



Comparison of reactant and analyte ions for ^{63}Ni Nickel, corona discharge, and secondary electrospray ionization sources with ion mobility-mass spectrometry

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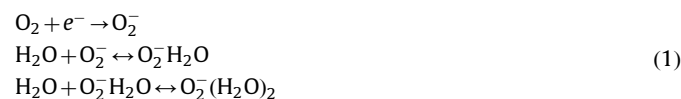
ABSTRACT

^{63}Ni Nickel radioactive ionization (^{63}Ni) is the most common and widely used ion source for ion mobility spectrometry (IMS). Regulatory, financial, and operational concerns with this source have promoted recent development of non-radioactive sources, such as corona discharge ionization (CD), for stand-alone IMS systems. However, there has been no comparison of the negative ion species produced by all three sources in the literature. This study compares the negative reactant and analyte ions produced by three sources on an ion mobility-mass spectrometer: conventional ^{63}Ni , CD, and secondary electrospray ionization (SESI). Results showed that ^{63}Ni and SESI produced the same reactant ion species while CD produced only the nitrate monomer and dimer ions. The analyte ions produced by each ion source were the same except for the CD source which produced a different ion species for the explosive RDX than either the ^{63}Ni or SESI source. Accurate and reproducible reduced mobility (K_0) values, including several values reported here for the first time, were found for each explosive with each ion source. Overall, the SESI source most closely reproduced the reactant ion species and analyte ion species profiles for ^{63}Ni . This source may serve as a non-radioactive, robust, and flexible alternative for ^{63}Ni .

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1. Introduction

The ^{63}Ni Nickel (^{63}Ni) ion source is the most common source used in standalone, commercial ion mobility spectrometry (IMS) systems [1]. This ion source's prevalence is due in part to its long-term stability and reliable ion chemistry. The ^{63}Ni source produces negative reactant ions via the following mechanism:



where the dominant reactant ion is a hydrated O_2^- ion [1]. This reactant ion is present in standalone systems using clean, dry air as both the sample and drift gas unless a more electronegative compound such as CH_2Cl_2 (commonly referred to as a dopant) is added to change the reactant ion chemistry [2–5]. The ^{63}Ni source also requires little or no maintenance and does not require an external power supply. However, there have been increasing financial, regulatory, and operational reasons to discontinue use of these sources and implement the use of non-radioactive ionization sources [6].

The second most common source in commercial, stand-alone systems is the corona discharge (CD) ionization source [7]. These sources are constructed in various configurations (e.g., point-to-plane geometry with a metal wire discharging to a metal surface) and operated in either a continuous or pulsed discharge mode [1]. The advantages of this source include greater ion current over the ^{63}Ni source, low cost assembly, and ease of operation [1]. The disadvantages of CD sources are the need for external high voltage supplies, long-term stability issues, and maintenance and/or replacement of the discharge component due to corrosion of the metal surface [1]. The pulsed operation may also induce time-dependent changes in the reactant ion chemistry and subsequent analyte ion chemistry [1,6,8]. This is due to the ionization mechanism which produces a cascading series of negative reactant ions through increasing concentrations of ozone and nitrogen dioxide neutrals: [9]



The reactant ion formation can be influenced by careful control of gas flow and concentration. When the corona discharge is pulsed on and off, this may prevent the buildup of ozone and

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nitrogen dioxide neutrals which, in turn, can lead to difficult operation [6,8,9]. A recent attempt has been made to address the long-term stability issues in CD sources by using an RF voltage applied on either side of a dielectric material. This new CD design has been termed distributed plasma ionization [10].

Secondary electrospray ionization (SESI) is a variant of electrospray ionization (ESI). Fundamental studies that first described SESI processes were performed by Fenn and co-workers. SESI was first developed for use as an ion source by Hill and used to analyze national security threats including explosives, chemical warfare agents, illicit drugs, and volatile organic chemicals (VOCs) in IMS, MS, and hybrid ion mobility mass spectrometers (IMMS) [11–18]. The SESI source consists of an electrospray apparatus with a fused silica or metal capillary for solvent introduction which connects to a high voltage source and is placed at the front of the IMS system's ion-molecule reaction region. Once neutral gas phase sample is quantitatively introduced into the ion-molecule reaction region of the IMS, one or more mechanisms may create ions. Separately, Fenn and Hill both suggested that interactions with the ESI droplets that contain the primary reactant ions and the neutral sample vapor produced ions with SESI. Fenn also suggested that charge exchange or chemi-ionization processes could create ions by SESI after desolvation of the ESI droplets [12,15,19,20].

Previous IMS research found that SESI achieved dynamic range gains over ^{63}Ni ionization and increased ionization efficiency and sensitivity over conventional atmospheric pressure chemical ionization (APCI) and electrospray ionization (ESI) [11,12,14]. This source can also introduce volatile and non-volatile dopants into the gas phase. Dopants are used to produce reactant ions in IMS; the radioactive source can only accommodate volatile dopants [2,13]. These reactant ions then provide a source of charge for ion-molecule charge transfer reactions. Disadvantages of this source include the need for an external high voltage supply, a solvent delivery system, and consumable costs for the solvent solutions (typically alcohol and DI water mixtures) [11].

When SESI was used to ionize vapor samples containing explosives, the SESI source provided lower detection limits for RDX over conventional ESI and ^{63}Ni ionization and greater response sensitivity for RDX, NG, and PETN using a non-volatile nitrate dopant instead of the traditional volatile chloride dopant [13]. Recently, SESI was used to achieve lower limits of detection for TNT and PETN on several atmospheric pressure ionization-mass spectrometers (API-MS) [16].

