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A new method and apparatus for on-site detection of trace levels of chemical warfare agents

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Abstract

A pre-concentration/fast gas chromatograph for the sampling of toxic vapors from air was developed. Pre-concentration is performed by filtering the contaminated air through a tube containing absorbing material. The sample is thermally desorbed and separated on a short chromatographic column using air as a carrier gas. Detection is performed with a commercial hand-held chemical warfare agent detector. The effects of the airflow rate, sample volume and system temperatures on the analytical performance were studied. Detection of organophosphorus vapors at concentrations in the range 4×10^{-4} to 4×10^{-5} mg/m^3 was achieved within 2.5 min. The ability to couple a portable detector to a pre-concentration/fast GC using air as a carrier gas encourages the development of a hand-held device for real-time on-site monitoring of low levels of CWA in the air.

Keywords: CWA; Pre-concentration; Fast-GC; On-site

1. Introduction

Chemical warfare agents (CWA) are extremely toxic compounds, which can become a severe threat to human health and life if dispersed in the atmosphere even at minute concentrations. Hence, a reliable and rapid on-site detection of these compounds at trace levels is of prime importance. Hand-held automatic CWA detectors are based on various technologies such as Ion Mobility Spectrometry (IMS), Flame Photometric Detector (FPD) or Surface Acoustic Wave (SAW). These technologies have been successfully adapted to field conditions in terms of ruggedness and portability. Their operation is simple and untrained personal can detect relatively low concentrations of CWA vapor in air (0.005–0.1 mg/m^3) [1,2]. However, such levels of CWA in the atmosphere are still unsafe for human inhalation. For example, the 8-h time weighted average values (TWA) of the nerve agents *O*-isopropyl methyl phosphonofluoridate (GB) and *O*-ethyl *S*-2-diisopropylaminoethyl methyl phosphonothiolate (VX) are 1×10^{-4} and 1×10^{-5} mg/m^3, respectively [2]. The common approach for the detection of trace levels of CWAs is to analyze environmental samples in the laboratory. Analytical performance of these techniques is very good and detection of TWA levels of CWAs as well as degradation and byproducts of CWAs is achievable even in complex matrixes such as soils [3]. However, real time monitoring of trace levels of CWAs is impossible with these techniques since in many cases they involve sample handling (e.g. extraction), delicate instrumentation and training of laboratory personal.

The sensitivity can be enhanced significantly by pre-concentration of the sample prior to detection [4]. Pre-concentration is achieved by cumulative adsorption of the analyte from the contaminated air stream onto a porous polymer, followed by thermal desorption. Drawing larger volumes of contaminated air through the pre-concentration tube (PCT) increases the amount of collected analyte, which improves the sensitivity. However, it should be noted that during sampling, analytes migrate in the sorbent bed, eventually penetrating through it, resulting in partial loss of the sample. The volume of air that causes penetration of the analyte through the sorbent bed is termed the breakthrough

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volume. Collection efficiencies of volatile and semi-volatile organic compounds (VOC and SVOC) have been studied extensively [5–9]. It was found that the breakthrough volume is primarily affected by the volatility of the analyte and the temperature and mass of the sorbent bed. At low analyte concentrations (ppm range), the effect of concentration on the breakthrough volume is negligible [5].

Pre-concentration of organic vapor was adopted for field applications by introducing automatic devices coupled to GC systems, for example MINICMS (CMS field products group, Birmngham, Al, USA) [10] and ACEM 900 (Dynatherm Analytical Instruments Inc., Kelton, PA, USA) [11]. Frishman and Amirav developed a fast GC/PFPD equipped with a small PCT (micro-trap) for the detection of organophosphorus (OP) and organosulfur (OS) compounds [12]. These instruments can detect 8-h TWA levels of CWA. But their operation depends on a supply of pure compressed gases and other consumable items. The requirement for supply of consumables items complicates deployment in the field. Thus, using air as a carrier gas can become a key issue for the development of a "consumable free" pre-concentration/pre-separation apparatus for coupling to existing detectors. One difficulty with this solution is that during thermal desorption and separation, oxygen and humidity in the air may degrade the analytes as well as the sorbent bed and column coating. Sanchez and Sacks demonstrated a separation of stable VOCs with a benchtop GC, using air as a carrier gas [13]. However, using air as a carrier gas for detection of low concentrations of CWAs presents greater challenge, since these compounds are reactive and thermo-labile. In order to meet this demanding task, the pre-concentration/pre-separation apparatus must be carefully designed. The operational parameters of the device must be specifically adjusted for this purpose.

