J Forensic Sci, Mar. 2004, Vol. 49, No. 2
Paper ID JFS2003219
Available online at: www.astm.org

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New Developments in SPME Part 2: Analysis of Ammonium Nitrate-based Explosives

ABSTRACT: Solid-phase microextraction (SPME) followed by gas chromatography-mass spectrometry (GC-MS) is a simple, reliable technique for the recovery and analysis of many organic explosives. However, this technique is impractical for the analysis of ammonium nitrate-type explosives due to the extreme polarity, low molecular weight, and high volatility of the amine moiety. This article describes an initial investigation of a derivatization process utilizing alkylchloroformates that converts ammonium nitrate and methylammonium nitrate into a form suitable for recovery by SPME and analysis by GC-MS.

KEYWORDS: SPME, explosives, ANFO, ammonium nitrate, methylammonium nitrate, GC-MS, ethylchloroformate, *n*-butylchloroformate, (−)-menthylchloroformate

Solid-phase microextraction (SPME) and gas chromatography-mass spectrometry (GC-MS) are accepted techniques for the recovery and analysis of many organic explosives (1–3). In that field, the technique has been shown to be rapid, capable of low detection limits, and extremely simple. Furthermore, as concentrated and dirty liquid extracts are not injected into the chromatograph, SPME-based analyses offer the potential for lower column and injector liner contamination, and therefore more reliable chromatographic performance over a larger number of injections.

Although SPME coupled to GC-MS is an extremely useful technique for the recovery and identification of many explosives traces in post-blast debris, it is not universal. For example, there are no reports of its application to the analysis of the ammonium nitrate-based explosives such as ammonium nitrate-fuel oil (ANFO), watergels, and slurries. While SPME is an impractical choice for recovery of ammonia or ammonium, GC-MS is an equally impractical technique for their identification. The low molecular weight of ammonia results in minimal retention on most common, low polarity phases, and necessitates data acquisition from a very low initial scan mass. As a consequence, recovery of ammonium nitrate traces from bombing debris has been limited to conventional solvent (usually aqueous) extraction, while identification has been accomplished by relatively specialized techniques such as ion chromatography (4) and capillary zone electrophoresis (5–7), or simple colorimetric tests (8).

The emergence of alkylchloroformates as reagents for the derivatization of primary and secondary amines (9), even in aqueous, polar, or protic solvents, offered the potential for a new analytical strategy for amine salt explosives residues contained in wet debris or aqueous extracts. The findings described here represent a preliminary investigation to establish whether high molecular weight alkylchloroformates could influence the recovery, chromatography, and mass spectrometry of amine salt explosives to such an extent that SPME followed by GC-MS would be feasible. As both SPME and GC-MS are well-established techniques for the recovery and identification of volatile hydrocarbons (2,10), this raised the possibility that SPME-GC-MS might be a comprehensive technique for the analysis of ANFO-type explosives, with not only the explosive ingredients but also the fuel oil being amenable to analysis. The ability to analyze ammonium nitrate-based explosives using GC-MS would be a benefit because this technique is widely available to forensic scientists, and it has a better level of discrimination than either ion chromatography or capillary ion electrophoresis.

In principle, derivatization-SPME can be performed in three modes: in-situ derivatization, where the analyte is mixed with the derivatization reagent then after an appropriate time the derivatized analyte is recovered by SPME; and two on-fiber modes whereby the analyte and the derivatization reagent are mixed within the SPME fiber. Instead of the sequential technique, it was decided to pursue on-fiber derivatization-SPME as this approach offered reduced consumption of derivatization reagent, the potential for better limits of detection, and better time-efficiency.

