TECHNICAL REPORT ARLCD-TR-81035

(12)

CHARACTERIZATION OF POLLUTANTS
AT
HOLSTON ARMY AMMUNITION PLANT

T. H. CHEN
C. CAMPBELL
W. J. FISCO

DTIC
ELECTE
NOV 17 1981
E

OCTOBER 1981

US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
LARGE CALIBER
WEAPON SYSTEMS LABORATORY
DOVER, NEW JERSEY

APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED

DTIC FILE COPY

81 11 16 085

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report ARLCD-TR-81035	2. GOVT ACCESSION NO. AD-A107340	3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* Characterization of Pollutants at Holston Army Ammunition Plant		5. TYPE OF REPORT & PERIOD COVERED
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) T.H. Chen, C. Campbell and W.J. Fisco		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS ARRADCOM, LCWSL Energetic Materials Division (DRDAR-LCE) Dover, NJ 07801		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS ARRADCOM, TSD STINFO Div (DRDAR-TSS) Dover, NJ 07801		12. REPORT DATE October 1981
		13. NUMBER OF PAGES 47
14. MONITORING AGENCY NAME & ADDRESS*(if different from Controlling Office)*		15. SECURITY CLASS. *(of this report)* Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

Approved for public release; distribution unlimited.

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Wastewaters	Inorganic ions	Direct injection
Analytical methodologies	Metals	Stopped-flow technique
Isotope dilution technique	Sampling	
Analysis	Degradation	
Nitramines	Concentration techniques	

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The development of reliable analytical methodologies for the identification and quantification of explosives and related pollutants in effluent wastewaters and the results obtained by direct instrumental techniques are described.

This study included the evaluation of sample degradation during storage, a comparison of solvent extraction and other concentration techniques, and the development of an isotope dilution technique.

DD FORM 1473 1 JAN 73   EDITION OF 1 NOV 65 IS OBSOLETE

20. ABSTRACT (cont)

The major pollutants quantified are, in the order of decreasing abundance, 1,3,5-trinintro-1,3,5-triazacyclohexane (RDX), 1-Acetyl-3,5,7-trinitro-1,3,5,7-tetraazacyclooctane (SEX), 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX), and 2,4,6-trinitrotoluene (alpha-TNT) for the organic compounds, and sulfate, chloride, sodium, potassium, and ammonium ions for the inorganic ions. The concentrations of copper, cadmium, and chromium were found to be, respectively, about 10, 1, and 0.02 ppb.

ACKNOWLEDGMENT

Accession For		
NTIS GRA&I	**X**	
DTIC TAB	☐	
Unannounced	☐	
Justification		
By		
Distribution/		
Availability Codes		
Dist	Avail and/or Special	
A		

SUMMARY

The four Holston Army Ammunition Plants' (HSAAP) wastewaters representing the effluents from the ends of 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) (WW1) and 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX) (WW2) production lines, the composite of the lower end of the production lines 1 to 5 (WW3), and the composite of the upper end of the production lines 1 to 5 (WW4) were analyzed using ultraviolet absorption spectrophotometry, high pressure liquid chromatography (HPLC), and ion chromatography (IC).

The organics in the wastewaters were found to decompose at room temperature with time, the extents of which depend greatly on the sample characteristics. Thus, during a storage period of about 7 months, the overall composition changed from about 10% for WW1 to several fold for WW4. In the latter, the changes were attributed to the degradations of nitramines to nitrate ions. The most striking degradation was observed in WW3 where 2,4,6-trinitrotoluene (α-TNT) disappeared in about 4 weeks. The inorganic ions were found to be quite stable.

The comparative studies on various concentration and isolation techniques for trace quantities of pollutants in the wastewaters revealed the variabilities in the results obtained, the possible sample contaminations by the impurities in the solvents used for extractions, and the loss of more volatile components. These findings, together with the fact that the extraction efficiencies of various compounds in an unknown mixture cannot be determined, indicate that unless these factors are carefully examined and taken into account in the analyses, the analytical data will be unreliable.

