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Solvating gas chromatography with chemiluminescence detection of nitroglycerine and other explosives

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Abstract

A separation technique known as solvating gas chromatography (SGC), which utilizes packed capillary columns and neat carbon dioxide as mobile phase, was used for the separation of nitroglycerine (NG) and other nitrogen-containing explosives including 2,6-dinitrotoluene (2,6-DNT), 2,4-dinitrotolulene (2,4-DNT), 2,4,6-trinitrotoluene (2,4,6-TNT), and pentaerythritol tetranitrate (PETN). SGC was coupled for the first time to a selective chemiluminescence thermal energy analyzer (TEA) detector for nitro-functional group specificity and sensitive detection of these compounds. TEA calibration curve for NG showed linearity in the sub-μg ml^{-1} range. Soil samples containing NG were used to test the validity of the technique. Detector response of SGC–TEA versus SGC–flame ionization detection for NG was also evaluated.

Keywords: Solvating gas chromatography; Explosives; Nitroglycerine

1. Introduction

Rapid identification of explosives is crucial in areas such as law enforcement forensics and military deployment safety and toxicology. Explosive residues can be present in materials such as soil and water, or on solid surfaces in areas surrounding a site for detonation and/or munitions storage. Complex matrices such as these can contain hundreds of compounds, and the need for a separation step prior to identification of the explosives is evident in order to reduce potential interferences and increase the likelihood for low-level detection.

Gas chromatography (GC) is typically the method of choice for the identification of explosive nitroglycerine (NG), and commonly used detection methods include electron-capture detection (ECD) [1,2] or chemiluminescence detection (thermal energy analyzer, TEA) [3–7]. Due to the nitro-specific selectivity of the TEA, GC–TEA is one of the most widely used techniques for screening high explosives [3], and recent work using high-speed GC–TEA with open tubular columns having small internal diameters has been reported [7]. The TEA selectivity has also been exploited through coupling with supercritical fluid chromatography (SFC) for the detection of explosives [8].

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High-performance liquid chromatography (HPLC) is also a useful method for analysis of high explosives, and reversed-phase methods are most commonly used. However, the TEA is not ordinarily used with reversed-phase HPLC since it is not compatible with aqueous mobile phases [3]. The TEA can be used when HPLC is used in the normal-phase mode, however, ultraviolet–visible (UV–Vis) detectors are usually employed for the analysis of explosives [3].

Other detection techniques such as laser optoacoustic spectroscopy [9–11], ion mobility spectrometry (IMS) [12–14], bioluminescence [15], and mass spectrometry (MS) [16–19] have also been used as detectors for the analysis of explosives. Recently, GC was also coupled with surface acoustic wave (SAW) detection [20–23]. A number of these methods (i.e., MS and IMS) have been used as stand-alone detectors. However, when explosives are present at low levels in complex matrices, positive identification based on a few m/z peaks proves difficult due to the possibility of a number of interfering compounds in the matrix and the lack of a separation step.

Solvating gas chromatography (SGC) [24–26] utilizes packed capillary columns together with the solvating power of carbon dioxide mobile phase. Although packed columns are inherently known for their high retention characteristics, the solvating properties of the mobile phase help promote movement along the column and allow for fast separations under SGC conditions. Instrument requirements are similar to SFC, except that the SFC restrictor at the end of the column is removed, resulting in a pressure gradient along the column. A pressure drop thus exists from supercritical conditions ($>$72 atm for carbon dioxide; 1 atm$=$101 325 Pa) at the column inlet to 1 atm at the outlet, which significantly increases the mobile phase linear velocity compared with SFC, while still taking advantage of the mobile phase solvating properties for rapid analyte elution. The benefits of SGC for rapid separations of nitroaromatic compounds have been described [27]. SGC is also capable of separating a wide variety of compounds, including polar and other environmentally-related analytes [28,29].