On-fiber derivatization-SPME involves exposing the fiber to the analyte, then exposing it to the derivatization reagent before desorption in the usual fashion (11–14). In this way, derivatization can take place immediately on the fiber, or within the injection port. According to Koster (15), it is also possible to rearrange the sequence of events so that the fiber is exposed to the derivatizing reagent before the analyte. Not only can this alternative mode of on-fiber derivatization-SPME be a more time-effective solution, it can offer better limits of detection in the case of low molecular weight analytes. If derivatization takes place within the fiber, and if the fiber is loaded with derivatization reagent before it is exposed to the analyte, then the situation arises whereby the analyte becomes "trapped" on the fiber. This takes place because the equilibrium between the analyte external to the fiber and the analyte within the fiber will be perturbed towards the latter because in the fiber the analyte is in its derivatized form, which will have a lower vapor pressure and lower water solubility. This phenomenon has been described by Koster (15).

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Received 21 June 2003; and in revised form 13 Sept. 2003; accepted 12 Oct. 2003; published 4 Feb. 2004.

This article describes an initial investigation into the scope and limitations of on-fiber derivatization-SPME-GC-MS as applied to recovery and identification of ANFO-type explosives.

Materials and Methods

Reagents

Ethylchloroformate [1], *n*-butylchloroformate [2], and (−)menthylchloroformate [3] were purchased from Aldrich Chemical Co. Inc. (Milwaukee). Specimens of Riogel 2 (ERT Explosives, South Australia) and Nitrex (Total Energy Systems, Western Australia) were obtained from Sgt M Thomas of South Australia Police Forensic Section.

Equipment

Gas Chromatography/Mass Spectrometry (GC-MS) was performed on a Hewlett Packard 5890A chromatograph using a ZB-1 column (30 m × 0.25 mm × 0.5 μm fused silica) with a Hewlett Packard 5971 series mass selective detector operating in the EI mode (70 eV) at a temperature of 310°C. The scanning range was 35–350 Da at a rate of 2.2 scans/s, a maximum sensitivity autotune was used routinely. Helium was employed as the carrier gas at 20 psi, which corresponded to a carrier gas linear velocity of 31.3 cm/s at 100°C. The injector temperature was set at 250°C; splitless mode was used. The oven was maintained at 35°C for 3 min, then heated at a rate of 40°C per minute up to 280°C, then maintained at that temperature for 2.5 min.

GC-MS was also performed on a Hewlett Packard 6890 chromatograph using a DB-1 column (15 m × 0.257 μm × 0.25 μm fused silica) with a Hewlett Packard 5973 mass selective detector operating in the EI mode (70 eV) at a temperature of 300°C. The scanning range was 35–350 Da at a rate of 2.2 scans/s, a maximum sensitivity autotune was used routinely. Helium was employed as the carrier gas, splitless mode and a pressure pulse of 20 psi for 30 s were employed followed by constant flow of carrier gas (either 64 cm/s for conditions A, or 61 cm/s for conditions B) throughout the temperature program. The injector temperature was set at 250°C; the oven was maintained at 35°C for 3 min, then heated at a rate of 10°C per minute up to 280°C, then maintained at that temperature for 2.5 min.

SPME

All fibers and SPME holders were purchased from Supelco (Bellefonte, PA). Unless specified otherwise, all experiments described below utilized 85 μm polyacrylate-coated fibers.

On-fiber SPME-derivatization of Ammonium Nitrate and Methylammonium Nitrate: Recovery from Aqueous Media

A solution of ammonium nitrate in water (0.5 mL, 1 mg/mL) was treated with an equal quantity of a solution of sodium hydroxide in water (1 mg/mL) in a 2 mL GC vial. The SPME fiber was immersed in the liquid for 1 min, exposed to the headspace above any of the three derivatizing reagents (10 μL) in a GC vial for 30 s, then thermally desorbed in the injection port of the GC-MS.

Recovery from Headspace

A solution of ammonium nitrate in water (0.5 mL, 1 mg/mL) was treated with an equal quantity of a solution of sodium hydroxide in water (1 mg/mL) in a 2 mL GC vial. The fiber was exposed to the headspace above the liquid for 1 min, exposed to the headspace above any of the three derivatizing reagents (10 μL) in a 2 mL GC vial for 30 s, then thermally desorbed in the injection port of the GC-MS.

