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Separation and identification of smokeless gunpowder additives by capillary electrochromatography

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ABSTRACT

This paper details a method for the separation and identification of fourteen organic compounds commonly found as constituents in commercial smokeless powders using a hexyl acrylate-based porous monolith. Capillary electrochromatography (CEC) coupled to UV and time of flight-mass spectrometry (TOF-MS) methods were both explored. The CEC–UV method provides an effective and efficient method for the detection of all components in the additive package of the powder. The TOF-MS procedure provides better sensitivity and selectivity allowing an additional confirmation of the presence of the subset of those compounds, which are detectable via positive and/or negative ion electrospray ionization mass spectrometry. Both methods were used for the analysis of smokeless powder components in a mixed standard as well as in the determination of the composition of the additive package of individual powders.

1. Introduction

Smokeless gunpowder is commonly used as a propellant for rifle and handgun ammunition. Based on nitrocellulose, it is manufactured worldwide and is readily available in bulk for sportsmen interested in reloading shells for application such as hunting and competitive target shooting. Because of the ease of purchase of smokeless powders, they can readily be diverted for use in improvised explosive devices. For example, of the pipe bomb incidents reported to the US Bureau of Alcohol, Tobacco, Firearms and Explosives between January 2005 and November 2009, at least 37% were reported as having smokeless or black powder as the explosive charge. It can be critical to identify the type and source of the powder following such an incident in order to determine the perpetrator of the bombing. Luckily, it is common for many unburned flakes of smokeless powder to be thrown clear of the device during the blast and these particles may be characterized if found. Morphology and chemical composition are key factors in the characterization of the various types of powder utilized in these devices.

There are three different classes of smokeless powder. Single-base powders contain only nitrocellulose. Double-base powders contain nitrocellulose and nitroglycerin; and triple-base powder contains nitrocellulose, nitroglycerin, and nitroguanidine. The class of smokeless powder used for small arms is generally double-base powder, and its energetic components are typically nitrocellulose and nitroglycerin. Rifle powders typically are single-based powders and may contain dinitrotoluene instead of nitroglycerin. In addition to the energetic components, modern smokeless powder formulations include stabilizers, plasticizers, flash suppressants, deterrents, opacifiers, and dyes.

Stabilizers present in the powder scavenge the nitric and nitrous acids produced by the decomposition of nitrocellulose and nitroglycerin. If left to accumulate, nitric and nitrous acids can catalyze a decomposition reaction in the powder. Interestingly, the concentration and variety of these nitrated stabilizers present in a powder may be used as a measure of its age or lot number [1,2]. For example, diphenyl amine, a common stabilizer, will react to produce a variety of nitro and nitroso diphenyl amines. As a result, determination of the identity and concentration of these products is an important component of any analytical or forensic assay. Other common stabilizers include methyl and ethyl centralites [3].

Plasticizers reduce the need for the use of volatile solvents during the formation and extrusion of the powder. Phthalates are common plasticizers and nitroglycerin, although the primary energetic material in smokeless powder, also functions as a plasticizer. Alkali or alkaline earth flash suppressants reduce muzzle flash when a weapon is fired. Deterrents and opacifiers are surface coatings that modulate the burn rate of the individual grains and enhance the burn reproducibility and efficiency of the powder, and dyes are sometimes added to assist in the visual identification of some

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brands of powder [3]. The sum of these additional components which are added to the nitrocellulose polymer is known as the additive package and can vary from one powder to the next, depending on the manufacturer's desired combustion rate and formulation.

Given the implications for law enforcement and national security organizations, considerable work has been devoted to the identification of smokeless powders by characterizing the additive package [4–8]. The ultimate goal is to identify the source of the smokeless powder found at a bombing scene by detecting the number and type of additives used in the manufacture of the powder. Characterization of age or lot number may also be possible in certain situations. In addition, the presence of smokeless powders on skin or clothing can be used as an indication that that individual has been in the presence of a fired weapon.

Many different procedures have been developed for the determination of components in smokeless powder, and a thorough review has been done by Meng and Caddy [9]. Because of the importance of proper identity of the components in the powder, chromatographic methods are commonly used for these samples. For example, gas chromatography coupled to flame ionization detection (FID) or mass spectrometry (MS) have been used for characterization of smokeless powders but require tight control of injector temperature. Otherwise, nitrated organic compounds such as nitroglycerin and nitrosodiphenyl amine may undergo thermal decomposition in the heated zones of the gas chromatograph [10]. To overcome the limitations imposed by gas chromatography, high performance liquid chromatography (HPLC) and HPLC–MS techniques have also been developed [8,11]. A significant amount of research has also been performed using capillary electrophoresis procedures [12,13]. However, since free zone capillary electrophoresis techniques cannot separate neutral molecules present in a sample, micellar electrokinetic chromatography (MEKC) techniques were developed [14,15]. MEKC based procedures can provide enhanced resolution of isomeric nitrotoluenes and nitrated diphenyl amines when compared to liquid chromatography. In a series of papers, the research group of MacCrehan and Northrop have demonstrated that capillary electrophoresis in the MEKC mode is an effective method for the analysis of these components in smokeless powders [14–16]. Unfortunately, coupling MEKC to mass spectrometers is awkward due to the use of non volatile surfactants in the buffer. There have been a few reports in the literature discussing interfacing of MEKC based methods to mass spectrometry using partial filling techniques, complex control of solute charges, pH, and wall effects; however, such techniques may be difficult to implement on a regular basis [17,18].

