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Developing a Quantitative Extraction Technique for Determining the Organic Additives in Smokeless Handgun Powder

ABSTRACT: Compositional analysis of the organic additives in smokeless handgun powder can provide forensic information to associate known and questioned samples. A reliable method for the quantitative extraction of smokeless powder additives would strengthen these measurements. To achieve quantitative recovery, both supercritical fluid extraction (SFE) and ultrasonic solvent extraction (USE) were evaluated as candidate techniques. Following a detailed evaluation of the solvent choice, the recovery of spiked additive compounds, and the effect of the powder matrix, a reliable USE technique was developed. When quantitative USE recovery of the target analytes, nitroglycerin (NG), diphenylamine (DPA), and ethyl centralite (EC), is coupled with additive measurement by micellar capillary electrophoresis (CE), compositional information can be obtained in less than 1 h.

KEYWORDS: forensic science, capillary electrophoresis, diphenylamine, ethyl centralite, gunpowder, nitroglycerin, supercritical fluid extraction, ultrasonic solvent extraction

The recovery and determination of the organic components in explosives and propellants is of particular interest to forensic and military analysts. For forensic work, the determination of the organic additives in smokeless powder residues, such as nitroglycerin (NG), diphenylamine (DPA), and ethyl centralite (N,N'-diethyl-N,N'-diphenylurea, EC), can be an excellent indication of the discharge of a firearm or the detonation of an explosive device. The organic additives in smokeless powder particles and gunshot residues (OGSR) have been extracted both qualitatively and semi-quantitatively (1–5). Qualitative determination of the presence of specific additives in a questioned sample is frequently used in conjunction with other independent methods, such as a morphological examination (6,7), for identification against known smokeless powder libraries. Recently, we have found that quantitative evaluation of additive composition can provide an added dimension to identification of both powders and handgun residues (1,2). We feel that quantitative measurements in forensic analysis can provide richer and more defensible information on a questioned sample, strengthening the value of such evidence in a court of law.

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For the military, recovery of high-energy explosives and propellant compounds by extraction is a more environmentally friendly means of disposing of surplus materials, rather than the traditional methods of open burning or detonation (8). Effective extraction and analysis techniques for smokeless powder and explosives have also helped the military more rapidly evaluate the stability of the energetic materials (9–15).

At the National Institute of Standards and Technology (NIST) we are currently evaluating the accuracy of smokeless powder compositional measurements by conducting an interlaboratory "round robin" measurement comparison exercise with two test handgun powder samples among both forensic and military participants. In order to assign a NIST value to these samples, we needed to develop a robust extraction method that provides quantitative additive recoveries.

Supercritical fluid extraction (SFE), in which a supercritical fluid (most commonly CO_2) is used to extract samples at elevated temperatures and pressures, has been investigated as an extraction method for propellants and explosives (9,11,12,14–17). Quantitative recovery of DPA and its nitrated derivatives from single-base powders has been studied (14,15). Thomas and Willson (15) evaluated SFE temperature and modifier addition and concluded that supercritical CO_2 modified with acetone was successful in achieving quantitative data for a majority of the stabilizer compounds. Other propellant extraction studies were aimed at providing qualitative results only; extraction procedures were not optimized for quantitative recoveries (9,11,12,16,17).

Direct solvent extraction has also been used to separate the additives from the matrix (5,8,11,13,18). In these studies, smokeless powder is placed in a solvent, typically dichloromethane or acetonitrile, and is stirred or allowed to stand for periods of several hours to two days. No quantitative data were presented in these studies.

A promising technique for smokeless powder extractions is ultrasonic solvent extraction (USE) (1,3,8). Typically, the sample is ultrasonically agitated in a solvent for a short period of time, after which the extract is analyzed. Ultrasonic agitation disrupts and dissolves solid samples, providing high, localized temperatures without bulk heating of the sample (19). USE is fast and easy to perform, and allows samples to be processed in parallel. However, recovery of the target analytes has not been thoroughly evaluated in previous studies (1,3,4). No detailed evaluation of the factors influencing USE additive recoveries has been made.