On-fiber SPME-derivatization of Ammonium Nitrate and Methylammonium Nitrate: Absorption Kinetics and Limits of Detection

Six solutions of ammonium nitrate and six solutions of methylammonium nitrate (0.5 mL, 1 mg/mL) were each basified with an equal quantity of a solution of sodium hydroxide in water (1 mg/mL). The SPME fiber was loaded with derivatizing reagent by exposing it to the headspace above n-butylchloroformate (10 μL) for 30 s, then immersed in one of the solutions of ammonium nitrate and methylammonium nitrate over six different time frames (1–60 min). The fiber was then thermally desorbed in the injection port of the GC-MS and the level of analyte recovery for each absorption time was calculated simply by measuring the chromatographic peak areas of the carbamate derivatives.

Solutions of ammonium nitrate and methylammonium nitrate in water (1 mg/mL) were basified with an equal quantity of sodium hydroxide solution (1 mg/mL) and then serially diluted (1:10) to yield solutions of various concentrations between 1 mg/mL and 1 ng/mL. The SPME fiber was exposed to the headspace above *n*-butylchloroformate (10 μL) for 30 s, and then to the headspace above each of the test solutions, starting with the most dilute, for 20 min at room temperature before analysis using GC-MS (the kinetics test described above indicated 20 min to be optimal). The limit of detection for the derivatized amines was reached when the intensity of the 62 Dalton ion (for ammonium nitrate) or 58 and 76 Dalton ions (for methylammonium nitrate) extracted from full scan data at the appropriate retention times achieved a value 3 times greater than the peak-to-peak background noise. The limits of detection were also measured using the same procedure as described above at 60°C.

In-situ Derivatization-SPME of Ammonium Nitrate and Methylammonium Nitrate: Limits of Detection

The six solutions of ammonium nitrate and methylammonium nitrate described in the previous experiment (1 mL) were treated with *n*-butylchloroformate (2 μL), sonicated at room temperature for 10 min, then subjected to liquid-phase SPME for 20 min at room temperature. GC-MS and estimation of the limits of detection were performed as described previously.

Recovery and Analysis of Explosives Exemplars

Solutions of Riogel and Nitrex in water (1 mL, 1 mg/mL) were treated with equal quantities of sodium hydroxide solution (1 mg/mL). The SPME fiber was exposed to the headspace above *n*-butylchloroformate (10 μL) for 30 s, and then to the headspace above each of the test solutions for 20 min at room temperature. GC-MS was performed using conditions A for Riogel and conditions B for Nitrex.

Cleaning of SPME Fibers

No special routine cleaning protocol was followed. Instead, the fiber was left in the injection port after thermal desorption for the

entire chromatographic run, or at least 10 min. If this procedure was followed, carry over was effectively eliminated.

Results and Discussion

Although several SPME stationary phases were assessed as to their efficacy, all the results discussed below apply to the 85 μm acrylate phase. Stableflex carbowax/divinylbenzene exhibited the best overall extraction, by a small margin, but that stationary phase was prone to "stripping" and we cannot recommend it; Wittmann (16) reported a similar experience.

Both ammonia and methylamine, generated by basification of their nitrate salts, reacted with ethyl-, *n*-butyl- and (−)-menthylchloroformate (structures [1], [2], and [3], Fig. 1) in aqueous solution under the influence of sonication to yield carbamate derivatives (structures [4], [5], [6], [7], [8], and [9], Fig. 1). All derivatives could be recovered using solution-phase SPME and analyzed using GC-MS.

In aqueous solution, derivatization using ethylchloroformate was least efficient by about an order of magnitude, while *n*-butyl- and (−)-menthylchloroformate were approximately equipotent. The detection limit for recovery of ammonia using *n*-butylchloroformate with an extraction time of 20 min was 1 μg/mL, while the limit for methylamine was 10 ng/mL. Figures 2, 3, and 4 show the mass spectral data and postulated fragment ion structures for derivatives of methylamine and ammonia. Derivatization using either *n*-butylchloroformate or ethylchloroformate is an effective, unambiguous way of discriminating between ammonia and methylamine; not only can the derivatives be distinguished using their retention times, their mass spectral data are also clearly distinguishable (see Figs. 2, 3). Although the (−)-menthyl derivatives of ammonia and methylamine can be separated chromatographically, their mass spectra are not distinguishable. Figure 4 is a mass spectrum representative of these two compounds, together with postulated structures for major ions. As can be seen, it would appear that the ions detected are formed by loss of fragments containing the amine moieties originating from the explosives, hence electron impact mass spectrometry cannot be used for discrimination. Hammarstrom (17) has reported previously that other menthyl derivatives behave similarly. (−)-Menthylchloroformate is therefore not recommended as a derivatization reagent except in circumstances where long retention times are advantageous.

