Analysis of Trace Amount of Bank Dye and Lachrymators from Exploding Bank Devices by Solid-Phase Microextraction and Gas Chromatography–Mass Spectrometry

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Abstract

Solid-phase microextraction (SPME) is a fast, solvent-free alternative to conventional sample preparation techniques. This technique involves exposing a fused silica fiber that has been coated with a stationary phase to an aqueous solution or its headspace to selectively extract compounds from their matrix. The fiber is then removed, and the analytes are thermally desorbed in the injector of a gas chromatograph. By sampling from the headspace above sample matrices, SPME can be used to extract target analytes from very complex matrices. In this study, SPME in the headspace is used in developing a method for the dye 1-methylaminoanthraquinone (MAAQ) and two lachrymators: orthochlorobenzalmalononitrile (CS) (tear gas) and 2-chloroacetophenone (CN) (tear gas). The focus is to develop a robust method to minimize sample preparation and to reduce matrix interferences encountered by other extraction techniques. In developing the method, several fibers are studied for their affinity for the compounds of interest. Although this method is developed for qualitative analysis, the extraction time and temperature profile are thoroughly investigated to provide the optimal conditions. The use of a salt solution is evaluated to increase the partitioning of MAAQ into the headspace. Using this method, qualitative extraction is achieved for the analysis of CN, CS, and MAAQ from its matrices. CN and CS are extracted in less than 5 min, though MAAQ needed more than 15 min to achieve a reasonable response. If more sensitivity is required, the use of a salt solution increases the response of MAAQ by 90-fold.

Introduction

A red dye [1-methylaminoanthraquinone (MAAQ)] and tear gases [orthochlorobenzalmalononitrile (CN) and chloroacetophenone (CS)] are used in bank security devices or "dye packs". These devices were invented as a way to nonviolently disrupt a bank robbery by permanently staining the stolen money a bright red color. This alerts people to the fact that the money was stolen. CS and CN tear gases are used as irritants that attack the mucous membranes in the eyes, nose, mouth, and lungs—ideally causing the suspect to abandon the money.

This method was developed with the intention that it may be used for the analysis of these compounds in a wide variety of matrices (plastic, paper, rubber, and cloth materials). The red stain produced by MAAQ on a material provides a visual mark, indicating where one can take a sample for examination. Although the tear gases do not produce a colored stain, an MAAQ stain may also contain tear gases because they can be transferred simultaneously during the deflagration of the security device. In developing a method that emulates a real-life situation, cloth material was spiked with serial dilutions of MAAQ, CS, and CN to provide a guideline for the lower working range from 2 to 200 ppm. Although solid-phase microextraction (SPME) is routinely used to analyze compounds below the level of 2 ppm, such concentrations are not relevant to this study because they correspond to MAAQ levels too low to produce a visible stain.

SPME is a well-established method that has attracted increasing attention for its simplicity, efficiency, precision, and ease of automation. Over the years, SPME has had a significant impact on forensics, food, flavor, and environmental analysis (1–7). Lately, there has been an increase in the use of this technique outside the field of analytical chemistry, such as biologists studying living plants and organisms in the wild (8–11).

By sampling organic analytes from the headspace above the sample matrix, SPME has been used to analyze volatile and semivolatile organics in very complex matrices (12–14). The headspace approach enables one to target analytes from any possible matrix because the fiber is not in direct contact with the matrix. For this method to be effective, analytes must be released from their matrix into the headspace. Volatile analytes tend to partition easily into the headspace, but semivolatile

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and low volatile compounds usually require external forces to be released into the headspace. One such method uses an organic solvent to enhance the release of the analyte from the matrix. However, the simplest and most effective way is the use of heat. Heating the sample to an elevated temperature provides enough energy for analyte molecules to overcome energy barriers, which bind them to the matrix, and as a result increase mass transfer.

