Short communication

Preconcentration and partial separation of nitroaromatic vapors using a methyltrimethoxysilane-based sol-gel

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A B S T R A C T

Typical trace vapor analysis involves sorbent trapping, followed by desorption and chromatographic separation. This communication describes a method for streamlining this process by combining sorbent sampling/preconcentration with partial separation achieved through temperature-programmed thermal desorption. A novel sorbent trap was formulated in which tubular glass liners for a programmable-temperature gas chromatograph inlet were coated with a sol-gel based polymer stationary phase synthesized from methyltrimethoxysilane precursor and installed into the inlet, which was directly connected to a mass-selective detector by a fused silica capillary transfer line. This method is shown to achieve partial separation of two nitroaromatic vapors in a total 3–5 min analysis time, which represents a tenfold improvement in speed in terms of the overall cycle time compared to an analogous conventional vapor analysis method. Both analytes proved to have a high dynamic range and loading capacity, with nitrobenzene achieving both high and low sampling extremes (0.32 ng–4 µg sampling concentration) with only a slight compromise in peak broadening. The multivariate curve resolution by alternating least squares algorithm (MCR-ALS) was shown to successfully resolve the overlapped elution profiles of the two nitroaromatic test vapors examined in this study.

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1. Introduction

Analysis of trace vapors in complex matrices is a challenging task with many important applications, such as detection of explosives at checkpoints. This difficulty is driven by the fact that such analytical tasks require not only great sensitivity, but also very high selectivity for accurate and precise results, and are complicated by intrinsic properties of the explosives including low vapor pressures and affinity to surfaces. Accordingly, standard laboratory analysis of trace vapor mixtures typically involves a multi-step process aimed to enhance analytical capability. Sorbent trapping is used to preconcentrate the sample, boosting method sensitivity. This is followed by desorption and subsequent chromatographic separation with, for example, gas chromatography (GC) to provide selectivity. Multichannel detection such as the mass selective detection in MS is often implemented as well, to further boost selectivity.

This sequence of steps leads to significant overall method complexity, cost, and analysis time. Recognizing that sorbent trapping and GC separation involve similar fundamental analyte-stationary phase interactions (albeit with different goals and optimization criteria) raises the possibility that these two steps might be effectively combined under the right conditions. This approach could significantly reduce analytical complexity and analysis time, enabling a more efficient alternative for both laboratory-based analytical systems and portable chemical detection systems. In such a system, an integrated sorbent bed would be used to sample and preconcentrate trace vapor. Once sampling is complete, the sorbent bed is then heated according to a method-dependent temperature program. Depending on the temperature program and the relative retention factors of the individual constituents of a sorbed mixture, differential migration out of the sorbent bed could be observed with the bed acting, in essence, as a very short chromatographic column providing a relatively low-resolution chromatographic separation.

Although the elimination of a traditional GC column would result in a reduction in resolving power, the use of a multichannel detector (e.g., a mass spectrometer, multi-wavelength optical detector, or sensor array) could provide sufficient analytical information to enable effective chemical analysis. Chemometric data analysis techniques have been shown to provide acceptable analytical results with neither full chromatographic resolution nor fully selective detection by leveraging chemical information from both. In this way a trade space between chromatographic performance

A

Sol-solution

Sol-gel coating

0.4 mm OD Teflon
Capillary

1 mm ID glass liner

tee fitting

B

1 mm ID

Bare silica CIS liner

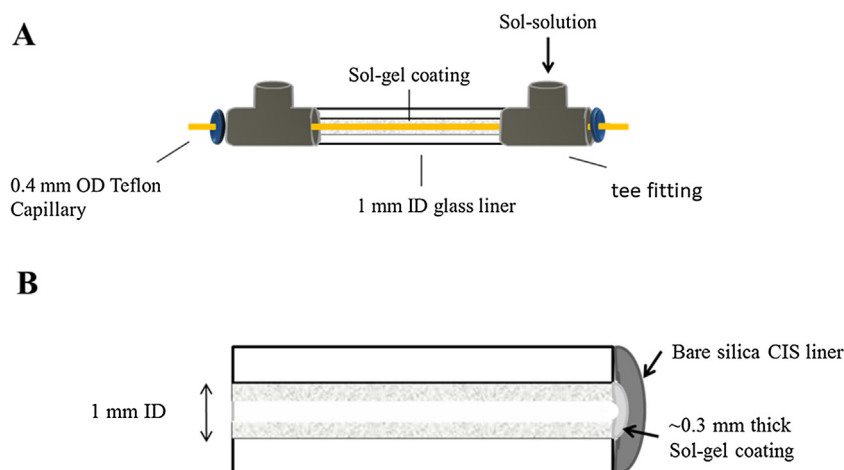~0.3 mm thick
Sol-gel coating

Fig. 1. A. Depiction of sol-gel coating apparatus. B. Depiction of cross-sectional view of sol-gel coating within PTV inlet liner.

and detection selectivity is enabled, allowing greater flexibility in analytical method optimization [1–4].