Smokeless powder is composed primarily of nitrocellulose (NC) propellant and may also contain additional propellants, such as NG. Stabilizers, such as DPA or EC, are added to neutralize the acidic nitrogen oxide decomposition products of NC and NG (20). The in-

dividual particles are coated with graphite to reduce static sensitivity. The manufacturing process determines how each of these is incorporated into the powder, with the goal of achieving specific burn rates (20).

The extraction protocol must be compatible with the final analysis procedure to be employed. Our method for this determination has been capillary electrophoresis (CE), which requires the sample extracts to be dissolved in a water-based detergent solution. This limits the range and amount of organic solvents that can be used for the extraction. Since NC is insoluble in water, a solvent system must be chosen that inhibits the complete dissolution of the NC yet still is able to extract the other polar analytes from the NC matrix. Large amounts of dissolved NC should be avoided since it precipitates on the addition of the CE run buffer, clogs the capillary, and affects the micellar separations.

The extraction technique must also minimize nitration reactions between the additives. When a powder is allowed to stand, particularly in extreme heat, NC and NG will release nitrogen oxides, which will in turn attack the stabilizers (13,21–23). As the powder ages, the stabilizers are nitrated by the free acid products and nitrous gases, producing such compounds as aromatic nitro and N-nitroso-derivatives. Care must be taken in the extraction process to avoid artifactual decomposition of NC and NG and subsequent reactions with the stabilizers.

We evaluated both SFE and USE to achieve quantitative recovery of the organic additives found in smokeless powder. Commercial reloading powders were extracted under a variety of conditions to optimize the recovery of the additives, NG, DPA, and EC.

Materials and Methods[3]

Reagents and Standards

Cellulose nitrate, with a similar nitrogen content to smokeless powder (12.5%), was purchased from Aldrich Chemical Company (Milwaukee, WI), and graphite was obtained from The Asbury Graphite Mills, Inc. (Asbury, Warren County, NJ). Trimethylchlorosilane and pyridine (both from Pierce, Rockford, IL) and dichloromethane (J.T. Baker, Phillipsburg, NJ) were used to silanize glassware for an SFE experiment. The buffer solution for the capillary electrophoresis (CE) was composed of 25 mmol/L sodium dodecyl sulfate (SDS) (sequanal grade, Pierce) and 10 mmol/L sodium borate buffer, pH 9.2, in Milli-Q water (Millipore, Bedford, MA) or HPLC grade water (J.T. Baker). Standards containing the additives, NG, DPA, and EC, in methanol (AccuStandard Inc., New Haven, CT) were diluted with the CE buffer for calibration. Crystalline standards of EC and DPA (both from TCI, Portland, OR) were dissolved in methanol for the spiking experiments. The internal standards for the CE and SFE, 2-methyl-6-nitroaniline (MNA) (Fluka, Milwaukee, WI) and 4-iodonitrobenzene (pINB) (TCI), were also dissolved in methanol.

Gunpowder

Commercial handgun powders distributed by Alliant (Radford, VA), IMR Powder Company (Washington, PA), Vihtavouri Oy (Lapua, Finland), and Winchester (Primex Technologies, St. Marks, FL) were purchased in 0.23 kg (1/2 lb) to 0.45 kg (1 lb) can-

[3] Certain commercial equipment, instruments, or materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

isters. Powder obtained in more than one container was combined and thoroughly mixed to ensure homogeneity before withdrawing samples.

Capillary Electrophoresis Analyses

All analyses were performed on a CE system with fixed wavelength detection at 214 nm and computer-based data collection software (Beckman P/ACE 5510, Brea, CA). Bare silica capillaries (Hewlett-Packard, San Fernando, CA) were used with an extended path length (200 μm window diameter), 75 μm inner diameter, and an overall length of 77 cm. A controlled temperature bath maintained the samples at 10°C during the CE analysis. Other conditions were as follows: 1 s pressure injection with a separation at 22 kV and 30°C for 20 min (1).

Supercritical Fluid Extractions

Extractions were performed on an automated SFE Isco SFX 3560 (Lincoln, NE). Two external pumps worked to deliver pure CO_2 (SFC/SFE grade CO_2, Air Products, Allentown, PA) and liquid solvent modifier blends. To prevent any photodecomposition of the analytes and internal standards, samples were shielded from direct light by a cardboard and black felt cover that surrounded the SFE. When the samples were removed from the SFE, the vials were covered with aluminum foil.

