Analytica Chimica Acta 795 (2013) 36–43

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Evaluation of false positive responses by mass spectrometry and ion mobility spectrometry for the detection of trace explosives in complex samples

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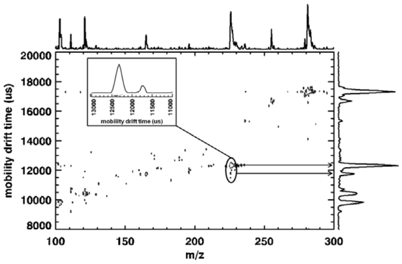
HIGHLIGHTS

- First study to use (−)SESI-IM-TOFMS to analyze complex mixtures of personal care products.
- The study demonstrated, by identifying mobility and mass interferents with explosive signatures, which, if used separately, neither IMS nor MS alone would prevent every false positive for explosives when detected in the presence of a complex sample matrix.
- Ingredients in common household cleaning products were shown to either enhance or suppress the ionization of explosives in a SESI-IM-TOFMS analysis.
- Mobility separation provided real-time separation of ion species that indicated overlapping isotope peak patterns

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 May 2013
Received in revised form 30 July 2013
Accepted 31 July 2013
Available online 6 August 2013

Keywords:
Ion mobility spectrometry
Mass spectrometry
Secondary electrospray ionization source
Interferences
Personal care products

ABSTRACT

Secondary electrospray ionization-ion mobility-time of flight mass spectrometry (SESI-IM-TOFMS) was used to evaluate common household products and food ingredients for any mass or mobility responses that produced false positives for explosives. These products contained ingredients which shared the same mass and mobility drift time ranges as the analyte ions for common explosives. The results of this study showed that the vast array of compounds in these products can cause either mass or mobility false positive responses. This work also found that two ingredients caused either enhanced or reduced ionization of the target analytes. Another result showed that an IMS can provide real-time separation of ion species that impede accurate mass identifications due to overlapping isotope peak patterns. The final result of this study showed that, when mass and mobility values were used to identify an ion, no false responses were found for the target explosives. The wider implication of these results is that the possibility exists for even greater occurrences of false responses from complex mixtures found in common products. Neither IMS nor MS alone can provide 100% assurance from false responses. IMS, due to its low cost, ease of operation, rugged reliability, high sensitivity and tunable selectivity, will remain the field method of choice for the near future but, when combined with MS, can also reduce the false positive rate for explosive analyses.

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http://dx.doi.org/10.1016/j.aca.2013.07.070

1. Introduction

The detection of trace quantities of organic compounds, such as an explosive, in real-world samples is important for human and critical infrastructure safety. The method of choice for detecting trace levels of explosive compounds has been ion mobility spectrometry (IMS) due to its sensitivity and selectivity, atmospheric pressure operation, and low cost [1]. Recently, however, a report suggested that mass spectrometry (MS) could supplant IMS as the preferred screening method for trace explosives detection [2].

Sample separation before mass analysis is normally required in order to reduce false responses [3]. MS, often with either a gas chromatography (GC) or liquid chromatography (LC) separation method, has been used to detect target threat compounds (e.g. chemical warfare agents [4,5], biological toxins [6], illicit drugs [7,8], explosives [9,10], etc.) in complex samples. The traditional gas chromatography (GC) and liquid chromatography (LC)-based separation methods often have lengthy separation times although recent improvements with fast GC have lowered separation times to 2.5 min or less [11]. Increased speed, however, comes with decreased resolving power (i.e. resolving power is the retention or drift time of an analyte divided by the analyte peak's width at half height). In addition, GC can only be used for volatile target compounds such as chemical and certain biological warfare agents. Low or non-volatile explosive compounds with thermal degradation issues may not be successfully detected with this method. GC also relies on costly helium gas for optimal separations (needed with complex samples) and the added complexity of temperature-programmed separation cycles [11]. LC–MS methods, including rapid UPLC methods, are able to analyze both volatile and non-volatile target compounds but suffer from unavoidable interferences with LC solvents and column materials that can coelute with the analyte peak [12]. Ever more complex samples can also cause increasing limits of detection (LOD) for target analytes due to increased chemical noise. An increase in the LOD can cause the instrumental dynamic range for that analyte to narrow, lessening the technique's ability to detect the analyte at a wide range of concentrations [13–16].