In view of the foregoing discussions, we have developed an isotope dilution technique for determining the ppm level α-TNT as part of our current efforts to develop more reliable analytical methodologies. Using this technique, a precision of 5.7% (relative standard deviation) and an accuracy of 0.2% (relative error) were obtained despite the presence of the large amount of impurities.

The major pollutants quantified so far are, in the order of decreasing abundance, respectively, RDX, 1-Acetyl-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, (SEX or QDX), HMX, and α-TNT for the organic compounds, and $SO_4^=$, Cl^-, Na^+, K^+, and NH_4^+ for the inorganic ions. The concentrations of copper, cadmium, and chromium were found to be, respectively, about 10, 1, and 0.02 ppb.

CONTENTS

TABLES

FIGURES

INTRODUCTION

Reliable analytical data on pollutants are essential to all environmental activities, such as the study of the sources of contaminants and their impact on the environment, development and evaluation of abatement technologies, setting of standards for regulatory control, and building of predictive models. However, the state-of-the-art of analytical methodologies for air and water analyses are still inadequate to deal with complex environmental analytical problems. We have, therefore, been developing reliable analytical methods for identifying and quantifying the pollutants in the wastewaters of Army Ammunition Plants in our pollution abatement program.

Much environmental analytical data are useless for the intended purposes due to improper sampling procedures, changes in composition during transport and storage, inadequate concentration methods, and the lack of criteria for evaluating the adequacy of analytical methods and results. In view of these facts, we focused our attention in this work on the problems of sample degradation and concentration techniques for trace quantities of pollutants and the development of an isotope dilution technique to improve the precision and accuracy of analytical data. These are among the areas where further work has been recommended by the Committee on Environmental Improvement of the American Chemical Society in its recent report (ref 1). We will also discuss the analytical data we obtained thus far on the four representative wastewaters from HSAAP in Kingsport, Tennessee. Three reports (refs 2 through 4) have appeared in the recent past which dealt with the identification and quantification of some pollutants, notably dimethylnitrosoamine, in the wastewaters of HSAAP. The aim of this work is to develop reliable analytical methodologies which can be used for obtaining reliable analytical data, to the maximum extent possible, on the pollutants in the wastewaters of the Army Ammunition Plants.

EXPERIMENTAL

Apparatus and Reagents

Military grade HMX was extracted with ethylenedichloride to remove RDX and triply recrystallized from acetone. The RDX obtained from HSAAP was treated with a buffer solution (pH=4.6) and recrystallized from a dimethyl sulfoxide-water mixture. The purity of RDX thus obtained was determined to be $99.84 \pm 0.19\%$ by a differential scanning calorimetric technique. Military grade α-TNT was recrystallized from carbon tetrachloride. Methylene chloride (MC) (Allied Chemical, Semi-Conductor grade), trichloroethylene (TCE) (Matheson Coleman & Bell), petroleum ether ("Baker Analyzed"), and acetone (Fisher Scientific Co., A.C.S.) were distilled and the fractions boiling, respectively, at 40°C, 86.5-87.5°C, 40-50°C, and 56°C were collected for use. Hexane (Matheson Coleman & Bell, Spectroquality) was used without further purification.

Recording of mass spectra, ultraviolet spectra, liquid chromatograms, and ion chromatograms were made using, respectively, a DuPont 21-490 Mass Spectrometer, a Beckman DK-2A Spectrophotometer, a Perkin-Elmer Series 3 Liquid Chromatograph with 65 T Detector and Sigma 10 Data System, and a Dionex System 14 Ion Chromatograph. A Perkin-Elmer Model 503 Atomic Absorption Spectrophotometer was used for analyzing cadmium, copper, and chromium.

1

A Chemtrix Type 60 Digital pH meter was used for pH measurements. A Buchi Rotavapor-EL was used in the freeze drying of the wastewaters.