Quantities (12 mg) of powder were weighed into extraction cartridges, and two strands of Teflon® wool (Alltech, Deerfield, IL) were then placed on top of the propellant to serve as the support for 10 μL of added SFE internal standard. Vessels containing only the Teflon® wool, empty cartridge blanks, and cartridges with powder standards spiked onto the wool were also extracted on the SFE.

Smokeless powder samples were initially extracted with conditions previously developed in our laboratory (24): 2 min static extraction and 50 min dynamic extraction with neat CO_2 at 70°C and 40.5 MPa (400 atm) with a restrictor temperature of 60°C. The extracts were depressurized and collected by liquid trapping in 10 mL of acetonitrile (J.T. Baker) and 10 μL of ethylene glycol (Eastman Kodak Company, Rochester, NY). Attempts to develop optimal temperature and pressure conditions for quantitative recovery will be briefly discussed here and can be found in more detail elsewhere (25). Extracts were concentrated at 30°C under a stream of nitrogen. The samples were dried to the ethylene glycol residual, and 250 μL of the CE buffer and 5 μL of the CE internal standard were added. The solution was vortex-mixed for 10 s, transferred to a 2 mL centrifuge tube, and then centrifuged for 5 min. A portion of the supernatant (200 μL) was transferred to a vial for CE analysis.

Ultrasonic Solvent Extractions

An ultrasonic bath (Branson, Shelton, CT) was used for the ultrasonic solvent extractions. Extraction solvents were 2-butanol and unstabilized tetrahydrofuran (both from Fluka, Milwaukee, WI), HPLC grade methanol and acetonitrile (both from J.T Baker), n-propanol (American Burdick and Jackson, Muskegon, MI), ACS grade 2-methyl-1-propanol (Fisher, Fairlawn, NJ), and HPLC grade glyme (1,2-dimethoxyethane) (Sigma-Aldrich). Either 10 mg of smokeless powder, 10 mg of nitrocellulose, or approximately 0.10 mg of graphite were weighed into a sealed 15 mL centrifuge tube, and 1.0 mL of solvent was added. The sample was vortex-mixed for 10 s and agitated in the ultrasonic bath at 0°C, 25°C, or 50°C for 5 min, 15 min, or 45 min. The mixture

was again vortex-mixed for 10 s and then centrifuged for 5 min. A 40 μL portion of the extract was added to 500 μL of the CE buffer and 10 μL of the internal standard. After this solution was vortex-mixed for 10 s, 200 μL was transferred to a CE vial for analysis. Sample preparation and extraction were performed under incandescent lighting.

The majority of the samples were analyzed in triplicate. To determine recovery correction factors, samples were extracted in replicates of ten. Concentrations of the additives in mg/L were calculated based on the internal standard method, using the peak area counts from a smokeless powder additives standard, an internal standard, and the samples. Average mg/g concentrations, with respect to the total matrix, and standard deviation of the mean were determined where noted.

Results and Discussion

SFE Recovery Collection Efficiency

The SFE recovery of the smokeless powder components in the absence of the gunpowder matrix was examined by spiking a standard solution onto a nonadsorptive matrix, Teflon® wool, and using the initial SFE conditions with pINB as the internal standard. Only 30% to 70% of the standard components were extracted. The observed losses were then investigated, beginning with the amount of ethylene glycol added to the collection vials to prevent losses associated with dryness on evaporation (4). Results from these experiments showed that the amount of ethylene glycol did affect analyte recovery (25). The addition of 40 μL of ethylene glycol was the most desirable, providing maximal analyte recoveries without deleterious effect on CE peak shape.