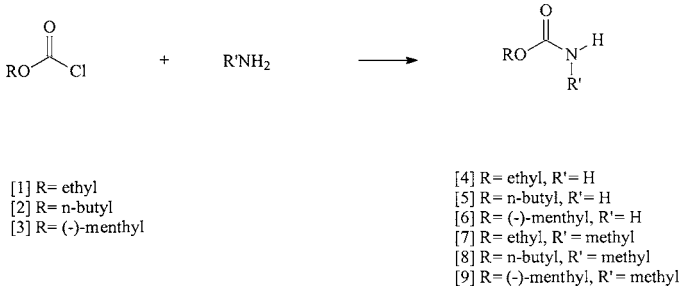

FIG. 1—*Structure.*

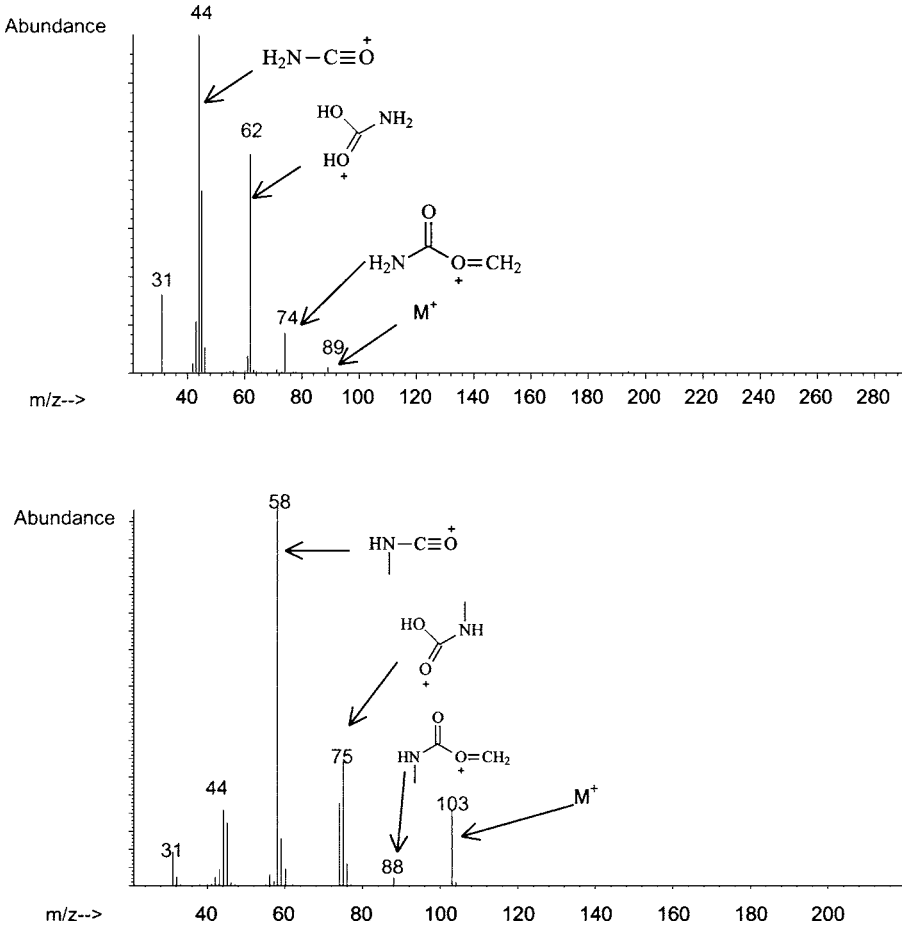

FIG. 2—*Mass spectral data for the ethylchloroformate derivatives of ammonia [4] (top) and methylamine [7] (below), the structures of postulated ion fragments are given.*

