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Desorption electrospray ionization–mass spectrometric analysis of low vapor pressure chemical particulates collected from a surface

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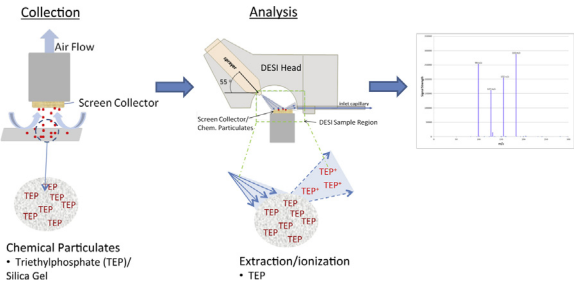
HIGHLIGHTS

- DESI–MS analysis of low vapor pressure chemical particulates collected from a surface.
- Investigated collection of low vapor pressure chemical particulates from surfaces.
- Successfully analyzed chemical particulates collected on sticky screen sampler using DESI–MS.
- Demonstrated μg level detection limits for chemical particulates.
- Normalized data against the total ion current (TIC) enabling good reproducibility.
- Successfully determined mass of TEP in a sample with 14% accuracy.

GRAPHICAL ABSTRACT



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ABSTRACT

The collection of a low vapor pressure chemical simulant triethyl phosphate sorbed onto silica gel (TEP/SG) from a surface with subsequent analysis of the TEP/SG particulates using desorption electrospray ionization–mass spectrometry (DESI–MS) is described. Collection of TEP/SG particulates on a surface was accomplished using a sticky screen sampler composed of a stainless steel screen coated with partially polymerized polydimethylsiloxane (PDMS). DESI–MS analysis of TEP/SG particulates containing different percentages of TEP sorbed onto silica gel enabled the generation of response curves for the TEP ions m/z 155 and m/z 127. Using the response curves the calculation of the mass of TEP in a 25 wt% sample of TEP/SG was calculated, results show that the calculated mass of TEP was 14% different from the actual mass of TEP in the sample using the m/z 127 TEP ion response curve. Detection limits for the TEP vapor and TEP/SG particulates were calculated to be 4 μg and 6 particles, respectively.

1. Introduction

Detection of low vapor pressure chemicals (LVPCs), which include energetic and toxic materials, is of significant concern for both military and civilian government agencies. Conventional chemical detectors, such as ion mobility spectrometers (IMS), surface acoustic wave (SAW) detectors, gas chromatographs (GC), and mass spectrometers (MS) [1–4] require the analyte be in the vapor phase for collection and analysis. Detection of trace levels of chemical vapors requires preconcentration of the chemical vapors where a sorbent tube is used to collect and concentrate the hazardous chemical vapor. Once collected onto the sorbent, the

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chemical vapor is thermally desorbed into the detector at significantly greater concentration then originally in the atmosphere. This approach has been enormously successful at enabling the detection of ppb(v) to ppt(v) levels of toxic chemical vapors using a variety of chemical detectors [2,5,6]. However, the use of conventional preconcentration media requires sufficient concentration of the chemical vapor to be present to enable collection a sufficient mass of the chemical vapor over an operationally relevant time frame for detection. LVPCs do not emit sufficient chemical vapor for direct analysis by conventional detectors due to the low vapor pressure of these materials (10^{-4}–10^{-8} torr) at ambient conditions [7]. Analysis of LVPCs is possible using preconcentration techniques however, because of the very low vapor concentration long collection times will be required to collect sufficient material for analysis. From an operational perspective rapid detection is essential and therefore preconcentration techniques targeted on collecting LVPC vapors are not applicable for LVPC analysis. The properties of LVPCs, particulate in nature and very low vapor pressure, require the development of new sampling and analysis methods capable of rapid collection and analysis of LVPC particulates from surfaces and as aerosols.

Desorption electrospray ionization–mass spectrometry (DESI–MS) is an atmospheric ionization technique that it enables the rapid analysis of surfaces for trace chemicals and biological with no sample preparation required [8–11]. DESI–MS utilizes an electrically charged solvent to extract and ionize trace chemical on surfaces. Droplets of the charged solvent impact the surface at approximately $150\,\mathrm{m\,s^{-1}}$ wetting the surface and extracting the analyte from the surface into the solvent. Subsequent solvent droplets impact the wetted surface causing the emission of secondary microdroplets containing the ionized analyte. Ionization can also occur through interaction of the analyte with gas phase solvent ions. DESI–MS analysis has wide applicability for a number of important detection and analysis needs such as the analysis of pharmaceuticals, explosives, and peptides and proteins, and chemical warfare agents sorbed onto solid-phase microextraction (SPME) fibers [10–12].