Also, the use of salt is known to affect the amount extracted depending on the compound and the salt concentration. In general, salting effects increase with increasing compound polarity. Saturation with salt can be used not only to lower the detection limit, but also to normalize the random salt concentration in natural matrices (15–17).

In this study, the use of temperature and salt played an important role in increasing the partition of the analytes in the headspace. For CN and CS, the use of temperature did not play such a significant role, although the concentration still increased with higher temperature.

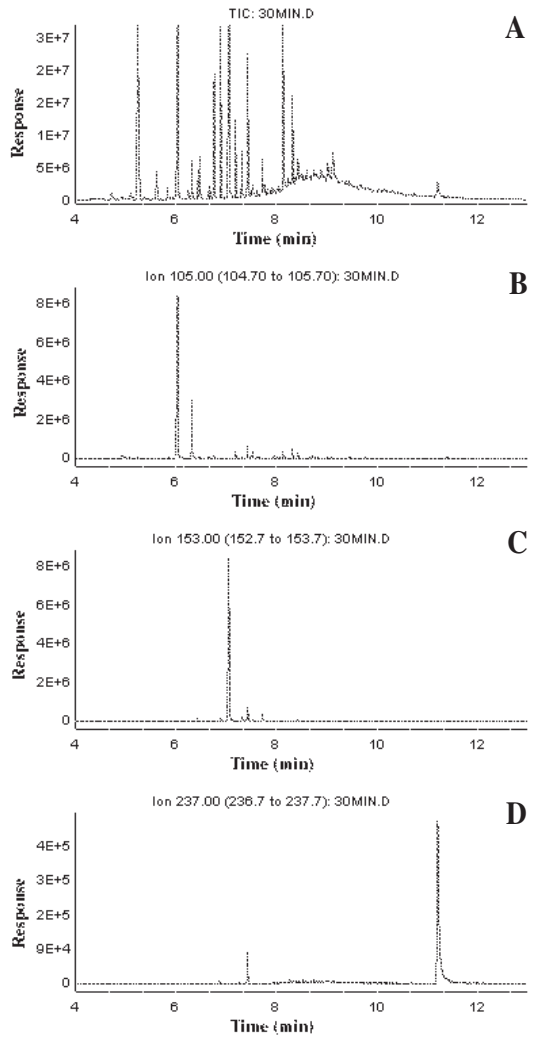

Figure 1. Total ion chromatogram of CN, CS, and MAAQ extracted from a cloth spiked at 100 ppm (A), extracted ion of CN (B), extracted ion of CS (C), and extracted ion of MAAQ (D).

Experimental

Materials

MAAQ and CN were purchased from Aldrich Inc. (Milwaukee, WI) at purities of 98% and 99%, respectively. CS was supplied from M.P. Laboratories, Inc. (Blairville, PA), at a purity of 100%. SPME fibers [100 µm polydimethylsiloxane (PDMS)–divinylbenzene (DVB)–carboxen (CA), 65 µm PDMS–DVB, and 85 µm polyacrylate (PA)] were purchased from Supelco Inc. (Bellefonte, PA). A manual SPME fiber holder and deactivated SPME glass liner (Supelco Inc) were used for all the analyses.

Instrumental analysis

All standards and samples were analyzed using an Agilent Technologies (Palo Alto, CA) 6890 gas chromatograph coupled to a 5973 MSD in electron impact ionization mode (ionization energy, 70 eV). A DB-5MS column (Agilent) with dimensions of 30 m × 0.25 mm × 0.25 µm was used for all experiments. The analysis was done in splitless mode with a constant flow of 1.2 mL/min of helium. The injector port, transfer line, and ion source were maintained at 250°C, 280°C, and 235°C, respectively. The mass spectrometry (MS) system was tuned with perfluorotributylamine by running the autotune program. The MS was run in the scan mode from 35 to 450 amu with a threshold of 150 and a scan rate of 3.50 s^{-1}. For desorption of the PA fiber, an injector temperature of 310°C was used. The oven temperature used for all analyses was from 60°C (held for 2 min) to a final temperature of 260°C with a ramp rate of 35°C/min (held for 15 min).