We consistently found the recovery of the internal standard, pINB, to be 50% or less, regardless of the ethylene glycol volume. A change in color of the crystalline standard from white to brown upon storage indicated the compound might be photosensitive and subject to decomposition. We evaluated the effect of light on pINB by exposing a mixture of the components to different light sources (25). All of the smokeless powder additives, NG, DPA, and EC, as well as the internal standard, were photo-degraded when exposed to a low pressure mercury lamp. For all subsequent experiments, care was taken to minimize photodecomposition losses by reducing the light exposure of the samples. A cardboard shield was constructed around the SFE apparatus, and samples stored for CE analysis were wrapped in aluminum foil. The extremely labile pINB internal standard was replaced with the less sensitive MNA for these studies. However, in subsequent work we have discovered difficulties with the solubility of MNA in the solvent system. We have been investigating the use of the water-soluble compound, quinazoline, as internal standard. Based on its solubility, separation from the analytes, and solution stability, quinazoline appears to be a suitable internal standard.

SFE recoveries of the smokeless powder standard components were improved by optimizing the ethylene glycol concentration and decreasing the light exposure, however, less than 90% recoveries were still noted. Although salinization was previously used to eliminate losses of these analytes on glassware (26), we found no significant difference in the recovery of the analytes from glassware treated with a 10% trimethylchlorosilane solution (25).

Optimizing SFE Conditions for Smokeless powder and Standards

With the recovery of spiked standards approaching 90%, we then evaluated conditions for the recovery of the native analytes

from a smokeless powder matrix containing NG and EC as the major additives. To evaluate the completeness of a single extraction, the extraction was repeated and evaluated. In addition, as carryover of the additives was previously noted, the SFE method was modified to include extraction of a blank cartridge between test samples (25).

Evaluating the effect of temperature on additive recovery between 70°C and 130°C revealed the presence of significant amounts of unrecovered analytes in the second extract (25). At higher temperatures (120°C and 130°C), we noted an increase in the proportion of nitrated stabilizer from reactions with propellant nitrogen oxide products. Because of these reactions, extraction at 110°C was the most efficient (Fig. 1).

Using the optimum temperature of 110°C, we then investigated the effect of extraction solvent composition and pressure/solvent density on recovery. According to work previously performed in our laboratory, acetonitrile, in limited quantities, was a more suitable modifier than methanol (24). However, care had to be taken in modifier addition, as 20% acetonitrile modifier dissolved the powder matrix and clogged decompression transfer lines. The addition of 5% acetonitrile modifier at 15.2 MPa (150 atm) and 40.5 MPa (400 atm) and increasing the pressure of neat CO_2 from 15.2 MPa (150 atm) to 51.7 MPa (510 atm) did not significantly improve the additive recoveries (Fig. 2).

The effect of the dynamic extraction volume passing through the sample was studied by filling the unused portion of the 7 mL cartridge with a solid glass rod. Although the number of solvent exchanges was increased from approximately 7 to 100, additive SFE recoveries were not significantly affected (25).

We additionally evaluated the optimal SFE recovery conditions (110°C and 40.5 MPa (400 atm)) by comparison to a previously developed ultrasonic solvent extraction (USE) method with methanol (3). USE recovered approximately 400% as much NG and 110% as much EC when compared to SFE (Fig. 3). While SFE has been successful at extracting the additives from single-
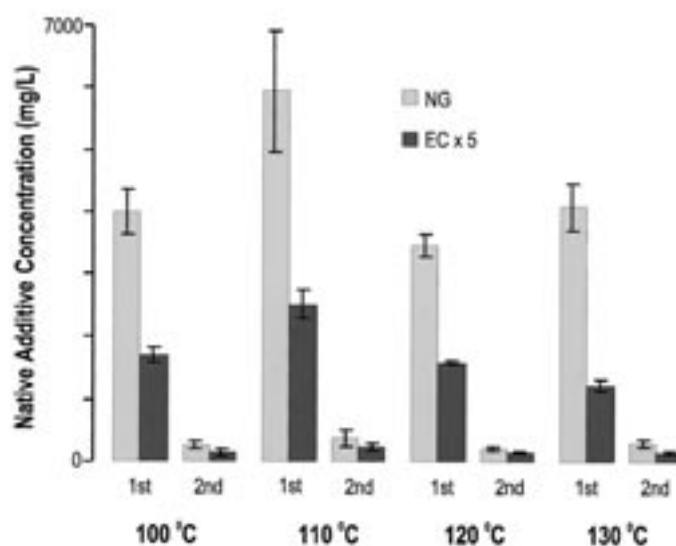