Method and Procedure

Estimation of Total Nitramine Content

Rapid estimations of total nitramine contents in the wastewaters were made by direct ultraviolet absorption spectrophotometry. This method is based on the fact that nitramines absorb strongly in the 200 to 260 nm region with the absorption maxima centering in the vicinity of 228 nm and with molar absorptivities at 228 nm ($\varepsilon_{228 \ nm}$) in the range of 0.6 to 2.1 x 10^4 M^{-1} cm^{-1} (ref 5). Thus, the approximate (within a factor of about 2) total nitramine contents can be obtained from the absorbances of wastewaters at 228 nm and the estimated average molar absorptivity and average molecular weight, whose values are close to the molar absorptivity and molecular weight of the most abundant nitramine component. The identity of the latter can usually be determined from information such as the sampling site, nature of effluents at this site, manufacturing process conditions, and solubility data. In the case of the HSAAP wastewaters obtained from the ends of RDX and HMX production lines, the pollutant in the highest concentration is determined to be RDX.

Identification and Quantification of Pollutants

Tentative identifications of major organic and inorganic pollutants were made by comparing the retention times of unknown peaks with those of external reference standards in the high pressure liquid chromatograms and ion chromatograms, respectively. For superimposing peaks, the assignment was made by spiking the sample with a standard. 1-Acetyl-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, which appeared as a shoulder of a major peak in a wastewater from RDX production line, was identified by this method. In later experiments, full spectrum scanning in the ultraviolet range using the stopped-flow technique was used to aid the identification of unknown liquid chromatographic peaks. The peak height method, using external standards, was employed in the quantification of both organic and inorganic pollutants, except for the nitrate ion where the method of standard additions was used. In the determinations of cadmium, copper, and chromium, the method of bracketting the samples was employed and the blind standards were used to validate the accuracy of the analysis.

Synthesis of α,α,α - trideuterio-2,4,6-trinitrotoluene (α-TNT-d$_3$)

A published procedure (ref 6) was modified for synthesizing α-TNT-d$_3$ because of the difficulties encountered in extracting the deuterated compound with CHCl$_3$. Addition of the latter essentially resulted in merely increasing the volume of the reaction mixture without affecting the desired separation of organic and aqueous layers. This arises possibly from the presence of a relatively large amount of acetone in acetone-D$_2$O mixture (3.5 : 1 by volume), which tends to make CHCl$_3$ miscible with the mixture. Our modification consists of adding a relatively large amount of water to the mixture so that CHCl$_3$ becomes immiscible with the aqueous layer. Following CHCl$_3$ extraction, the organic layer was separated from the aqueous layer and evaporated to dryness at room temperature under a flow of air. The residue obtained was dissolved in acetone and the solution centrifuged. The supernatant

solution was drawn out using a syringe and evaporated to dryness at room temperature. The synthesized compound was not purified. A small amount of the deuterated compound was transferred to a capillary tube and introduced via a solid probe into a mass spectrometer for the isotopic purity determination. In order to obtain a steady vapor pressure of α-TNT without rapid sample depletion, a low filament current setting ($50\,\mu A$) was used to maintain the unheated ion source temperature at about 100°C. This in turn held the unheated solid probe at a steady, relatively low temperature of about 73°C. This condition permitted mass spectrometric (electron impact mode at 70 ev) examination of the isotopic purity of α-TNT-d_3 for a relatively long period by slow, repetitive scanning (200 sec/decade) of ion currents at M/e 227, 228, 229, and 230. The composite ion current intensitities at these M/e's were found to be in the ratios of $\sim 0 : 3.3 \pm 0.3 : 16.0 \pm 1.0 : 137.2 \pm 10.0$ (average of 3 scans). The intensities were resolved into those of molecular ions of M/e 228, 229, and 230 using equations 1, 2, and 3. The coefficients f_1, f_2, and f_3 represent the intensity ratios of minor ion fragments, which contribute to the observed composite ion current intensities, to the major fragment in the molecular ion cluster. These values were computed from the molecular ion cluster of undeuterated α-TNT (M/e 226, 227, 228, and 229).

$$I^C_{230} = I_{230} + f_1 I_{229} + f_2 I_{228} \tag{1}$$

$$I^C_{229} = f_3 I_{230} + I_{229} + f_1 I_{228} \tag{2}$$

$$I^C_{228} = 0 \cdot I_{230} + f_3 I_{229} + I_{228} + f_1 I_{227} = 0 + f_3 I_{229} + I_{228} + 0 \tag{3}$$

where

$I^C_{230}, I^C_{229}, I^C_{228}$ = Observed composite ion current intensities at M/e 230, 229, and 228 respectively.

