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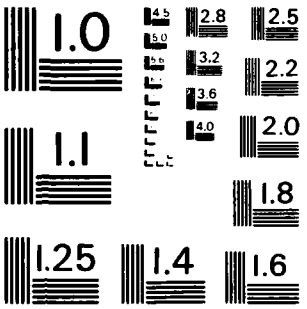

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CHEMICAL SYSTEMS LABORATORY

US Army Armament
Research and Development Command
Aberdeen Proving Ground, Maryland 21010

TECHNICAL REPORT
ARCSL-TR-83027

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY ANALYSIS OF 2-CHLOROETHYL ETHYLSULFIDE AND ITS DECOMPOSITION BY-PRODUCTS BY DERIVATIZATION

By

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May 1983

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A new and sensitive technique for the analysis of 2-chloroethyl ethylsulfide, a sulfur mustard type compound, and its major decompositon by-product is presented. 2-Chloroethyl ethylsulfide, ethyl 2-hydroxyethylsulfide, and ethyl vinylsulfide are derivatized to novel chromophore-bearing phenylsulfonylfilimines separately and in a combined mixture. These are then separated by reverse-phase high performance liquid chromatography and quantitated by ultraviolet detector response. Quantities of these sulfides as low as 20 nanograms are detected.

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PREFACE

The work described in this report was conducted under Project 1L161101A91A, Task Enhancement Reaction Technique for Simultaneous Detection/Quantification. This work was started in January 1981 and completed in October 1981. The experimental data are contained in Notebooks 9915 and CSL 81-0151.

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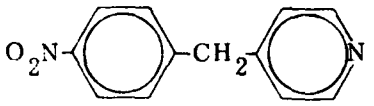
HIGH PERFORMANCE LIQUID CHROMATOGRAPHY ANALYSIS OF 2-CHLOROETHYL ETHYLSULFIDE AND ITS DECOMPOSITION BY-PRODUCTS BY DERIVATIZATION

1 INTRODUCTION

The ability to easily detect, separate, and quantitate trace amounts of sulfur mustards and their decomposition by-products in aqueous solution is needed in combat situations for the detection of agent use as well as in the laboratory for the analysis of intelligence samples. The degradation by-products along with the agent are more likely to be encountered rather than the agent alone. In addition, this need is apparent also in the area of environmental studies and in general analytical methodology for the identification of alkylsulfides in an aqueous matrix.

Sulfur mustards currently are analyzed by colorimetry using 4-(p-nitrobenzyl)pyridine (DB-3 (I)[1,2]



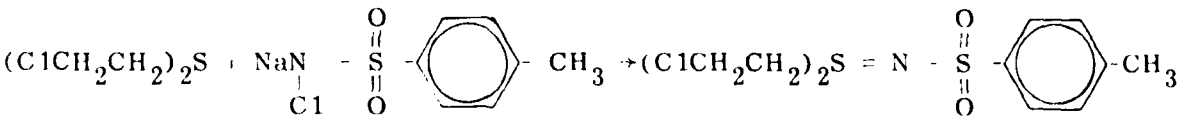
I

This is a general test and gives positive results for practically all alkylating agents and false positives for some acylating agents. In addition, this test cannot be used for the decomposition by-products.

Gas chromatography (GC) has also been employed.[3] However, water samples cannot be analyzed directly by GC but must undergo a lengthy extraction and workup procedure before analysis can be performed.

The sulfur mustards and their by-products do not absorb or fluoresce in the ultraviolet (UV) or visible spectral range. Thus, they are not amenable by themselves to high performance liquid chromatography (HPLC) analysis using a UV or fluorescent detector.

The arenesulfonylsulfilimines were discovered shortly after World War I by Mann and Pope.[4] It was shown then that bis-(2-chloroethyl)sulfide (Mustard Gas) (II) was swiftly converted in aqueous solution to crystalline and innocuous S-bis-(2-chloroethyl)-N-tolylsulfonylsulfilimine (III) by treatment with sodium toluenesulfochloramide (chloramine-T) (IV) according to the following reaction:



II IV III

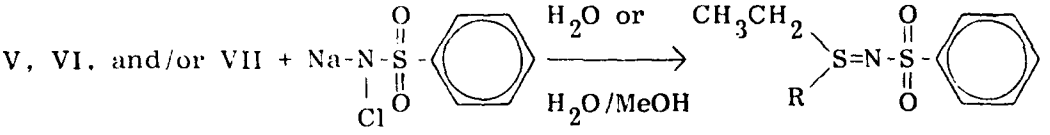
Since then, the reaction of alkylsulfides with salts of various N-chloroarenesulfonylsulfonamides, e.g., chloroamine-B or -T, has been widely used as a facile means of preparing crystalline and innocuous derivatives of alkyl sulfides for characterization purposes.