The fundamental operating principles of the chemiluminescence TEA have been described previously [8]. Briefly, nitrosyl radicals formed during pyrolysis of the nitro-containing analytes are reacted with ozone to form a nitrogen dioxide molecule in an electronically-excited state. During relaxation back to the ground state, a photon is emitted which is then detected using a photomultiplier tube (PMT). This allows for sensitive and specific detection of nitro-containing species, and is ideal for explosives detection, most of which contain nitro functional groups. With this detection technique, compounds without nitro functional groups, which may be present in the sample, do not contribute to the analytical signal.

In this paper, we describe the coupling of SGC with a chemiluminescence TEA for the selective identification of NG and other nitro-containing explosives. Since SGC is most commonly used with flame ionization detection (FID), the SGC–TEA detector response was compared with SGC–FID using an NG standard solution. Soil samples containing NG obtained from a sand pit used for the training of law enforcement officers were also extracted and analyzed.

2. Materials and methods

2.1. Chemicals

Standard explosives were purchased from Supelco (Bellefonte, PA, USA). Carbon dioxide mobile phase and oxygen for the TEA ozonator were purchased from Scott Specialty Gases (Plumsteadville, PA, USA). Spectra-grade acetonitrile for NG sample extraction and making of the explosives standard solutions was from Fisher Scientific (Fair Lawn, NJ, USA). Soil samples containing NG were obtained from the Federal Bureau of Investigation Academy (Quantico, VA, USA). It has been noted [30] that standard explosives can undergo degradation in as little as a few minutes when exposed to air at ambient temperatures. Thus, all standards and soil samples were kept in the refrigerator until just prior to use, and then returned to the refrigerator as quickly as possible.

2.2. Column materials

Spherical porous (80 Å) 10 μm ODS-bonded silica particles were obtained from Phenomenex

(Torrance, CA, USA). Fused-silica tubing (250 μm I.D.×365 μm O.D.) was purchased from Polymicro Technologies (Phoenix, AZ, USA). Stainless steel zero dead volume unions were from Valco Instruments (Houston, TX, USA).

2.3. Preparation of packed capillary columns

Fused-silica capillary columns (75 cm×250 μm I.D.) were packed using a CO_2 slurry method previously described [31]. Briefly, a 1 m section of fused-silica capillary was fitted with a zero dead volume connector (Valco) with a 2 μm stainless steel screen to prevent loss of the silica particles from the end of the column. The column was placed in a sonicator bath and the silica particles were introduced into a packing vessel. The particles were then slurry packed using supercritical CO_2 from 50 atm to 300 atm until the column was completely filled. The column was then conditioned with sonication at 300 atm for 45 min to allow for further particle settling in the column and then allowed to slowly depressurize overnight.

2.4. Preparation of soil samples

Two soil samples (Federal Bureau of Investigation Academy, 50 g each) were shipped packed in dry ice to prevent analyte decomposition, and were immediately transferred to a refrigerator upon receipt. Sample 1A was a mix of soil and sand found on the surface of the sand pit site, and sample 1B was almost strictly humic soil from approximately 5–8 cm below the surface. A 10-g amount of each sample was placed in a clean, dried, and labeled glass vial fitted with a PTFE-lined cap. Spectra-grade acetonitrile (1 ml) was added and each vial was sonicated in a bath for 15 min to promote partitioning into the organic solvent phase. The contents of the vials were then allowed to settle and the acetonitrile supernatant was transferred to a separate vial where it was then placed in the refrigerator for subsequent analysis.

2.5. SGC–TEA apparatus

SGC–TEA experiments were carried out using a Lee Scientific Model 600 GC/SFC oven with a Lee Scientific Model 600 supercritical fluid syringe pump fitted with a helium actuated A90 rotary injection valve (Valco). The injection volume and injection time were 0.20 μl and 200 ms, respectively. A 5 cm×15 μm I.D. fused-silica capillary (Polymicro Technologies) was used as a split line (12:1 split ratio). The packed capillary column was connected via a stainless steel transfer line which ran from the injection valve to the split connection inside the oven. The detector was a modified TEA Model 543 chemiluminescence detector (Thermedics Detection, Chelmsford, MA, USA) which included a heated transfer line from the oven, a pyrolyzer unit, ozonator, and electronics. Modifications to the TEA were similar to modifications done by Douse [32]. The transfer line between the SGC column and the TEA pyrolyzer unit consisted of a 50 cm length of large bore (530 μm I.D.×700 μm O.D.) fused-silica tubing. The long length of the transfer line was necessitated by the fixed distance between the outlet of the SGC column and the inlet to the pyrolyzer. Data were acquired using a Spectra-Physics SP4270 integrator (Thermo Quest, San Jose, CA, USA). A diagram of the SGC–TEA system is shown in Fig. 1.