$I_{230}, I_{229}, I_{228}, I_{227}$ = Ion current intensities of molecular ions of M/e 230, 229, 228, and 227 respectively.

$f_1 = I_{228}/I_{227} = 9.95 \times 10^{-2}$ std. dev. 5.2×10^{-3} (fast scan)
$\qquad\qquad\qquad\quad\; 9.85 \times 10^{-2}$ std. dev. 4.5×10^{-3} (slow scan)

$f_2 = I_{229}/I_{227} = 2.24 \times 10^{-2}$ std. dev. 3.2×10^{-3} (fast scan)
$\qquad\qquad\qquad\quad\; 2.29 \times 10^{-2}$ std. dev. 1.5×10^{-3} (slow scan)

$f_3 = I_{226}/I_{227} = 4.17 \times 10^{-2}$ std. dev. 3.7×10^{-3} (fast scan)
$\qquad\qquad\qquad\quad\; 3.82 \times 10^{-2}$ std. dev. 2.8×10^{-3} (slow scan)

The computed ion current intensities of molecular ions of M/e 230, 229, and 228 were, in turn, used to calculate the isotopic compositions. The deuterated product was found to contain $91.3 \pm 0.9\%$, α-TNT-d_3, $6.76 \pm 0.03\%$ α-TNT-d_2 and $1.93 \pm 0.07\%$ α-TNT-d_1.

Deuterium-hydrogen Exchange of Deuterated α-TNT With Water

This exchange study was made to determine the applicability of α-TNT-d_3 as a diluent in the isotope dilution technique for analyzing α-TNT in wastewaters.

An aqueous solution of deuterated α-TNT (1 mg/25 mL) was prepared in duplicate and set aside at room temperature for 12 days. These solutions were then evaporated to dryness at room temperature to determine the extent of deuterium-hydrogen exchange by the mass spectrometric technique already described. The average isotopic compositions of two samples were found to be 89.2 ± 0.4%, 5.10 ± 0.30%, and 5.72 ± 0.06% for α-TNT-d_3, α-TNT-d_2, and α-TNT-d_1 respectively. Comparison of these results with the corresponding values of 91.3 ± 0.9%, 6.76 ± 0.03%, and 1.93 ± 0.07% for the original composition indicate the extent of deuterium-hydrogen exchanges to be about 2% or less in approximately a 20-day period, which includes the additional period needed to isolate the samples by room temperature evaporation. This study establishes that α-TNT-d_3 can be used as a diluent in an isotope dilution technique since the diluent and the undeuterated α-TNT were extracted with a suitable solvent shortly after the dissolution of diluent in water.

Isotope Dilution Technique

An aqueous solution containing about 50 ppm each of α-TNT and α-TNT-d_3 was prepared and four 100 mL aliquots were used for obtaining solid samples for determining I^C_{230}, I^C_{227}, I^C_{212}, and I^C_{210} by a slow repetitive mass spectrometric scanning technique described earlier. The four samples were isolated from water by room temperature evaporation and solvent extractions using ten 10 mL portions of MC, TCE, and petroleum ether, respectively, followed by solvent removal by evaporation at room temperature. In all cases, the samples were brought to constant weights.

Mixtures of α-TNT and α-TNT-d_3 of known compositions were prepared by weighing, for each composition, the desired amounts of α-TNT and α-TNT-d_3 successively into a 5 mL weighing bottle and dissolving in a small volume of acetone. This solution was then evaporated to dryness at room temperature to insure homogeneous mixture for the isotopic ratio determination.