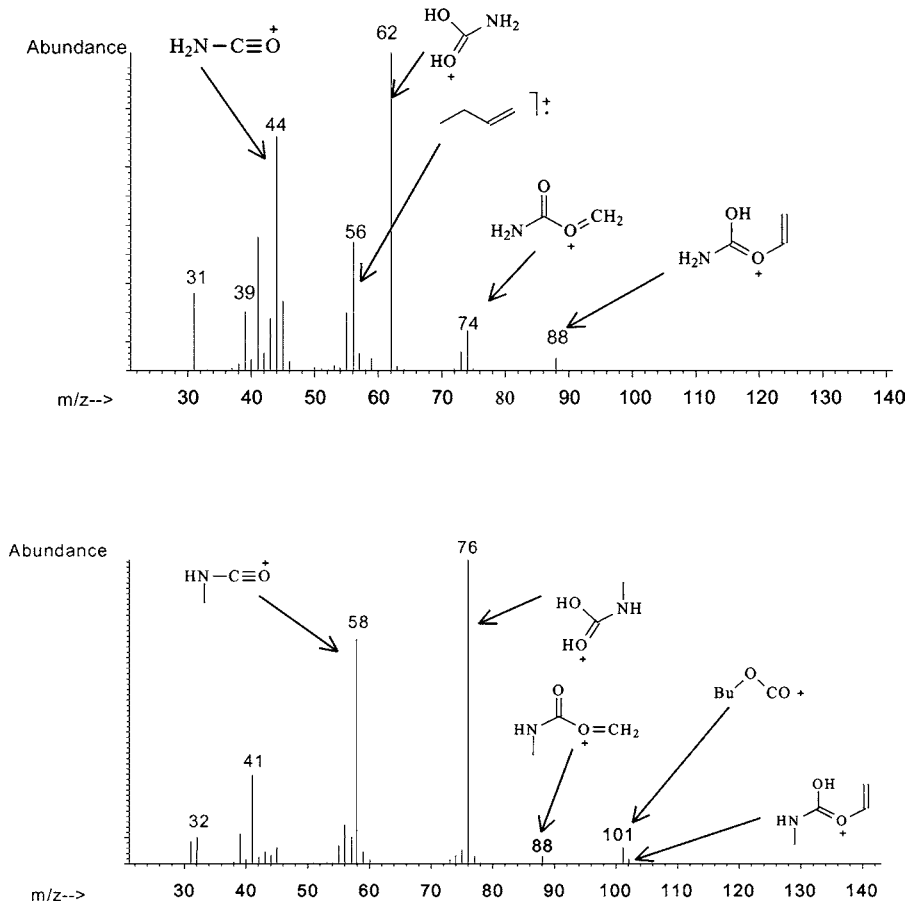

FIG. 3—*Mass spectral data for the n-butylchloroformate derivatives of ammonia [5] (top) and methylamine [8] (below), the structures of postulated ion fragments are given.*

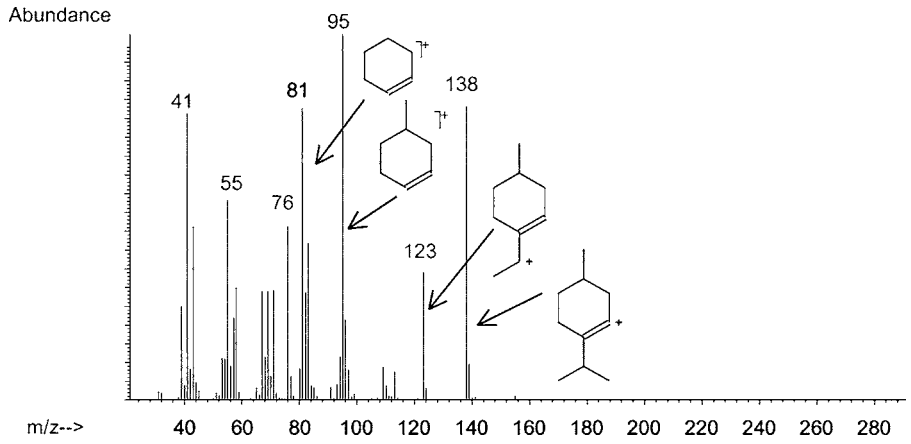

FIG. 4—*Representative mass spectral data for the (−)-menthylchloroformate derivatives of ammonia [6] and methylamine [9], the structures of postulated ion fragments are given.*