Sol-gel polymers present an interesting alternative to traditional packed sorbent materials for this approach. These materials are more thermally stable and easier to prepare than organic polymers [5,6]. The thickness, porosity, and surface area can also be easily manipulated, increasing their versatility for a variety of applications and the final product is a rigid monolithic material [7–11]. Sigman et al. created in-house sol-gel sorbent tubes for the extraction of a series of explosive vapors. Sol-gel sorbents were prepared by loading the polymer material on stainless steel tubes which were then attached to the base of a GC injection port [12]. Molecularly imprinted sol-gel sorbents were recently tested by Lordel et al. for the selective extraction of nitroaromatic explosives, showing their potential to be used as highly selective sorbents with large capacity for analytes in complex matrices [13]. Walker et al. used imprinted sol-gel sensor films for TNT detection, again proving high selectivity for TNT with a low limit of detection for the template molecule. However, the use of sol-gel sorbents is still a relatively new approach and its use for explosive detection is still in its infancy [14].

To determine the capabilities of a consolidated preconcentration/separation method, a sol-gel sorbent sampling trap was made in-house and evaluated by connecting it directly to a conventional GC detector, bypassing the GC column and relying on temperature-programmed thermal desorption from the sorbent to achieve partial separation of a mixture of nitrobenzene and 2,4-dinitrotoluene.

2. Materials and methods

2.1. Reagents and standards

All sol-gel materials, including acetic acid, polyethylene glycol, ethanol, methyltrimethoxysilane, and sodium hydroxide for liner pretreatment were purchased from Sigma-Aldrich (St. Louis, MO). Nitrobenzene (1512 ng/min @ 110 °C) and 2,4-dinitrotoluene (827 ng/min @ 100 °C) permeation tubes, used for vapor generation, were purchased from KIN-TEK Laboratories (La Marque, TX). 1000 μg/mL ampules of nitrobenzene and 2,4-dinitrotoluene standards, used for calibration and quantitation, were purchased from AccuStandard (New Haven, CT). Diluted liquid standards were made using methanol as the solvent, also purchased from Sigma-Aldrich.

2.2. Sorbent liner fabrication

The sorbent liner was prepared by coating a sol-gel polymer onto the interior walls of a straight (without notch) bare silica liner with an internal diameter of 1 mm and 70 mm in length (Gerstel Cooled Injection System liner, Mulheim an der Ruhr, Germany).

2.2.1. Liner pretreatment

Prior to polymer coating, the liner required a pretreatment strategy to ensure strong binding between the polymer and liner as well as high mechanical stability within the liner. To accomplish this, the ends of a clean liner were manually etched with a 0.75 mm diamond coated drill (Triple Ripple, Lewis Center, OH). This was done to *physically* increase the surface area available for covalent bonding of the sol-solution to the glass, thereby improving the mechanical stability of the sol-gel within the liner. Following the etching process, the liner was rinsed with 15 mL of 5 M sodium hydroxide (NaOH) to ensure that the newly exposed glass surface was fully activated/hydrolyzed. Finally, the liner was rinsed with water and allowed to dry.

2.2.2. Sol-gel synthesis and polymer coating

The sol-gel sorbent used in this work was previously developed by Giordano et al. [15] for use in electrochromatographic separations of explosives and their degradation products in seawater. Briefly, sol-gels were prepared by combining an aqueous solution of 100 mM acetic acid containing 0.2 g/mL polyethylene glycol (8000 molecular weight), with ethanol, and the sol-gel monomer-methyltrimethoxysilane (C1-TMOS). Polyethylene glycol served as a porogen while the acetic acid served as an acid catalyst for the hydrolysis process. The solution was gently stirred at room temperature for 2 h. A 1:1 v/v mixture of diethylamine and acetonitrile was added as base catalyst, to initiate the condensation process. Sol-gels synthesized from this formulation have a pore diameter of 58 Å, a total surface area of 11 m^2/g, and a pore surface area of 7 m^2/g [16].

In order to coat the liner, it was mounted between two stainless steel Swagelok® "tee" fittings (Solon, OH), with 1/8 in. perfluoroalkoxy (PFA) ferrule hex nuts (Savillex, Eden Prairie, MN) on the inner ends, holding the liner firmly in place. A 0.4 mm (external diameter) Teflon capillary (Polymicro Technologies, Phoenix, AZ) was tightly stretched through the middle of the glass liner (Fig. 1A). The sol-solution was injected into the top of the apparatus and allowed to solidify in the space around the capillary. To decrease air exposure to the polymer during the condensation process, which could potentially dry out the polymer, the liner, still connected