Sampling of Wastewaters

For the sampling, transport, and storage of the representative HSAAP wastewaters, the brown glass bottles, originally containing high purity solvents for HPLC, were thoroughly rinsed with tap and distilled water. Before sampling, the containers were rinsed four times with the wastewater to be sampled, filled with wastewater, and capped. After an equilibration period of at least 1 hour, the contents of the containers were discarded, and the containers refilled with fresh samples.

Solvent Extraction

A one liter aliquot of wastewater filtered with No. 40 Whatman paper was extracted with eight 100 mL portions of TCE in the usual manner. The solvent in the extract was removed using a rotary vaporator, and the residue transferred successively to smaller beakers by thorough scraping with a stainless steel spatula and

acetone solvent. Finally, the residue was dried in a 5 mL or 10 mL beaker to constant weight at room temperature.

Room Temperature Evaporation

A one liter aliquot of wastewater filtered with No. 40 Whatman paper was evaporated at room temperature in a 1,000 mL beaker and the residue was transferred and dried to constant weight in the manner described above.

Freeze Drying

A 400 mL aliquot of wastewater filtered with No. 40 Whatman paper was freeze dried using a rotary vaporator with the rotating sample flask immersed in a bath maintained at -10 to -15°C with an ice-salt mixture. The sample was partially frozen at the beginning of drying under vacuum (~ 2 torr), but it became frozen after several hours. About 40 hours was needed for the removal of 400 mL water. The residue was treated in the manner described earlier to obtain a constant weight.

Preconcentration and Elution of Pollutants

A Waters SEP-PAK C18 cartridge (Waters Associates, Inc.) was used for removing the high polarity compounds. A 50 mL aliquot of wastewater was injected with a syringe through the cartridge, prewashed with acetonitrile and distilled water, followed by water removal by pumping air through the cartridge. The cartridge was then eluted successively with 10 mL each of acetonitrile, methylene-chloride, and hexane, respectively, into three separate 30 mL beakers and the solutions were evaporated to dryness at room temperature. Each residue was subseqently transferred to a 1 mL beaker with the eluting solvent and dried to constant weight at room temperature.

Sample Degradation

The degradation of wastewaters was examined at various storage periods using ultraviolet absorption spectrophotometry and HPLC by direct injection of wastewaters.

Wastewater Storage

Except for a period of several months after sampling, all wastewaters and the residues obtained by solvent extraction, room temperature evaporation, freeze drying, and preconcentration-elution technique were stored in a refrigerator until several hours before use when they were removed and allowed to equilibrate to room temperature.

RESULTS AND DISCUSSION

Representative Wastewaters

Four samples, WW1, WW2, WW3, and WW4, representing respectively, the wastewaters from the end of RDX production line, the end of HMX production line, the composite of the lower end of the production lines 1 to 5, and the upper end of the production

lines 1 to 5, were obtained from HSAAP. Additional pertinent information on the samples was summarized in table 1.

More elaborate representative sampling, such as the additional sampling at other plant sites, time-composite, and seasonal samplings were not made since this work was in the initial phase of developing analytical methodologies.

Estimated Total Nitramine Content

The total nitramine contents of HSAAP wastewaters were estimated from the ultraviolet absorption spectra shown in figure 1. The results are summarized in table 2. Since RDX was determined to be the most abundant species, the average molecular weight and the average molar absorptivity values very close to the molecular weight and the molar absorptivity of RDX were used in this estimation. Although this estimate is only approximate (within a factor of two), this useful information can be obtained very quickly.