When SPME was performed by directly immersing the fiber into basified solutions of ammonium nitrate or methylammonium nitrate in water followed by on-fiber derivatization using ethylchloroformate, *n*-butylchloroformate, and (−)-menthylchloroformate, all but the latter yielded carbamate derivatives. The performances of ethylchloroformate and *n*-butylchloroformate were about equal for recovery of methylamine, but the latter was slightly more efficient for recovery of ammonia.

Ammonia and methylamine could both be recovered from the headspace above basified solutions of their nitrate salts using derivatization-SPME. Ethylchloroformate and *n*-butylchloroformate were both found to be much better than (−)-menthylchloroformate for this task. Derivatization took place irrespective of whether the fiber was exposed to the analyte before the alkylchloroformates, or vice versa. However, when the fiber was exposed to the derivatization reagent first, a two-fold (approximately)

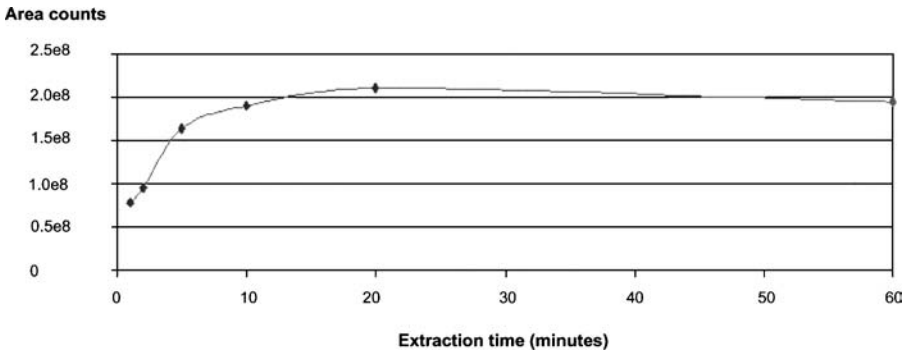

FIG. 5—*Plot of extraction time versus total ion peak area for headspace recovery of methylamine from a basified solution of its nitrate salt in water (1 mg/mL) at 60°C followed by derivatization using n-butylchloroformate.*

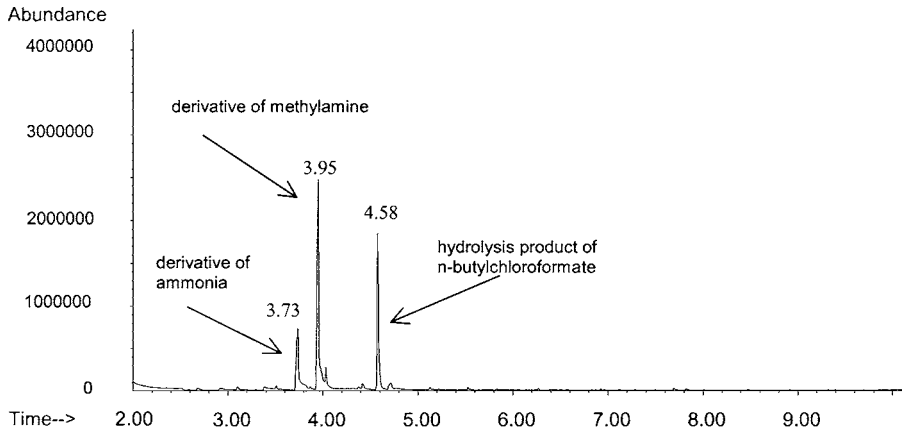

FIG. 6—*Total ion chromatogram (GC-MS conditions A) relating to SPME sampling of headspace above a basified solution of Riogel 2 at 60°C followed by derivatization using n-butylchloroformate. The peak at 3.73 min is due to the derivative of ammonia [5], the peak at 3.95 min is due to the derivative of methylamine [8], while the peak at 4.58 is due to a hydrolysis product of the derivatization reagent.*