Quantitative analysis using DESI–MS is challenging due to the different experimental parameters involved in the use of ambient ionization techniques. Some of these experimental parameters include the type of surface being analyzed, the chemical and physical properties of the solvent system, and the reproducibility of sample introduction into the DESI stream [13]. Quantitative DESI–MS analysis has been reported for the pharmaceuticals propranolol and carbamazepine, both as the pure component in water (background free) as well as mixed with urine/water (biological background) [14]. Using internal standards good precision was achieved with relative standard deviations (RSDs) of 5% and ~10% for the background free and biological background samples, respectively. The reproducibility of DESI data for use in analysis of mouse brain tissue samples was investigated using an imaging DESI–MS system [15]. In this case no internal standards were used but the ratio of the two most intense peaks in the DESI–MS spectrum were used to normalize the analyte signals over different analytical runs. This analytical approach resulted in RSDs for analysis of two different rat brain tissue samples of 7.2% and 4.7% indicating good precision.

DESI–MS can be used for the detection and analysis of LVPCs because of its ability to rapidly extract and ionize analytes directly from surfaces, as well as when sorbed into different matrices. For example, the LVPC pesticides dicrotophos and malathion immobilized into an inert matrix (diatomaceous earth or Hi-Sil) were successfully analyzed using DESI–MS [16]. The pesticides were loaded onto the inert matrices at 0.1 wt%, 1 wt%, and 10 wt% by controlled evaporation of a mixture containing the inert matrix and a solution of the pesticide. Analysis of the immobilized pesticides was accomplished by first fixing the particulates onto double sided tape mounted to a microscope slide. Mass spectra for both dicrotophos and malathion using DESI for extraction and ionization were reported, however, detection limits were not determined due to the imprecise nature of the sample mounting procedure utilized.

In the current work we report the collection and analysis of a LVPC particulate consisting of the nerve agent simulant triethyl phosphate (TEP) immobilized onto silica gel (SG). A sticky screen sampler was utilized to collect the TEP/SG particulates from a contaminated surface followed by DESI–MS analysis of the TEP/SG particulates. The sticky screen sampler enables the quantitative collection of the particulate sample from a surface and reproducible sample introduction into the DESI stream thereby minimizing sampling errors. The TEP ion signals are normalized using the total ion current (TIC) signal generated for each analytical scan by the DESI–MS system minimizing the signal strength variation caused by changes in ambient atmospheric conditions as well as any changes in the DESI spray conditions.

2. Experimental

Triethylphosphate, 99%, (TEP) and silica gel (SG) powders (200–425 mesh) were purchased from Sigma–Aldrich and used as received. Samples of the triethylphosphate/silica gel (TEP/SG) containing 5 wt%, 11 wt%, and 24 wt% of TEP were prepared by pipetting a specific volume of a known concentration of TEP in ethanol onto a known mass of SG suspended in ethanol [17,18]. The TEP/SG suspension in a beaker with a stir bar was then covered with parafilm and stirred for 1 h. After stirring the parafilm was removed from the beaker and the beaker covered with a cover glass. The beaker and cover glass were then placed into a chemical hood and the TEP/SG suspension stirred for 24 h during which time the solvent evaporated leaving behind the TEP/SG particulates. After 24 h the particulates of TEP/SG were removed and air dried to constant weight. All of the prepared TEP/SG particulates were free flowing powders with no evidence of liquid TEP on the surface.

Sticky screen samplers were prepared using precut and formed stainless steel screens (304SS, mesh 100; 150 μm × 150 μm square holes). The clean pre-formed screen is placed into the sticky screen holder and fixed in place using a pressure fitting. The screens are coated by spraying a mixture of dimethylsiloxane with curing agent (Sylgard 184, Dow Corning, USA), volume ratio of 10:1, onto

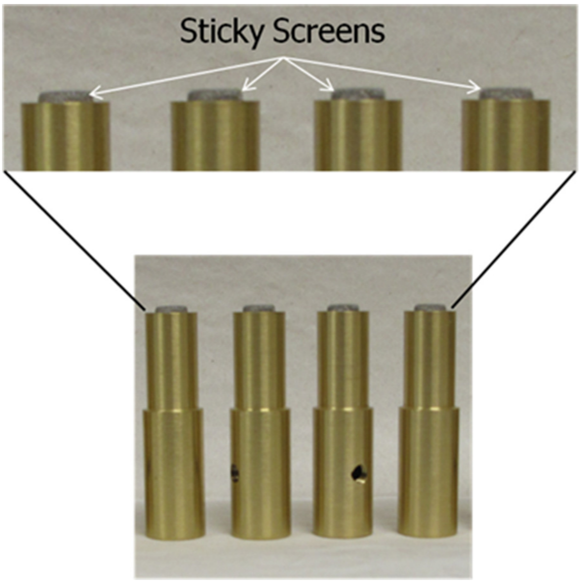

Fig. 1. Sticky screen samplers showing sticky screens mounted in brass jackets.