FIG. 1—*Comparison of different SFE extraction temperatures for the first (1st) and repeat (2nd) extractions of native additives in smokeless powder samples. Shaded bars represent mean additive concentrations (mg/L), with the range of concentration values represented by the error bars. EC concentrations are multiplied by 5 to be seen on the same scale as NG. Other SFE conditions included: 2 min static extraction and 50 min dynamic extraction with neat CO_2 at 40.5 MPa (400 atm).*
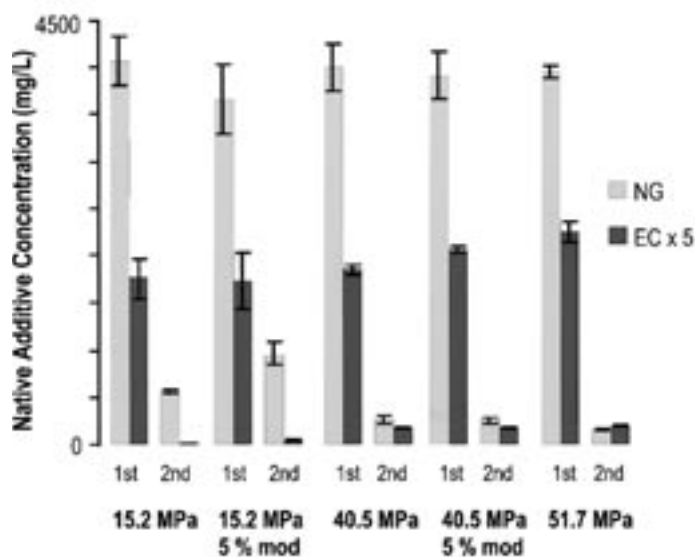
FIG. 2—*Comparison of various SFE pressure and modifier conditions for the first (1st) and repeat (2nd) extractions on the same samples. Extractions were performed with either neat CO_2 or CO_2 modified with 5% acetonitrile. Shaded bars represent mean additive concentrations (mg/L), with the range of concentration values represented by the error bars. Other SFE conditions included: 2 min static extraction and 50 min dynamic extraction at 110°C.*
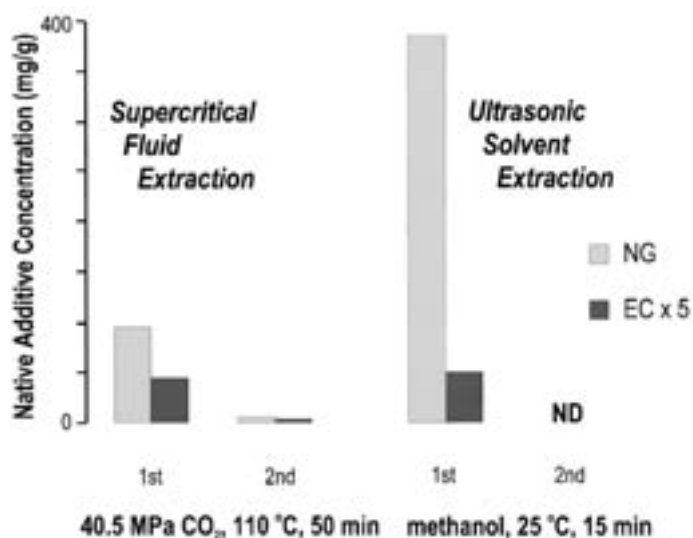

FIG. 3—*Initial differences observed between SFE and USE in the extraction of the smokeless powder additives. No additives were detected (ND) in the second extraction with the USE technique.*

base powders (containing only a stabilizer, such as DPA) (11,14,15), this technique did not prove suitable for quantitative extractions of double-base powders (which contain stabilizer plus an additional propellant, NG). NG may readily react with the stabilizers under the SFE temperature and pressure conditions, affecting recoveries of all additives. Since the SFE recovery parameters were bound by dissolution of the matrix and the nitration reactions at higher temperatures, quantitative recovery with USE was pursued instead of SFE, and a new protocol for smokeless powder extraction was developed (1,25).