In the present paper, we describe the design and analytical performance of a new PCT/fast gas chromatograph (PCT/FGC) aimed to detect low levels of CWA vapors in the field. The PCT/FGC described in the present paper is unique and innovative in two aspects: (a) air is used as the carrier in the fast chromatographic separation of CWA and (b) the system is an "add-on" unit that may be coupled to commercial, hand-held CWA detectors. In the present work the PCT/FGC capabilities were demonstrated with a commercial system, namely AP2C™ based on FPD technology.

2. Experimental section

2.1. Materials

Triethylphosphate 99.5% purity (TEP, BDH, Wesel, Germany) and tributylphosphate 99.5% purity (TBP, Fischer analytical, Zurich Switzerland) were used without further purification. Bis (2-chloroethyl) sulfide (sulfur mustard—HD), *O*-ethyl *S*-2-diisopropylaminoethyl methyl phosphonothiolate (VX) and *O*-isopropyl methyl phosphonofluoridate (sarin, GB) were synthesized in IIBR at purity levels higher than 95% as measured by NMR.

2.2. Analytical methods

Vapors of the CWAs and simulants were generated by bubbling dry nitrogen through 2–5 g of the liquid chemical at a controlled temperature. The vapor-saturated air stream was diluted with clean air in order to obtain the desired concentration. This method enables efficient and reliable addition of organic vapor to the air stream in a very wide concentration range. However, if a sample contains volatile impurities their concentration in the air stream will be higher than in the liquid sample. Thus, the air stream was sampled and analyzed with GC/FPD and GC/MS in each experiment. Sampling was preformed by bubbling a known volume of the contaminated air through organic solvent (hexane or isooctane, both of analytical grade, from Aldrich). GC/FPD analysis of these samples was performed with Agilent 6890 (Agilent, Wilimngton, DE, USA) gas chromatograph equipped with FPD. A capillary fused silica column (30 m length × 0.25 mm i.d. × 0.25 μm film thickness—DB5MS, Agilent, Wilimngton, DE, USA) was used for chromatographic separations. Column temperature was held at 50 °C for 0.5 min then heated at a rate of 20 °C/min to 300 °C. The sample (2 μL) was injected to the GC at splitless mode, injector temperature was 200 °C and the detector temperature was 250 °C. Nitrogen was used as a carrier gas at a constant flow of 2 mL/min. GC/MS analysis were performed with an Agilent 6890 (Agilent, Wilimngton, DE, USA) equipped with Programmed Temperature Vaporization inlet (PTV, CIS-4, Gerstel, Baltimore, MD, USA) and mass selective detector (5973/N, Agilent, Wilimngton, DE, USA). Ionization method was EI (70 eV), mass spectrometer was operated at full scan mode (50–500 a.m.u.). The sample (50 μL) was injected to a packed liner containing Tenax inside the PTV. After the injection, PTV temperature was held at 50 °C for 0.5 min in order to trap the analytes on the Tenax while the solvent was flashed away from the inlet. After venting the solvent the injector was heated to 250 °C at a rate of 700 °C/min. Helium was used as a carrier gas at a constant flow of 2 mL/min. Both GC/MS and GC/FPD were calibrated with standard solutions containing known concentrations of the analytes. The flow system and the PCT/FGC were installed inside a climatic chamber, in order to control climate conditions during the experiments (Fig. 1a). The PCT/FGC was challenged with CWAs vapor at air temperature of 25 °C and 50% relative humidity.

2.3. PCT/FGC design and principle of operation

A scheme of the PCT/FGC is shown in Fig. 1b and c. The PCT is made of a Pyrex tube (o.d. = 3 mm, i.d. = 1.8 mm, length = 88 mm), filled with 15 mg of Tenax-TA (35/60 mesh size, Alltech associates Inc., Deerfield, IL, USA). The PCT is fitted inside a small homemade oven made of a thin-walled