increase in recovery was noted. This suggests that derivatization can take place on the fiber with the result that the analyte becomes "trapped" to some extent on the fiber as described earlier. However, it was found that full derivatization does not take place instantaneously on the fiber. When an experiment was conducted whereby the SPME fiber was exposed to ammonia, then exposed to ethylchloroformate, and finally exposed to *n*-butylchloroformate, a mixture of *n*-butyl and ethyl carbamates was formed.

As can be seen in Fig. 5, maximal extraction of explosives from headspace is achieved after about 20 min at room temperature. Even after this time, however, compared to direct extraction from the aqueous phase, headspace extraction results in detection limits 10 and 100 times higher for ammonia and methylamine, respectively.

Two commercial ammonium nitrate-based explosives were analyzed using SPME and on-fiber derivatization using *n*-butylchloroformate. Figure 6 depicts a total ion chromatogram obtained from analysis of a solution of Riogel 2 (a typical emulsion explosive). This explosive contains both ammonium nitrate (about 44%) and methylammonium nitrate (about 25%) as well as sodium nitrate (about 11%), aluminum dust (about 5%), water (about 11%), and cross-linking compound (about 4%). Presumably the latter acts as fuel because fuel oil is not present in this explosive. As commented upon above, the detection limit for methylammonium nitrate is lower than that for ammonium nitrate, a finding that is illustrated graphically by the relative intensities of the two peaks due to these substances in Fig. 6.

Figure 7 shows total ion and extracted ion chromatograms obtained from analysis of a sample of Nitrex, which is a pre-mixed ammonium nitrate-fuel oil product. Clearly it is possible to recover and detect both the fuel and explosive substances from traces of Nitrex.

Conclusions

A simple, practical method has been developed for rendering the amine moieties present in ammonium nitrate and methylammonium nitrate amenable to recovery by SPME and analysis using GC-MS. This paper presents the first reported instance where these explosives have been characterized using this methodology. This is of significance because GC-MS facilities are usually available to forensic laboratories, and GC-MS has substantially more discrimination power than color tests, ion chromatography, or capillary ion electrophoresis, which are commonly applied to analysis of these explosives. The method involves derivatization of the explosives using either ethyl chloroformate or *n*-butyl chloroformate. It is versatile in that derivatization can be performed on-fiber or in aqueous solution, and SPME can take place either in headspace or aqueous solution. Our experiments have indicated that compared to headspace sampling, sampling of the aqueous phase offers detection limits better by at least an order of magnitude (i.e., about 1.0 μg/mL and 0.1 μg/mL for ammonia and methylamine, respectively). These detection limits are modest, but acceptable. Experiments making use of more