This paper describes a precolumn enhancement reaction technique for the reverse-phase HPLC analysis of 2-chloroethyl ethylsulfide (V), a sulfur mustard type compound, and its major decomposition by-products, ethyl 2-hydroxyethylsulfide (VI), and ethyl vinylsulfide (VII), in aqueous solution. These compounds were derivatized with sodium benzenesulfochloramide (chloramine-B) (VIII), which contains a strong

$CH_3CH_2SCH_2CH_2Cl$ $CH_3CH_2SCH_2CH_2OH$ $CH_3CH_2SCH{=}CH_2$

V VI VII

UV chromophore, on a microscale in aqueous alcohol to form novel UV absorbing phenylsulfonylsulfilimines separately and in a combined mixture as indicated in the following equation:



VIII

where R = $ClCH_2CH_2$- = V ⟶ IX

= $HOCH_2CH_2$- = VI ⟶ X

= CH_2=CH- = VII ⟶ XI

Compounds IX, X, and XI were separated by reverse-phase HPLC and quantitated by UV detector response.

2 MATERIALS

2.1 Instrumentation.

HPLC analyses were carried out using a Waters Associates High Pressure Liquid Chromatograph consisting of two Model 6000A Pumps, a U6K Injector, a Model 440 UV Detector, a 730A Data Module, and a 720A Systems Controller. Separation was carried out using a Waters Associates Radial-PAK C18 (10 µ) Column.

Infrared spectra were recorded on a Perkin-Elmer 283-B Spectrophotometer. ^{1}H NMR spectra were recorded using a Varian A-60-D Spectrometer. GC-MS analyses were carried out using a Hewlett-Packard 5985A equipped with a 10 m x 0.25 mm ID glass, WCOT, SP2100 Column.

2.2 Chemicals.

Water used for HPLC was distilled and deionized (10-14 megohm-cm). Acetonitrile and methanol were HPLC grade (Burdick and Jackson, Muskegon, MI). Compounds V and VII were obtained from Fairfield Chemical Co., Inc. (Blythewood, SC). Compound VI was obtained from Aldrich Chemical Co., Inc. (Milwaukee, WI). Compound VIII was obtained from Eastman Kodak (Rochester, NY) and purified. All chemicals used gave analytical data consistent with their chemical structure.

3 METHODS

3.1 Preparation of the IX, X and XI Standards for HPLC.

Quantities of each of the three sulfilimines were prepared for use as standards to determine optimum chromatographic conditions and effectiveness of analytical derivatization. The sulfide (1.0 mole) and VIII (1.1 mole) were stirred together in 10 ml of 30% cold methanol for one hour. A white crystalline precipitate appeared almost immediately in all cases. The precipitate was filtered off, washed with a small quantity of water, dried, and washed with ether. The precipitate was then recrystallized from ethanol. Spectral data were in agreement with the assigned structures.

3.1.1 S-Ethyl-S-Chloroethyl-N-phenylsulfonylsulfilimine (IX).

The recrystallized product was obtained by the general procedure outlined above: yield 89%; m.p. 109-110°. (Found: C, 42.9; H, 5.1; Cl, 12.8; N, 5.1; and S, 22.9. Calc. for $C_{10}H_{14}ClNS_2O_2$: C, 42.9; H, 5.0; Cl, 12.7; N, 5.0; and S, 22.9.)

3.1.2 S-Ethyl-S-2-hydroxyethyl-N-phenylsulfonylsulfilimine (X).

The recrystallized product was obtained by the general procedure outlined above except that water alone was used as the reaction solvent and ether: chloroform was used for recrystallization. The yield was 83%; m.p. 75-76.5. (Found C, 45.8; H, 5.8; N, 5.6; and S, 24.5. Calc. for $C_{10}H_{15}NS_2O_3$: C, 45.9; H, 5.8; N, 5.4; and S, 24.5.)

3.1.3 S-Ethyl S-vinyl-N-phenylsulfonylsulfilimine (XI).

The recrystallized product was obtained by the general procedure outlined above: yield, 82%; m.p. 86.5-88. (Found C, 49.1; H, 5.2; N, 6.0; and S, 26.5. Calc. for $C_{10}H_{13}NS_2O_2$: C, 49.3; H,5.4; N, 5.8; and S, 26.4.)

3.2 Chromatographic Procedure.

Analytical separations were performed under the following conditions: sample size, 20 ul; flow rate, 1.5 ml/min; column temperature, ambient; mobile phase, 30% acetonitrile:water; UV detector, 254 nm.

Standard solutions of IX, X, and XI were injected onto the column and their retention times determined. Calibration curves conforming to Beer's Law were obtained by injecting known concentrations (1.0 ug, 2.0 ug, 4.0 ug, 10.0 ug, and 20.0 ug per ml) of the sulfides as sulfilimine derivatives onto the column in triplicate and measuring the resulting peak areas.

3.3 Analytical Derivatization.

To one equivalent of each of the sulfides in one ml of methanol is added two equivalents of VIII. The mixture was heated with stirring at 60°C for one hour. After cooling, 20-µl samples were introduced onto the column through a continuous flow loop injector. Peak areas were measured and computed with an on-line integrator (Data Module).