2.6. SGC–FID apparatus

SGC–FID experiments were carried out using a Lee Scientific Model 501 SFC instrument with a helium actuated A90 rotary injection valve (Valco) and equipped with an FID system using nitrogen as make-up gas to optimize sensitivity. The injection volume and injection time were 0.20 μl and 200 ms, respectively. A similar 5 cm×15 μm I.D. fused-silica capillary (Polymicro Technologies) was used as a split line (~12:1 split ratio). The packed capillary column was connected via a stainless steel transfer line in a similar fashion to the SGC–TEA instrument. Data were acquired using EZ Chrome version 6.6 (Scientific Software, San Ramon, CA,

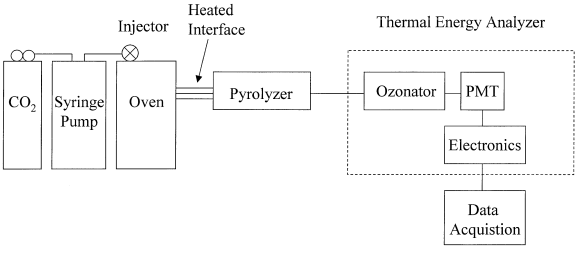

Fig. 1. Schematic of the SGC–TEA system.

USA) with an SS420 analog-to-digital converter (Scientific Software) sampling the FID signal at 60 Hz with an IBM-compatible Pentium 166 personal computer running Windows 95.

3. Results and discussion

3.1. Solvating gas chromatography

One of the principal advantages of SGC is the ability to control mobile phase properties using either temperature or pressure. In open tubular column GC, only temperature is typically manipulated. The added pressure variable for SGC gives the operator an additional tool for method development. At high inlet pressures, carbon dioxide mobile phase possesses increased solvating power and becomes more liquid-like, thus increasing its ability to elute highly retained compounds. This solvating power can be greatly altered by changes in either the column inlet pressure or column temperature, which leads to shortened method development times. An attractive aspect to pressure programming is the ability of a system to rapidly re-equilibrate following the end of a run. Typical oven cool-down times (without cryo accessories) can range between 3 and 10 min depending on the initial and final temperatures. However, newer syringe pumps for carbon dioxide mobile phase have recovery times less than 20 s, leading to increased sample throughput. This may be especially important in military battlefield or deployment situations where rapid sampling and analysis serves primarily as a protective pre-screening technique.

A benefit in coupling SGC to the TEA is that carbon dioxide mobile phase does not give rise to added background noise. Since it does not contain nitro or nitroso functional groups, the limit of detection for the TEA is not increased. In addition, the selective nature of the TEA gives rise to the possibility of using certain organic modifiers in the carbon dioxide mobile phase to elute highly retentive compounds that are not rapidly eluted either by raising the temperature or pressure. Organic modifiers cannot be used with FID due to a significant rise in baseline signal when modifiers such as dichloromethane or methanol are used.

3.2. Identification of NG in soil

Explosive residues close to detonation sites are of particular interest from an environmental standpoint. While persistence of these compounds may represent a threat to the environment, they also are key indicators for forensic studies. Two soil samples from an explosives training ground were obtained to analyze whether NG could be detected in the samples using the SGC–TEA apparatus. Similar samples were previously analyzed using GC–MS and were known to contain NG concentrations ranging in the sub-μg ml^{-1} range. A calibration curve (average peak area of three replicate injections vs. μg NG ml^{-1}) was constructed and showed good linearity for the concentration range of 0.1–0.5 μg ml^{-1}, with a line equation of $y=1.95\cdot10^{5}x-1.53\cdot10^{4}$ and a correlation coefficient $R^2=0.996$. TEA response using SGC for NG determination was obtained in the low pg range, which agrees with data obtained using SFC–TEA with carbon dioxide mobile phase [8]. SFC–TEA sensitivity for other explosives using carbon dioxide mobile phase can be found in Ref. [8].