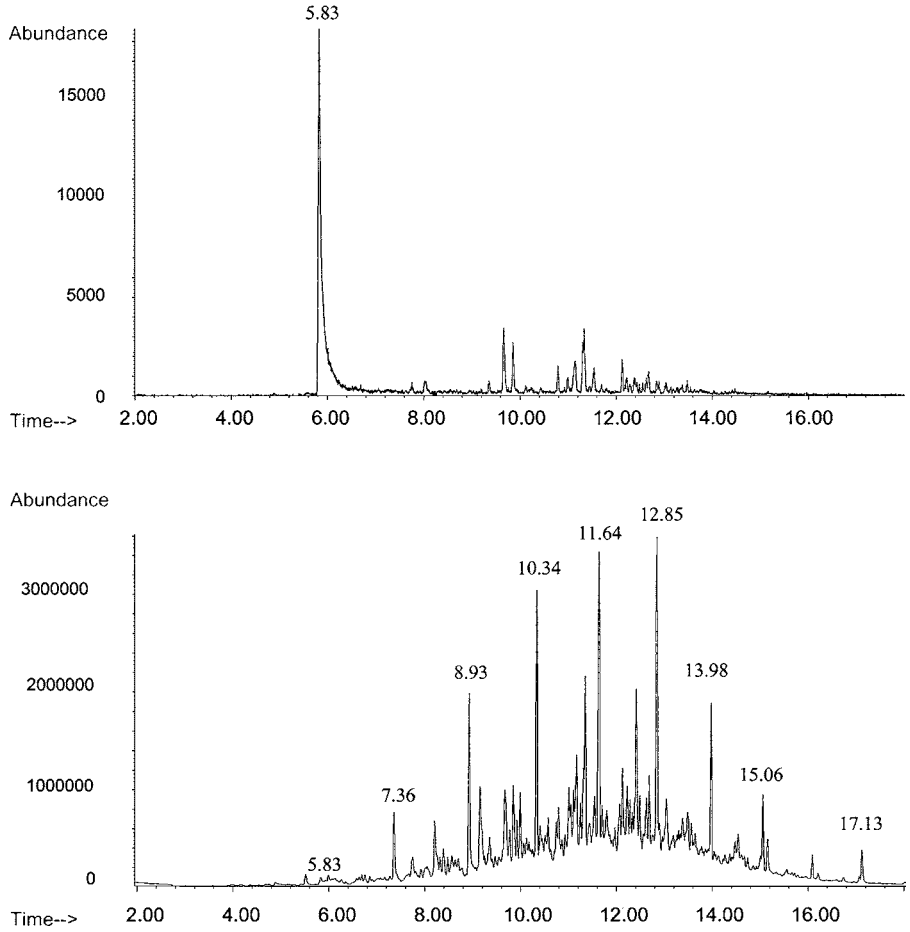

FIG. 7—*Bottom: Total ion chromatogram (GC-MS conditions B) relating to SPME sampling of headspace above a basified solution of Nitrex at 60°C followed by derivatization using n-butylchloroformate. The complex envelope between 7 and 17 min is due to fuel oil. Top: Extracted ion chromatogram derived from the total ion data plotted for the 62 Da ion abundance. The peak at 5.83 min is due to the derivative of ammonia [5].*

modern equipment, such as the 5973 mass selective detector, resulted in detection limits approximately 2 orders of magnitude lower. (−)-Menthyl chloroformate can also be used as derivatizing reagent, however, it is not as versatile as the other two chloroformates, and although the menthyl derivatives of methylamine and ammonia can be resolved by gas chromatography, their mass spectral fragmentation patterns are identical. The technique described here can be readily integrated into standard explosives residues recovery protocols, which usually involve aqueous extraction of debris. All that is required is to raise the pH of the extract above 7 and then either sample the headspace above the extract, or the liquid phase directly.

In bombing cases where ammonium nitrate is detected, a significant issue germane to the investigation is whether it actually originated from an explosive, or naturally from soil. If the source is an explosive, then the issue as to whether the device contained a commercial explosive or an improvised explosive based upon fertilizer becomes relevant. In order to resolve these questions, the discovery of methylammonium nitrate can be of great significance because it is not present in fertilizer, nor is it a natural product in soil. Its presence in bombing debris therefore provides very strong evidence that a commercial explosive was involved, and will allow the exclusion of those explosives that only contain ammonium nitrate. The technique described in this article is a very efficient and highly discriminating test for the detection of methylammonium nitrate.

Although not absolute proof of an explosive, the presence of both fuel oil and ammonium nitrate in debris strongly suggests the involvement of one. The method described allows detection and identification of both ammonium nitrate and fuel oil in one step. Previously two separate tests involving two totally different techniques would have been required to accomplish this. SPME is a particularly effective method for the recovery of hydrocarbons and the discrimination between very closely related petroleum products, as evidenced by its growing involvement in the field of arson accelerant analysis.

Several avenues for decreasing the detection limits further are currently being investigated, for example the impacts of agitating the aqueous phase, adding salt to it, and varying the absorption temperature are being examined.

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