Sample Degradation

The wastewaters which were found to be essentially neutral (table 3) degraded with storage time at room temperature. The extent and the nature of composition changes depend greatly on the sample characteristics. The overall changes during the course of approximately 7 months are shown in figures 2 to 5. The wastewater obtained from the end of RDX production line (WW1) decomposed to the extent of about 10% throughout the whole absorption range while the sample from the end of the HMX production line (WW2) shows more pronounced change ($\sim 30\%$) in the 200 to 220 nm range. In contrast, the more complicated sample (WW3), which includes discharges from buildings where α-TNT is incorporated into RDX and HMX, WW1, and WW2, exhibits an interesting crossover of absorption patterns near 220 nm. This suggests the degradation of some nitramines to form compounds which absorb strongly at shorter wavelengths. The wastewater obtained from the upper end of RDX and HMX production lines (WW4) degraded to the greatest extent with dras . crossover of absorption curves. This drastic change was attributed to the decomposition of nitramines to nitrate ion on the basis of the excellent matching of the absorption pattern of the decomposed WW4 to that of nitrate ion, as shown in figure 6. This conclusion was substantiated by the fact that the nitrate ion concentration as determined by ultraviolet spectrophotometry (18.4 ppm) using $\varepsilon_{203nm} = (9.49 \pm 0.11) \times 10^3 \, M^{-1}cm^{-1}$ (ref 7) agreed well with that determined by HPLC (16.6 ppm, see table 7).

The degradation of individual components in the wastewaters can be seen in figures 7 through 9. The most striking change was the disappearance after about 4 weeks of a peak (the peak with an arrow in fig. 7), tentatively identified as α-TNT. These degradation studies demonstrated the importance of preserving the integrity of the environmental samples to obtain meaningful analytical data, which will represent the true composition of samples at the time of sampling.

Isolation of Trace Quantities of Pollutants

Table 4 shows the solid isolated by various techniques. The data in parentheses are obtained by the second analyst from samples stored for longer periods. The results obtained by the first, more experienced analyst (data without parentheses)

6

on WW1 and WW4 samples in columns 2 and 3, indicate that freeze drying isolated about 15% more pollutants than the room temperature evaporation method. This means that at least 15% of the pollutants was lost by the latter method. This table also shows that TCE extracts only a small fraction of the total solid content, perhaps part of the nitramines in WW1. It may be noted that the two numbers, 179.9 and 46.4 under column 3, represent the residues obtained by further extractions of the solid isolated by room temperature evaporation with H_2O and TCE, respectively. It appears then that TCE extracts the pollutants more efficiently from the solid already isolated than from the wastewater directly. However, further work is being done to confirm this observation. It should be pointed out that the solvent extaction efficiencies of various component species in the unknown mixture cannot be determined. Further, the use of a large volume of solvent may introduce impurities. Examples of this will be illustrated in the next section.

The amounts of relatively nonpolar pollutants isolated by Waters SEP-PAK are shown in the last column. Except for WW4, the results were not too reproducible. However, since only one cartridge was used (the only one available to us), further work will be needed. Comparison of these results with those in the next to the last column, indicates that MC is a poor solvent for nitramines as expected from the solubility data.

The results in table 4 and the foregoing discussion point out the problems associated with common isolation techniques such as the loss of more volatile components, the introduction of impurities, and the incomplete extraction of pollutants. Unless these factors are carefully controlled and the results properly corrected for them, the analytical data obtained are likely to be unreliable.

Isotope Dilution Technique

In view of the shortcomings of concentration and isolation techniques, we have developed and examined an isotope dilution technique for analyzing α-TNT in the wastewaters as part of our current efforts to develop more reliable analytical methodologies. Recently, St. John, et al. (ref 8) used d_5-TNT and other isotopically substituted explosive compounds as diluents in determining TNT and other explosives in air by the isotope dilution technique. In their method, field ionization mass spectrometry was employed in the isotopic ratio determinations. Figure 10 shows the molecular ions, M/e 230 and 227, and their most abundant corresponding fragment ions, M/e 212 and 210, which were used to obtain figure 11. As can be seen from the latter, the peak height ratios $I_{210}/(I_{210} + I_{212})$ and $I_{227}/(I_{227} + I_{230})$, are linear with the content of α-TNT in the mixture throughout the whole composition range. From the percentage of α-TNT determined by figure 11 and the amount of deuterated α-TNT added, the content of α-TNT can be readily computed.