In this way, concentrations of V, VI, and VII were prepared individually and in combined mixtures at 1.0 µg, 2.0 µg, 4.0 µg, 10.0 µg, and 20.0 µg/ml for detection as the sulfilimines species.

4 RESULTS AND DISCUSSION

From the literature,[5] arenesulfonylsulfilimines show a strong absorption peak around 230 nm (log E4.0-5.0) and a weak absorption peak in the area of 270 nm (log E3.0-4.5). As seen in table 1, compounds IX, X, and XI show strong absorption peaks at 224-226 nm as well as a weak absorption at 272 nm. Another weak peak also was observed for all three compounds at 265 nm. Also in table 1, the log E values at 254 nm for IX, X, and XI are shown.

Table 1. UV Spectra of IX, X, and XI in Acetonitrile

Compound	λ_1(nm)	Log E_1	λ_2(nm)	Log E_2	λ_3(nm)	Log E_3	Log E_{254}
IX	224	3.9	265	2.7	272	2.6	2.7
X	225	3.9	265	2.7	272	2.6	2.7
XI	226	4.0	264	2.8	272	2.7	2.9

The qualitative capability for this technique is illustrated in figure 1 in which the complete separation of IX, X, and XI as well as VIII is achieved in 15 minutes.

The retention times for the phenylsulfonylsulfilimine derivatives and excess chloramine-B reagent under the stated conditions are shown in table 2. Excess chloramine-B reagent is unretained on the column and does not interfere with the analysis.

Table 2. Retention Times of the Phenylsulfonylsulfilimine Derivatives

Compound	Retention Time (Min)
VII	1.05
X	3.32
XI	6.72
IX	11.00

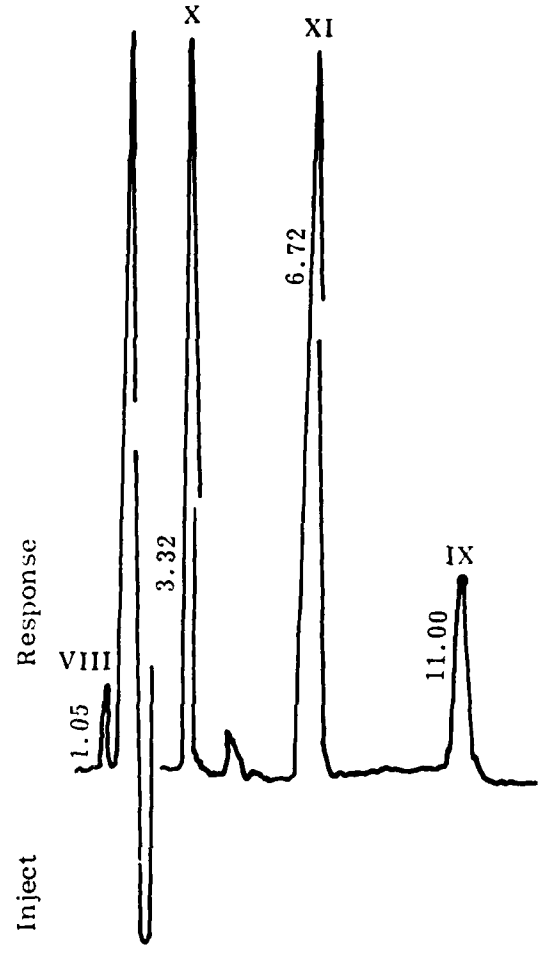


Figure 1. Chromatogram for the Separation of VIII, IX, X, and XI

Quantitation also was readily achieved by reverse-phase HHLC. The reactions were reproducible and detector response was linear for V, VI, and VII in concentrations of 1.0-20.0 ng/ml. The overall efficiency of the derivatization reaction for the three sulfides was 85-99% by comparison with standardized materials. The detection limits for V, VI, and VII were 10, 12, and 21 ng, respectively. The limits of detection are based on the method described by Hubaux and Vos[6] using a 95% confidence level with α and β being equal to 5% (i.e., one out of 20 datum may fall outside 2 standard deviations of the fitted curve).

5 CONCLUSIONS

A new and sensitive technique for the simultaneous detection, separation, and analysis by reverse-phase HPLC of 2-chloroethyl ethylsulfide, a sulfur mustard type compound, and its major decomposition by-products by a novel precolumn enhancement derivatization procedure is described. The techniques involve the reaction

of these nonchromophoric sulfides with N-halogeno-N-metalloarylsulfonamidates on a microscale to attain any UV or visible absorbing or fluorescing arenesulfonylsulfilimine species. These arenesulfonylsulfilimine derivatives can then be facilely separated on a low polarity C-18 column by reverse-phase HPLC. Quantitation of these sulfides by ultraviolet detector response can be achieved easily in quantities as low as 20 nanograms.

As a corollary achievement, several novel phenylsulfonylsulfilimine derivatives have been synthesized.

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