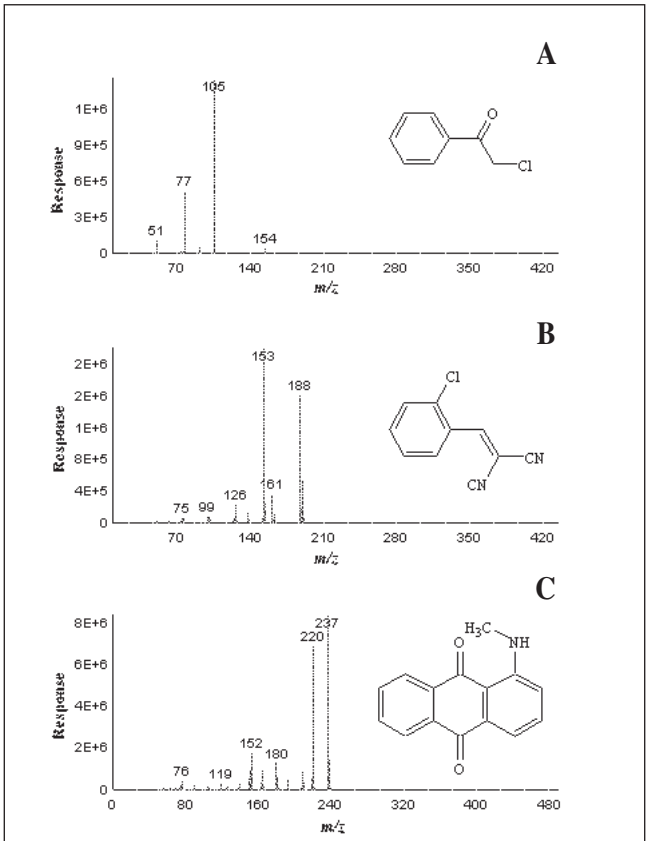

Figure 2. EI spectrum of CN, CS, and MAAQ.

Results and Discussion

Identification

A successful analysis of all the compounds was made with positive identification within a 30-min extraction at temperatures greater than 75°C (Figures 1 and 2). However, for extractions of less than 30 min, the response for MAAQ was significantly less, though CN and CS did not show any significant loss in response. From the beginning of this study, it was known that MAAQ would pose some problems because it is less volatile than the other two compounds. To influence it into headspace would require external forces.

To find the optimal parameters and factors that would provide a successful analysis, the following factors were studied: (*i*) appropriate fibers, (*ii*) extraction temperature, (*iii*) extraction time, and (*iv*) effect of salting.

Fiber comparison

For the selection of a fiber, the general principle of "like dissolves like" applies. As a result, three fibers (PDMS–DVB–CA, PDMS–DVB, and PA) were used because of their ability to extract polar and semipolar compounds. Although this method will not be used for quantitation, the extraction profile was investigated to find the optimal extraction time and appropriate fiber that will provide the maximum response.

For CN, all of the fibers extracted the compound very well. When comparing the fiber, PDMS–DVB and PA extracted CN better than 3× more than PDMS–DVB–CA at the lower extraction time and approximately 2× more at the higher extraction time (Figure 3). It has been known that PA tends to favor polar aromatic compounds (5).