In table 5, the results of α-TNT analyses at the ppm level by the isotope dilution technique are summarized. Four residues, isolated by different methods from an aqueous solution containing α-TNT and α-TNT-d_3 in the ratio of essentially 1:1 were analyzed in order to evaluate the isotope dilution technique under various conditions. In columns 1, 2, 3, and 4 are, respectively, the concentrations computed from the amounts taken, the weights of residues isolated, $I_{210}/(I_{210} + I_{212})$, and $I_{227}/(I_{227} + I_{230})$ in figure 11. Comparison of columns 1 and 2 shows that the room temperature evaporation caused about 15% weight loss of α-TNT whererea in the

7

case of MC extract, the weight loss was about 2%. The greater weight loss in the former is attributable to a much longer period required to remove the relatively nonvolatile water. In contrast, the TCE and the petroleum ether extracts gained weights corresponding to approximately 38% and 76% of the original concentration, respectively. The gains are due obviously to the impurities in the contaminated solvents although the solvents were distilled before use. As shown in the lower mass spectra of figures 12 and 13, the contaminants included the impurities with molecular weights exceeding 230. Despite the presence of large amounts of impurities, a precision of 5.9% (relative standard deviation) and an accuracy of 0.2% (relative error) were obtained by the isotope dilution technique.

Major Pollutants in the Wastewaters

In view of the sample degradation problems and the uncertainties involved in the concentration and the isolation of pollutants from the wastewaters, we are reporting the results obtained by the direct HPLC and IC techniques using the direct injection of 100 μl samples. The results obtained are shown in tables 6 and 7, and figures 14 through 17.

The precision and accuracy of the values for RDX and HMX in table 6 have been determined to be about $\pm$ 10% taking into account the degradation of samples and the quantification method used. It should be pointed out that the estimated value for α-TNT in table 6 was obtained by extrapolation back to the time of sampling (12/19/78) based on the results determined about 1 week (12/27/79) and 3 weeks later (1/10/79) assuming a linear rate of decomposition.

As can be seen from table 7, the wastewaters were not analyzed until about five months later. However, the concentrations of inorganic ions have apparently changed only to the extent of 5% or less based on the comparison of the two sets of values for Cl^- and $SO_4^=$ determined 8 months apart. This finding is not surprising in view of the relatively stable nature of these ions. Except for K^+ and NH_4^+, the precision and accuracy of the results have been determined to be about $\pm$ 10%.

It should be pointed out that the accuracies stated above refer to the results obtained using external standards, which do not take into account the possible interferences of many compounds in the complex wastewaters.

Other Results

HPLC With Full Spectrum Scanning by Stopped-Flow Technique

In later experiments, full spectrum scanning of HPLC peaks using the stopped-flow technique were employed to substantiate the identifications of the unknown components based on the observed retention times. An example of this is shown in figure 18 where the assignment of the no. 6 peak as RDX from retention time is strengthened by the close matching of the absorption curves of RDX and the no. 6 peak. The use of the logarithm of absorbance enables the direct comparison of the spectral features of the standard and the unknown with different concentrations.

8

Metal Priority Pollutants in the Wastewaters

Table 8 shows the concentrations of cadmium, copper, and chromium as determined by direct atomic absorption (AA) spectrophotometry (flameless). The typical absorption signals are shown in figure 19. In these experiments, some scattering of the data has been observed. When this was encountered, the experiments were repeated until reproducible results were obtained in six consecutive determinations.

REFERENCES

1. "Cleaning our Environment: A Chemical Perspective," American Chemical Society, Washington, D.C., October 1978, pp 4, 37, and 38.

2. D.O. Helton, W. Burton, G. Rehagen, and C.C. Lee, MRI Progress Report No. 10, Midwest Research Institute, Kansas City, Missouri, April 24,1979.

3. S.L. Kistner, Report USAEHA-32-24-0180-79, Army Environmental Hygiene Agency, Aberdeen Proving Ground, Maryland, September 14, 1979.