Capillary electrochromatography (CEC) is a hybrid of liquid chromatography and capillary electrophoresis that uses a fused silica capillary with a diameter of 50–100 μm that has been filled with a stationary phase. Due to embedded charges in the wall and on the stationary phase, the mobile phase can be electroosmotically driven with lower diffusion than is found in pressure driven systems [19]. The partitioning of the analytes between the mobile phase and stationary phases as well as differences in electrophoretic mobilities result in highly efficient separations. CEC has been applied to the study of explosives using both packed columns [20] and sol-gel stationary phases [21], but the explosives analyzed by the technique have so far been limited to high explosives such as nitroaromatic and nitramines.

The goal of this project was to develop a method for the analysis of smokeless powders using monolithic CEC that would be compatible with MS detection. In addition, we were interested in determining if monolithic CEC system could provide the high resolution necessary to separate geometric isomers of dinitrotoluene and nitrodiphenyl amine, which can aid in the determination of lot to lot variations in the composition of powders. Also, CEC methods may permit preconcentration of the sample, improving the sensitivity of the assay [22].

2. Materials and methods

2.1. Reagents and materials

Fused-silica capillaries with an inner diameter of 75 μm and a UV-transparent coating were purchased from Polymicro Technologies (Phoenix, AZ, USA). Hexyl acrylate (HA), 1,3-butanediol diacrylate (BDDA), 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS), 2,2′-azobisisobutyronitrile (AIBN), trimethoxysilylpropyl acrylate, and smokeless powder additive standards (Fig. 1) were obtained from Aldrich Chemical (St. Louis, MO, USA). Diphenylamine standard was purchased from Acros Organics (Morris Plains, NJ, USA).

2.2. Monolith preparation

Monolithic columns were prepared following a method adapted from Ngola [23]. A polymerization solution was prepared using 1380 μl hexyl acrylate and 590 μl 1,3-butanediol diacrylate. To this was added 0.0145 g AMPS and 4 μl trimethoxysilylpropyl acrylate. A sodium phosphate buffer was made from a solution containing 3 mM sodium dihydrogen phosphate and 4 mM disodium hydrogen phosphate, adjusted to pH 6.8 with a 1.0 M sodium hydroxide solution. The porogenic mixture was composed of 3 parts by volume acetonitrile, 1 part by volume ethanol, and 1 part by volume sodium phosphate buffer. The monomer mixture was mixed with the porogen in a 1:2 ratio and 9.4 mg of the radical photoinitiator AIBN were added to the solution. The mixture was sonicated to remove dissolved air, leaving a clear solution.

The capillary was pretreated by flushing with acetone for 10 min and then with 1.0 M sodium hydroxide for 1 h before treating the inner wall with 20 μl trimethoxysilylpropyl acrylate in 1 ml 6 mM acetic acid for one hour. The capillary was then rinsed with deionized water for 30 min before being dried with a flow of nitrogen gas [24]. One end of the capillary was immersed in the polymerization solution, which was pushed through the capillary using pressurized nitrogen.

After filling, the ends of the capillary were sealed and a 1 cm piece of aluminum was wrapped around the capillary at the location of the UV window. The capillary was then placed under a 365 nm UV lamp (UVP, Upland, CA, USA) for 1 h at room temperature to initiate polymerization. After curing, the capillary was cut to the appropriate length and installed into the CE instrument (Agilent, Santa Clara, CA, USA). To remove residual monomer and porogen, a gradual voltage from 0 to 30 kV was applied to the capillary for 1 h and then the voltage was kept at 30 kV for 5 h (or until the baseline was stable) with an eluent made of 80% acetonitrile–20% phosphate buffer. Both ends of the capillary were pressurized with 10 bar of nitrogen gas to avoid bubble formation within the column during this step. When switching to CEC–MS, an additional short conditioning was performed with a gradual voltage from 0 to 30 kV for 30 min and then held at 30 kV until the current was stable. A pressure of 2 bar was applied on the inlet side of the capillary during this step. The column was conditioned on a daily basis prior to injection of the samples. This was performed by passing a freshly prepared eluent made of 75% acetonitrile–25% phosphate buffer through the column until the current and the baseline were both stable.

2.3. Instrumentation

Separation of the smokeless powder standards and samples was performed using an Agilent G1600AX CE instrument with