In the extraction of CS, the PDMS–DVB and PA performed just as well as for the extraction of CN (Figure 4). However, at the longer extraction time, it was observed that PDMS–DVB performed better than PA. Compounds tend to have a longer migra-

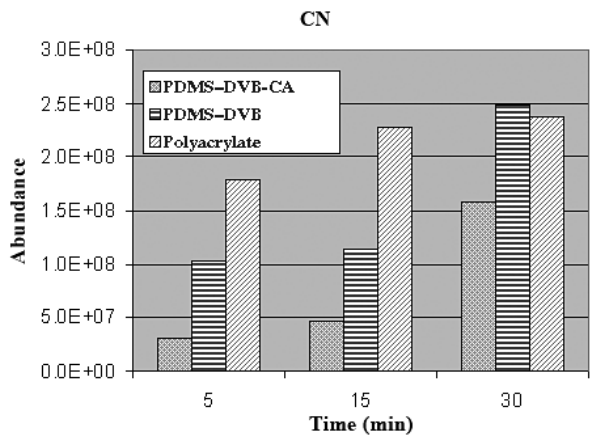

Figure 3. Bar graph depicting average area response (n = 3) versus time for CN using three different fibers from cloth spiked at 100 ppm.

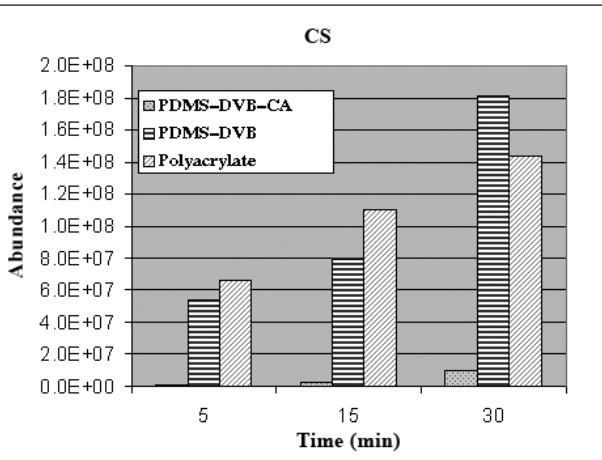

Figure 4. Bar graph depicting average area response (n = 3) versus time for CS using three different fibers from cloth spiked at 100 ppm.

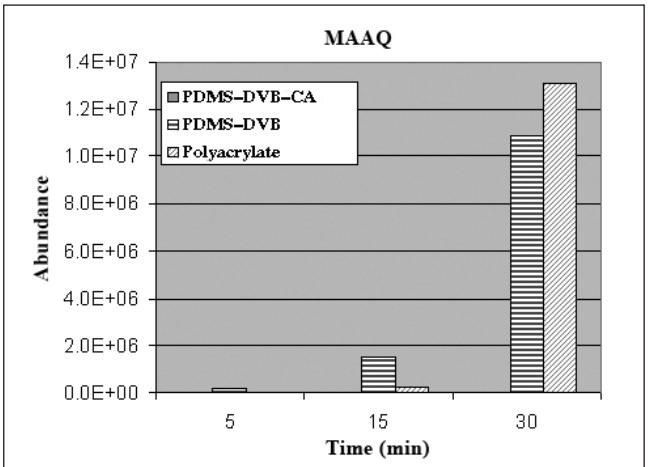

Figure 5. Bar graph depicting average area response (n = 3) versus time for MAAQ using three different fibers from cloth spiked at 100 ppm.