Quantitative Recoveries with USE

Since USE gave higher recoveries than SFE, we further evaluated quantitative recovery of the native additives with the USE technique on a smokeless powder sample. A 10 mg sample was extracted twice in 1.0 mL of methanol for 15 min (3). No additives were detected in the second extraction; however, we could not be certain that the first extraction had recovered 100% of the additives. Standard additive solutions were then spiked onto the powder and extracted with methanol for 15 min. The recoveries were less than 100% in both the first and second extractions. We subsequently investigated the factors affecting USE recovery.

To determine where the observed losses were occurring in the extraction protocol, an additive standard solution was spiked onto two different smokeless powders (Powder 1 containing NG and EC and Powder 2 containing NG and DPA) before extraction, after extraction but before centrifugation, and directly into the CE run buffer without extraction. No losses of the additives were observed from those standards spiked into the CE run buffer, but significant losses (10% or more) were noted for the standards spiked onto the powder before and after USE.

The effect of the smokeless powder matrix was further examined by studying its two major components, NC and graphite. These model matrix components were added in amounts comparable to those expected in powder samples. NC, with similar nitrogen content to smokeless powder, was added in 10 mg quantities to extraction tubes. Graphite was added to separate extraction vials in 0.10 mg portions, which were representative of the amounts (0.1% to 1.0%) used in powder coatings. Standard solutions were spiked onto each of these materials and extracted in 1.0 mL of methanol for 15 min. Both NC and graphite had an effect on the recovery of the additives, but NC seemed to inhibit the recoveries to a greater extent.

A number of extraction solvents were evaluated to maximize recovery from the model matrix components, including: acetonitrile, 2-butanol, 2-butanol:methanol (1:3), glyme, methanol, 25 mmol/L SDS in methanol, 2-methyl-1-propanol, n-propanol, and tetrahydrofuran (Fig. 4). To correct for any viscosity effects on the amount of the residual solvent injected into the CE, each solvent system was referenced to a calibration standard prepared with the same solvent. Although recoveries with 2-methyl-1-propanol were the largest, it was not considered further because of its formation of an immiscible solvent layer with NC during the extraction process, and its limited solubility in the run buffer.

2-Butanol appeared to be a promising extraction solvent, with recoveries generally above 90% for both model matrices. To determine if 2-butanol was able to extract the additives from a real matrix, standards from crystalline DPA and EC were prepared and spiked onto smokeless powder. The DPA standard was spiked onto a powder without DPA (Powder 1), while a powder that did not contain EC (Powder 2) was spiked with an EC standard. We then further investigated extractions with 2-butanol, comparing the results with methanol.

During a methanol extraction, smokeless powder samples would either completely dissolve or swell in the solvent. In the 2-butanol extraction, there was no dissolution or swelling of the matrix. For the extraction to be successful, it was necessary for the powder to swell or dissolve slightly, but not completely. While the percent recoveries for the spiked material were approximately 92%, the recoveries of the native additives in the powders were much lower than those obtained with methanol. These powders should have contained between 200 mg/g and 300 mg/g of NG and between 6
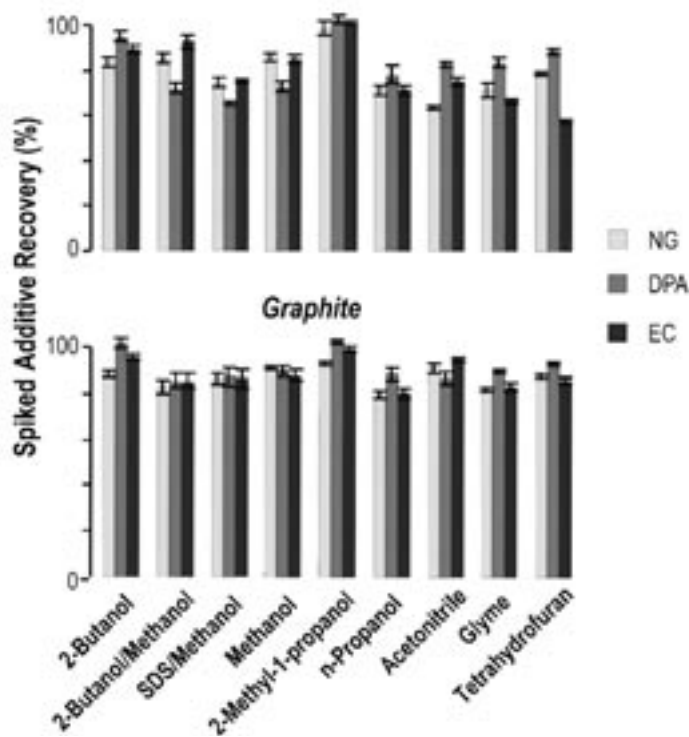
FIG. 4—*Comparison of different USE solvent systems on the extraction of spiked standard additives from nitrocellulose and graphite. Error bars represent two standard deviations of the mean.*

