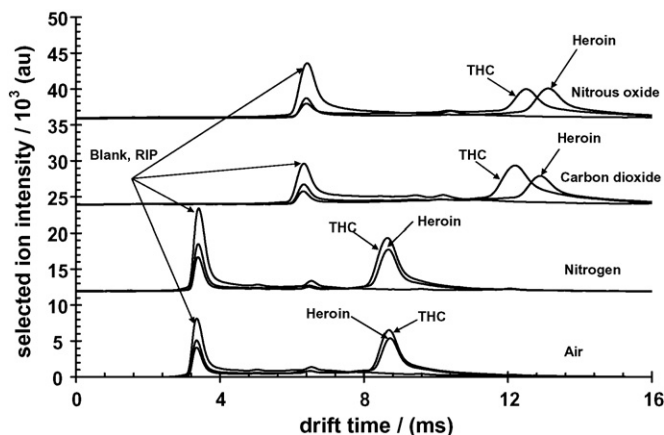
Fig. 6. Ion mobility spectra of heroin and tetrahydrocanabinol (THC) in different drift gases: air, nitrogen, carbon dioxide and nitrous oxide. The spectra illustrates the two compounds can be resolved with high-polarizability drift gases carbon dioxide and nitrous oxide.

relative mobility of THC was measured to be 0.71 ± 0.01 and the relative mobility of heroin was 0.75 ± 0.01. As shown in Fig. 6, THC and heroin could not be separated in air but were well separated in carbon dioxide and nitrous oxide.

4. Conclusion

Reduced mobility values for drugs and explosives measured in various drift gases indicate that relative mobilities of some drugs and explosives vary significantly and reproducibly. This variance in relative mobility among drift gases demonstrated that confirmatory tests for explosive or drug detection may be performed rapidly in the field by simply changing drift gas composition. For example, a small carbon dioxide cylinder could be attached to the back of a commercial IMS unit and used to switch between air and carbon dioxide drift gases to confirm results for drugs and explosives and reduce the incidence of false positive responses. In addition, the choice of drift gas can have a modest effect on separation selectivity (similar to GC stationary phases), in some cases enabling the resolution of hard-to-resolve compounds by the prudent choice of the IMS drift gas.

The use of secondary drift gases for confirmation is somewhat limited in IMS instruments with low resolving powers such as those currently used in the field. Instruments with higher resolving powers, however, would reduce the number of false positive responses to drugs and explosives due to better ion mobility discrimination between the target compound and interfering ions as well as the potential of using secondary gases for added identity confirmation.

Acknowledgements

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