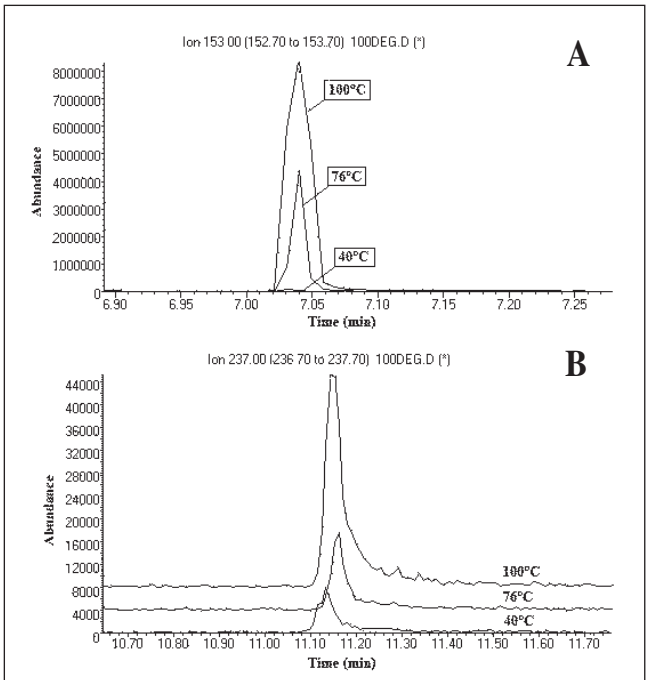

Figure 6. Extracted ion chromatogram showing response of CS (A) and MAAQ (B) with the increase of temperature.

tion time into the PA phase (5,10). PDMS is considered a "liquid-like" phase, which allows compounds to migrate more easily than a more "plastic-like" PA phase. The PDMS–DVB–CA did not perform as well as the other two phases, which is probably because of the CA phase.

For the MAAQ extraction, the factors that influenced the extraction were the length of time the fiber was exposed to the headspace and how fast MAAQ partitioned into the headspace (Figure 5). At the lower extraction time, PDMS–DVB performed better than PA, which can be attributed to the migration into the fiber.

Although PDMS–DVB and PA extracted the analytes by a different process, both fibers exhibited excellent performance. For PDMS–DVB, the extraction process is a combination of absorption and adsorption, respectively, but PA is purely absorption. The liquid phase of PDMS allows compounds to migrate much easier into the coating than PA. The DVB is suspended in the PDMS and works well at a low concentration because of the limited number of binding sites. At a high concentration, this process undergoes competition for the active sites, or compounds are dislodged because of the competition for the active sites.

On the other hand, PA extracts using the absorption process, commonly referred to as the "sponge process". Because PA takes a longer time to absorb the analyte, it also needs a hotter temperature to remove it. This required a temperature of at least 310°C for 5 min to completely remove all the analyte from the fiber. In comparison, the PDMS–DVB only needed a temperature of 250°C for 5 min.

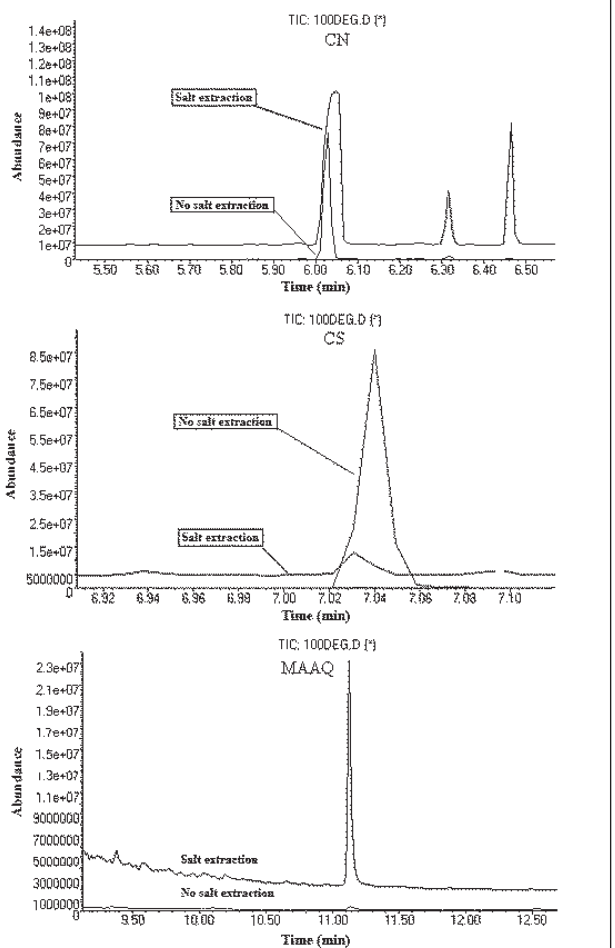

Figure 7. Total ion chromatogram showing the effects of salt on the response of CN, CS, and MAAQ.