Each sample extract was analyzed in triplicate using the SGC–TEA instrument, and the average TEA response was recorded. The RSD for sample injections was approximately 5%. Fig. 2 shows a chromatogram for soil sample 1A with a signal-to-noise (S/N) ratio of approximately 90:1 and a peak area corresponding to 0.158 μg ml^{-1} (260 pg injected) of NG. Sample 1B had an NG concentration of 0.207 μg ml^{-1} (340 pg injected).

3.3. Separation of explosives mixtures with TEA detection

Nitroaromatic compound detection is of interest because high explosives such as 2,4,6-trinitrotoluene (2,4,6-TNT), as well as its degradation products such as 2,4-dinitrotoluene (2,4-DNT) and 2,6-dinitrotoluene (2,6-DNT), can be found in surrounding areas following a detonation. Coupled with the selectivity of the TEA, nitroaromatics can be rapidly separated and identified at low levels. An SGC separation of nitroaromatic compounds in approximately 4 min using neat carbon dioxide as mobile

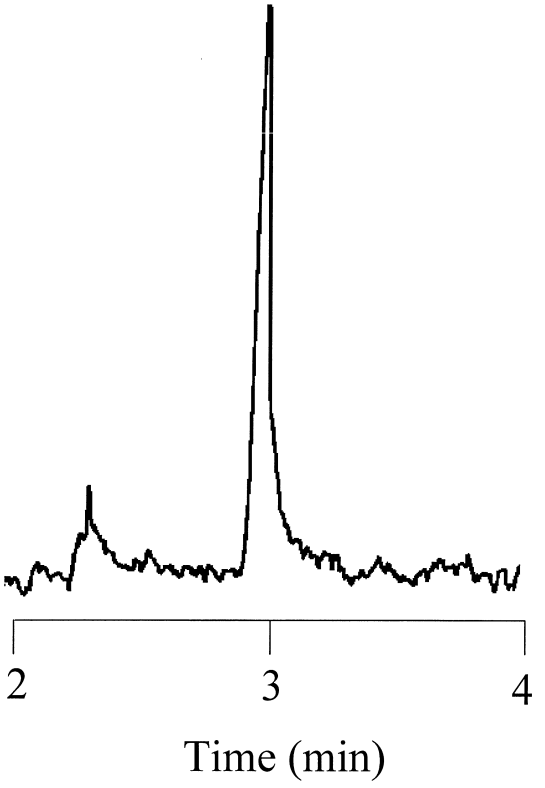

Fig. 2. SGC chromatogram of NG contained in soil sample 1A (S/N~90:1). Conditions: 65 cm×320 μm I.D. column packed with ODS-bonded porous (10 μm, 80 Å) particles, neat CO_2 mobile phase, 250 atm, 130°C isothermal oven, 740°C pyrolyzer, 250°C transfer line, 200 nl injection, 12:1 split ratio.