FIG. 5—*Comparing the extraction of the native additives from smokeless powder using methanol and 2-butanol:methanol (1:3). Powder 1 and Powder 2 are the materials for the interlaboratory comparison exercise. Error bars represent two standard deviations of the mean. Shaded bars of EC and DPA represent concentrations multiplied by a factor of 5.*

TABLE 1—*The effect of USE extraction time and temperature on the recovery of the native additives from Powders 1 and 2. Data represent the mean concentration recovered in mg/g and (mean standard deviation).*

USE Condition	Powder 1 (mg/g)		Powder 2 (mg/g)	
	NG	EC	NG	DPA
Temperature				
0°C	263 (4)	8.9 (0.1)	187 (1)	5.28 (0.02)
25°C	281 (1)	10.1 (0.2)	189 (2)	5.31 (0.05)
50°C	278 (6)	10 (1)	186 (1)	5.5 (0.1)
Time at 25°C				
5 min	278 (4)	9.6 (0.5)	198 (4)	5.3 (0.1)
15 min	287 (3)	9.7 (0.2)	198 (1)	5.25 (0.02)
45 min	284 (9)	9.5 (0.5)	192 (2)	5.0 (0.1)

mg/g and 10 mg/g of either EC or DPA (1). Instead, each had recoveries of less than 90 mg/g of NG and less than 3 mg/g of the stabilizers. Because of the disparity in the concentrations of native additives recovered from the powder, it was apparent that the simulated matrix of NC and graphite was not a complete representation of the properties of the smokeless powder matrix.

Since 2-butanol and methanol seemed to complement each other in their extraction qualities, a simple visual observation was made to determine if a combination of these two solvents might provide appropriate extraction behavior. The two powders were extracted for 15 min in 1.0 mL of 2-butanol:methanol (1:3, 1:1, and 3:1) and examined to observe the extent of dissolution or swelling. The higher the concentration of 2-butanol, the less the powder appeared to swell or dissolve. It appeared that the more NC that dissolved, the greater the interference on the complete extraction of the additives. A solvent system that minimized but not entirely eliminated the dissolution of NC was desirable. 2-Butanol:methanol (1:3) provided good matrix swelling and was investigated further for its USE recovery.