Temperature effects

For CS and MAAQ, increasing temperature shows a significant increase in response, though temperature did not play a significant role for CN (Figure 6).

Going from 40°C to 100°C increased the response for CS by 100× and MAAQ by 4× using the polyacrylate fiber. Heating a sample can provide enough energy for analytes to overcome the energy barriers that bind them to the matrix. However, the absorption of analytes by the fiber is an exothermic process. This means that although higher temperatures are good for the release of analytes from their matix, they can adversely affect the absorption of analytes by the coating because of the decrease of the partition coefficient.

Salting

The use of salts, such as sodium chloride, can either increase or decrease the amount extracted, depending on the compound and salt concentration. For this study, a 25% salt solution of sodium chloride was used. The salting has a positive effect on CN and MAAQ, but a negative effect on CS (Figure 7). The increase in response for CN and MAAQ was by 2× and 90×, respectively. However, the drop in sensitivity for CS was 5-fold. Regardless of the drop in response for CS, it was still sensitive enough to make a positive identification.

The drop in sensitivity for CS is not from the salting but from the conversion of CS to 2-chlorobenzaldehyde. To understand this mechanism, water solutions spiked with CS were prepared and extracted at room temperature and at 100°C. It appears

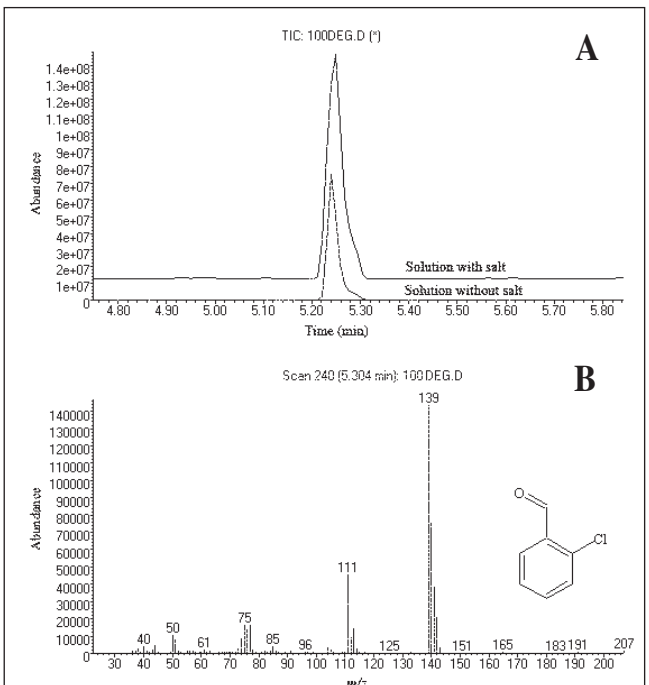

Figure 8. Total ion chromatogram of CS with and without salt (A) and spectra of 2-chlorobenzaldehyde (B).

that this process undergoes a nucleophilic attack in the presence of moisture and heat does not play a predominant role in the conversion. Also, it appears that it does not go to completion, but it comes to equilibrium with the headspace. Although this process takes place, the fibers (PDMS–DVB and PA) are able to extract the presence of CS in a sample and make a positive identification.

Conclusion

In any analytical procedure, sample preparation has always been the limiting factor. SPME has revolutionized the approach to sample preparation and provides chemists with an additional tool for selectively extracting analytes from very complex matrices. Overall, this approach is a cost benefit in analysis and instrument downtime.

In the study, PDMS–DVB and PA were found to be the best fibers for this analysis. Overall, temperature and salting had positive effects in the analysis of these compounds. With the use of robotic autosamplers, this approach to sample extraction and analysis can be automated.

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