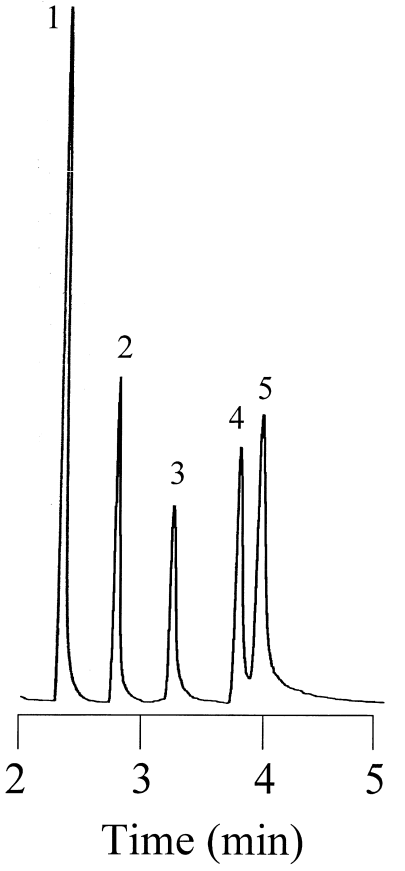

Fig. 3. SGC separation of a standard explosives mixture. Conditions as in Fig. 2. Injected amounts: 0.33 μg NG, 3.3 μg all others. Peaks: (1) nitroglycerine, (2) 2,6-dinitrotoluene, (3) 2,4-dinitrotoluene, (4) 2,4,6-trinitrotoluene, (5) pentaerythritol tetranitrate (PETN).

phase and the TEA as a selective detector is shown in Fig. 3.

Peak tailing was evident in all chromatograms obtained with the SGC–TEA system (see Figs. 2 and 3). When the same packed column was placed in an SGC–FID instrument, no peak tailing was observed. Thus, the tailing is most likely attributed to the fused-silica transfer line between the outlet of the SGC column and the pyrolyzer. As was mentioned earlier, the 50 cm transfer line was fixed due to the configuration of the TEA.

3.4. SGC–TEA versus SGC–FID

In a previous study of explosives using SFC–TEA, the TEA exhibited detection limits in the low pg (10^{-12} g) range [8]. All SGC studies to date, except one, have used FID [24–29] due to the ease of use of FID and its broad applicability to a wide variety of compound classes. In general, FID has a reported sensitivity of ~10^{-13} g s^{-1} and a linear dynamic range of over seven orders of magnitude [33]. However, for rapid separations of ultra-trace compounds having very narrow peak widths, this level of mass flow sensitivity may not provide adequate detection.

To compare the detection capability for low levels of NG using both SGC–FID and SGC–TEA systems, a standard NG sample containing 0.40 μg ml^{-1} was introduced (0.2 μl injection), which corresponds to ~6 pg on-column after taking into consid-

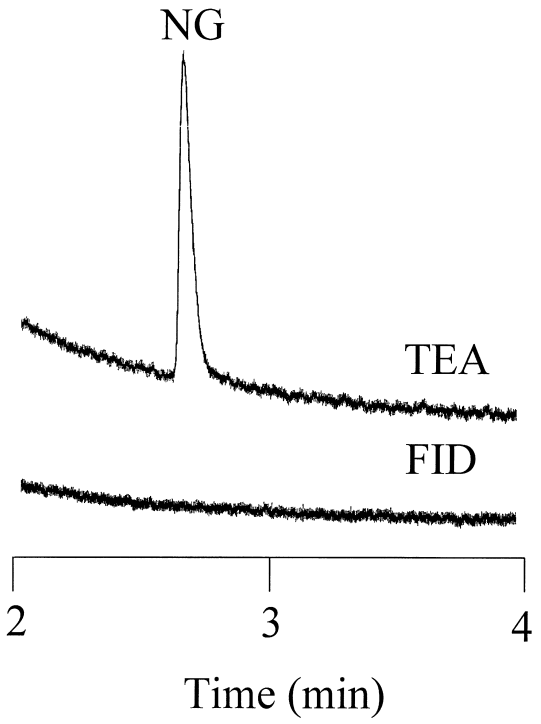

Fig. 4. Chromatograms of standard NG obtained using TEA and FID (0.0004 mg ml^{-1}). Conditions as in Fig. 3.

eration the split ratio (12:1). Both systems used the same column, split line, inlet pressure and temperature. Fig. 4 compares the two signals obtained. The TEA gives a strong NG peak with S/N ~32:1, while FID failed to detect the compound. The peak width at half maximum ($w_{1/2}$) is approximately 4 s (base width=8 s), necessitating an FID sensitivity of 0.75 pg s^{-1} for detection, which is near its limit of detection. SGC is capable of performing separations with half-height peak widths on the order of 200 ms, thus, for sensitive and selective detection of compounds such as NG or nitroaromatics, a detector with increased sensitivity over FID, such as the TEA or mass spectrometer, is required.

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