If gains are realized in detection sensitivity and specificity for explosives using an ionization source other than conventional ^{63}Ni , then a comparison of the proposed alternative sources' reactant and analyte ions must be performed. Table 1 summarizes the ion species and reduced mobility (K_0) values for explosives in the peer-reviewed literature for the CD and SESI ion sources (K_0 values are used to identify analytes in IMS); [1] a thorough review is available of the K_0 values produced by ^{63}Ni ionization sources for these explosives and others [21].

These summaries highlight problems with accurate ion species identification and K_0 value calculation. Specifically, there is a range of ion species for each explosive across the various ion sources. There is also a range of K_0 values for the same ion species found with the same source and across the ion sources. The determination of ion species produced by various ionization sources is important because the ion species determines the K_0 value for that analyte ion. If the analyte ion found with the ^{63}Ni source, used as a benchmark for portable and hand-held IMS systems, does not match the ion(s) produced for an explosive by another ion source, then the K_0 values will not match.

Correlation of K_0 values is especially critical when field-portable standalone IMS units are used for explosives and contraband

Table 1

Summary of reduced mobility values found in the literature for the CD, SESI, and ESI ion sources and for the explosives used in this study.

Compound	Species	K_0	Ion source	Mass ID.	Reference
TNT	TNT-H ⁻	1.55	CD	No	2003 Khaymian [26]
TNT	TNT-H ⁻	1.53	CD	No	2011 Roscioli [27]
TNT	TNT-H ⁻	1.58	CD	Yes	2009 Laakia [28]
TNT	TNT-H ⁻	N/A	SESI	Yes	2009 Fernandez [29]
TNT	TNT-H ⁻	1.59	ESI	No	2010 Hilton Wu [30]
TNT	TNT ⁻	1.55	CD	No	2002 Tabrizchi [31]
TNT	TNT-NO ⁻	1.97	CD	Yes	2009 Laakia [28]
TNT	TNT+O ⁻	1.53–1.55	CD	Yes	2009 Laakia [28]
NG	NG+NO ₃ ⁻	1.31	SESI	No	2004 Tam Hill [13]
NG	NG+Cl ⁻	1.40	SESI	No	2004 Tam Hill [13]
NG	NG-H ⁻	1.45	SESI	No	2004 Tam Hill [13]
RDX	RDX+NO ₃ ⁻	1.27	CD	No	2003 Khaymian [26]
RDX	RDX+NO ₃ ⁻	1.436	CD	Yes	2009 Ewing [9]
RDX	RDX+NO ₃ ⁻	1.46	CD	No	2011 Roscioli [27]
RDX	RDX+NO ₃ ⁻	1.35	SESI	No	2004 Tam Hill [13]
RDX	RDX+NO ₃ ⁻	1.42	ESI	No	2010 Hilton Wu [30]
RDX	RDX+NO ₂ ⁻	1.47	CD	No	2003 Khaymian [26]
RDX	RDX+NO ₂ ⁻	1.49	CD	Yes	2009 Ewing [9]
RDX	RDX+NO ₂ ⁻	1.40	SESI	No	2004 Tam Hill [13]
RDX	RDX+NO ₂ ⁻	1.48	ESI	No	2010 Hilton Wu [30]
PETN	PETN+NO ₃ ⁻	1.21	CD	No	2003 Khaymian [26]
PETN	PETN+NO ₃ ⁻	1.21	CD	No	2002 Tabrizchi [31]
PETN	PETN+NO ₃ ⁻	1.10	CD	No, indirect ^a	2011 Choi [32]
PETN	PETN+NO ₃ ⁻	1.14	SESI	No	2004 Tam Hill [13]
PETN	PETN+NO ₃ ⁻	1.19	ESI	No	2010 Hilton Wu [30]
PETN	PETN+NO ₂ ⁻	1.27	CD	No	2003 Khaymian [26]
PETN	PETN+NO ₂ ⁻	1.27	CD	No	2002 Tabrizchi [31]
PETN	PETN+NO ₂ ⁻	1.17 ^b	SESI	No	2004 Tam Hill [13]

^a 'Indirect' means that the mass and mobility measurement were not taken during the same experimental run.

^b Although the authors did not assign this species as PETN+NO₂⁻, the data seems to indicate this was the species detected by the IMS.

detection. The most persistent example in the literature of K_0 value discrepancies for explosives is the TNT-H⁻ species. A literature report using ^{63}Ni -IMS and chloride ion reactant ion chemistry found the K_0 values of ten explosives and taggant chemicals [22]. The author calculated the value for the TNT-H⁻ ion two ways. First, the author used a calibrant compound's K_0 value and then calculated the K_0 value for the unknown species using the equation:

$$K_{0,\text{unk}} = K_{0,\text{std}} \times \frac{t_{d,\text{std}}}{t_{d,\text{unk}}} \quad (3)$$

where $K_{0,\text{unk}}$ is the K_0 value of the unknown compound, $K_{0,\text{std}}$ is the K_0 value of the reference standard, $t_{d,\text{std}}$ is the drift time (ms) of the reference standard and $t_{d,\text{unk}}$ is the drift time (ms) of the unknown compound [23,24]. The second calculation method used the IMS instrumental parameters (the preferred method used by this study) and the standard reduced mobility equation:

$$K_0 = \left(\frac{L^2}{V \times t_d} \right) \left(\frac{T_0}{T} \right) \left(\frac{P}{P_0} \right) \quad (4)$$

where the squared length of the IMS drift region (L , cm) is divided by the voltage applied to pulse the ions into the IMS drift region (V , volts) multiplied by the analyte drift time (t_d , seconds) and corrected for standard temperature (T , Kelvin) and experimental pressure (P , Torr) [25].

The first calculation method found a K_0 value for the TNT-H⁻ ion was $1.45 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ while the second calculation method found a value of $1.59 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The author then chose to use the $1.45 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ value to calculate every other species' K_0

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