IMS is an ion detection method that separates ions based on their size-to-charge ratios in the gas phase. The size of an ion is typically measured as its collision cross section (Ω), which is dependent on the ion's mass and shape [17]. IMS has been used to detect target compounds including explosives, chemical warfare agents, and illicit drugs since the 1970s [18,19]. Commercial IMS systems were first deployed in the 1980s at airport security checkpoints to detect explosives and illicit drugs in complex samples [20]. Over 40,000 ambient pressure IMS systems are deployed now at transportation security checkpoints in airports and at border crossings as part of passenger and hand luggage screening efforts [1,21]. Ambient pressure IMS uses air as a carrier gas, has fast analysis rates (under 6 s per sample), and, depending on the ion source, can separate and detect both volatile and non-volatile analytes.

Although IMS false positive responses are extremely low, the use of IMS systems in increasingly diverse operating environments has the potential to cause false positive responses [21]. Contaminants from 20 personal care products (PCPs) (fragrances, cosmetics, sun screens, etc. containing a range of low molecular weight compounds [22,23]) were investigated using ^{63}Ni-IMS to find any mobility interferents with 22 compounds of interest to national security including explosives, illicit drugs, and chemical warfare agents [24]. The IMS analysis revealed that four of the 20 cosmetic products contained mobility interferences for the analytes of interest [24]. Another study found that two compounds, 2,4-dichlorophenoxyacetic acid and 2,4-dichlorophenol, overlapped with mobility peaks produced by thermal degradation products of TNT in a ^{63}Ni-IMS analysis [25]. An evaluation of gaseous interferents with TNT found that 17 suspected contaminants commonly found in airport settings decreased TNT sensitivity [26].

Little work has been conducted to determine the extent to which mass spectrometry would experience similar types of interferences when trying to detect trace amounts of target analytes in the presence of complex mixtures. Resolving power (R_p) is one of several factors that influence successful identification of a compound in the presence of a mixture in laboratory-based mass spectrometers. R_p values of lab-based MS instruments can span a range between 4000 and 40,000, compared with a common resolving power range of 20–40 for IMS [27]. So far, miniaturized ion traps built for target analyte detection achieve slightly more than unit mass resolution [28]. Thus, many believe that since the resolving power of MS is so large, all ions will be well separated, and false positive responses will be reduced by several orders of magnitude. This improved false positive rate would then justify the added expense and weight of vacuum pumps and the field operation of vacuum equipment. MS also has the added advantage of MS–MS analysis and isotope ratio identification of unknown compounds. On the other hand, the use of MS is not expected to improve the false negative response rate since these rates are primarily dependent on the ionization process and the efficiency of sample transfer to the ion source. Interferences may compete with target compounds for charge at APCI sources which may lead to suppression or masking of the analyte.

The goal of this study was to evaluate common complex matrices for false positive responses with explosives. Eighteen samples of common household products underwent an ion mobility mass spectrometry analysis (IMMS) and their responses were characterized by mobility, mass, and mobility-mass.

2. Materials and methods

2.1. Vapor generation and sample introduction

The sample vapor generator has previously been described [29]. After ensuring clean blank spectra, small amounts of each sample (3–5 mg per sample) were thermally desorbed from the sample holder by heating the sample holder to 160–180 °C with an ultra-high temperature heating tape from Omegalux (Stamford, CT). An AHP Series in-line gas heater by Omegalux was connected with Swagelok (Solon, OH) fittings to the sample holder and heated N_2 gas (160–180 °C as measured by a thermocouple) swept the neutral sample vapor into the IMS at a rate of 90.0 mL min^{-1}. Since the IMS was operated in an open-ended configuration, air was also present near the ion source to induce atmospheric pressure chemical ionization of the analytes. No dopant species were used to create reactant ions. The sample introduction setup was used to generate vapor over a period of 5 min so as to collect many spectra that were averaged to produce a high signal:noise average IMMS spectra.

2.2. SESI-IM-TOFMS

The negative mode operation of the ion mobility-time-of-flight mass spectrometer (IM-TOFMS) with secondary electrospray ionization has been described in detail [30,31]. The SESI source was chosen over the traditional radioactive ^{63}Ni ionization source because a previous literature report showed increased sensitivity for explosives over ^{63}Ni [32]. The ESI source sprayed a 1:1 (v:v) methanol:water ESI solvent at a rate of 4 μL min^{-1} using a KD Scientific Inc. model 210 syringe pump (Holliston, MA). The analyte ions were then pulsed into a 17.99 cm drift region by a Bradbury–Nielsen ion gate with a 200 μs pulse width. Heated (150–200 °C) nitrogen drift gas flowed at a rate of 1000 mL min^{-1} countercurrent to the