Single component standards of NG, DPA, and EC were spiked onto three different powders that did not contain each respective additive. These samples were extracted for 15 min with methanol and with 2-butanol:methanol (1:3). There was a significant increase in the amount of the spiked additives that were extracted using 2-butanol:methanol over those extracted with only methanol. Mean recoveries (% recovery $\pm$ 1 SD/$\sqrt{n}$, $n = 3$) for spiked NG, DPA, and EC with methanol were 88% $\pm$ 1%, 88% $\pm$ 2%, and 90% $\pm$ 1%. Using 2-butanol:methanol (1:3) as the extraction solvent, mean recoveries of spiked NG, DPA, and EC were 96% $\pm$ 2%, 99% $\pm$ 1%, and 100% $\pm$ 2%. An increase was also observed in the concentrations of the native additives recovered with 2-butanol:methanol (Fig. 5).
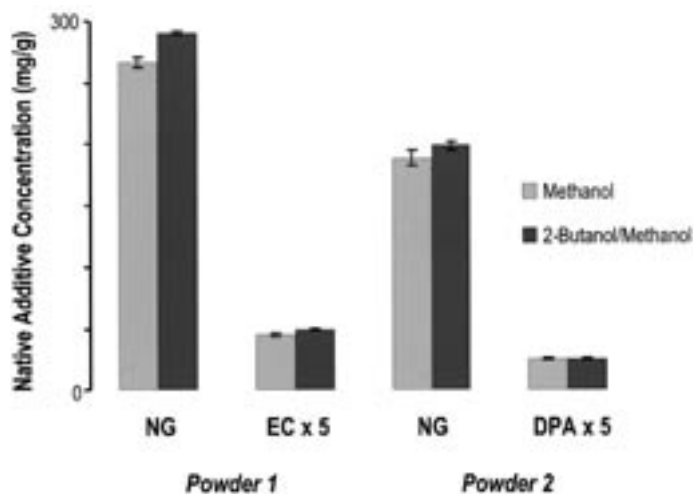
We evaluated the robustness of the 2-butanol:methanol (1:3) USE technique by examining the effect of extraction time and temperature on the recovery of the additives. Portions of Powders 1 (containing NG and EC) and 2 (containing NG and DPA) were extracted for 5 min, 15 min, and 45 min. No significant differences were observed in the recoveries of the additives at the three extraction times for all smokeless powder compositions (Table 1). An extraction time that is too short, such as 5 min, may not sufficiently dissolve or swell the matrix (25), while an extended extraction time might induce nitration reactions between the analytes via the high effective energy available with ultrasound (19). We concluded that the most desirable extraction time for the handgun powders was about 15 min, although shorter or longer extraction times did not significantly affect the recovery of the additives. Subsequent investigations of a ball-type rifle powder demonstrated that longer extraction times are needed to achieve complete extraction of all additives. Additive recovery should be complete in these type powders in a 75 min extraction with this solvent system. In the evaluation of unknown smokeless powder samples, a 75 min extraction is recommended.

The effect of temperature was then investigated by extracting smokeless powder samples with 2-butanol:methanol (1:3) for 15 min at approximately 0°C, 25°C, and 50°C. While a slight increase

in NG and EC concentration was observed at 25°C for Powder 1, there were no significant differences between the three temperatures (Table 1). As mentioned before, elevated extraction temperatures might increase the proportion of stabilizer derivatives and inhibit complete recovery of the additives. A lower extraction temperature may also limit the ability of the solvents to swell the matrix. We chose to continue extracting at 25°C, but the extraction recoveries were not sensitive to temperatures from 0°C to 50°C.

Frequently in analytical studies, extraction recovery factors are carefully evaluated and reported. However, seldom are these known recovery factors used to correct the determined values on unknown samples. Given that we chose very realistic smokeless powder matrix samples that were free of selected analytes to use as model matrices for spiking experiments, we could be confident in using recovery correction factors to achieve a more accurate determination of the native analytes. We determined the recovery factors for the optimized USE conditions by spiking known amounts of NG, DPA, and EC into three different smokeless powders that were free of the respective target analyte. The mean recoveries ($n = 10$) for NG, DPA, and EC were found to be: 96% ± 1%, 95.6% ± 0.3%, and 98% ± 1%. These factors will be used in all future calculations to correct the recoveries of the native additives from the gunpowder.

Conclusions

In order to develop a quantitative extraction of the organic additives from smokeless powder, supercritical fluid and ultrasonic solvent extraction methods were extensively evaluated, examining the effect of parameters such as temperature and solvent systems on recovery. While SFE was an attractive technique because of its automation possibilities, quantitative recoveries of the target analytes were not achieved. Possible reactions between NG and/or NC with the stabilizers, the potential for dissolution of the NC matrix accompanied by clogging of transfer lines, and carryover of NG to subsequent samples contributed to our abandonment of SFE as an extraction method for the smokeless powder samples.

USE proved to be a highly suitable technique for the extraction of the smokeless powder additives. An extraction protocol was developed that involved a 15 min extraction in 2-butanol:methanol (1:3) at room temperature. This solvent system minimized any NC interferences and maximized the recovery of the additives. Recovery factors were then determined for correcting that value assignment.

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