4. B.R. Stidham, Report HDC-51-79, Holston Defense Corporation, Kingsport, Tennessee, December 1979.

5. W.A. Schroeder, P.E. Wilcox, K.N. Trueblood, and A.O. Dekker, Anal. Chem., vol 23, 1951, pp 1740-1747.

6. S.A. Shackelford, J.W. Beckmann, and J.S. Wilkes, J. Org. Chem., vol 42, 1977, pp 4201-4206.

7. T.H. Chen, Explosives and Propellants, vol 4, 1979, p 18.

8. G.A. St. John, J.H. McReynolds, W.G. Blucher, A.C. Scott, and M. Anbar, Forensic Sci., vol 6, 1975, pp 53-66.

Table 1. Sampling information on HSAAP wastewaters

Wastewater	Location	Description/designation	Date/time
WW1	Bldg H-4	4RC1-1106 & 4RA5-211	12/19/78 2:00 p.m.
WW2	Bldg. H-5	5HAS2-5533 & 5HAS2-5534	12/19/78 12:00 noon
WW3	Near Bldg. N-2		12/19/78 2:10 p.m.
WW4	Near Bldg. E-1 Manhole No. 148		1/17/79 2:00 p.m.

Table 2. Estimated total nitramine contents in HSAAP wastewaters

Wastewater	Estimated concentration ppm
WW1	~ 42
WW2	~ 15
WW3	~ 16

Average $\varepsilon_{228 \text{ nm}} = 1.00 \times 10^4$ M^{-1} cm^{-1}

Average molecular weight = 222

13

Table 3. pH of HSAAP wastewaters (4/3/79)

Wastewater	pH
WW1	6.56 ± 0.10
WW2	6.98
WW3	6.74
WW4	6.77

Table 4. Pollutants isolated from HSAAP wastewaters by various methods (ppm)

Wastewater	Freeze drying	Room temperature evaporation	Solvent extraction TCE	MC	SEP-PAK
WW1	322.2	274.3 $\begin{cases}179.9\ (H_2O)\\46.4\ (TCE)\end{cases}$	13.7		
WW2	220.3	(180)		(8.2)	33.3
	234.0	(140)		(7.5)	10.0
WW3	204.0	(150)		(2.1)	15.8
	202.2	(134)		(2.1)	9.3
WW4	261.0	219.6		(1.3)	8.5
				(1.6)	8.1

Table 5. Analysis of α-TNT by isotope dilution technique

Concentration calculated ppm mixture	Concentration observed, ppm		
	Obtained from residue weight mixture	Isotope dilution technique using $I^C_{210}/(I^C_{210}+I^C_{212})_{\alpha\text{-TNT}}$ $I^C_{227}/(I^C_{227}+I^C_{230})$	
93.3	79.3 Room temperature evaporation	49.7	48.4
93.3	91.1 Methylene chloride extract	45.4	42.7
93.3	128.8 Trichloroethylene extract	48.2	43.6
93.3	163.8 Petroleum ether extract	45.7	42.9

Avg. 45.8
Std. dev. 2.7 (5.9%)
Rel. error 0.2%

Mixture: α-TNT 45.7 ppm

α-TNT-d$_3$ 47.6 ppm

Table 6. Nitramines found in the wastewaters of HSAAP by direct HPLC

Compound	Concentration in ppm		
	WW1	WW2	WW3
RDX	21.0	5.1	12.0
HMX	0.85	1.7	
SEX	2.5	2.5	
α-TNT			~ 2 (12/19/78)
			~ 0.4 (12/27/79)
			~ 0.04 (1/10/79)

15

Table 7. Inorganic ions found in the wastewaters of HSAAP by direct IC

Ions	Date of analysis	Concentration in ppm			
		WW1	WW2	WW3	WW4
Na^+	1/7/80	21.0	20.9	16.5	16.7
NH_4^+	1/7/80	~ 0.5	2.0	~0.2	0.2
K^+	1/7/80	2.0	2.5	2.0	1.7
Cl^-	5/11/79	--	--	20.4	11.1
	1/4/80	26.8	29.5	19.0	11.9
$SO_4^=$	5/11/79	71.8	72.2	53.4	43.0
	1/4/80	70.7	70.3	51.7	40.3
NO_3^-	5/14/80				16.6

Table 8. Cadmium, copper, and chromium found in HSAAP wastewaters (by direct AA-flameless)

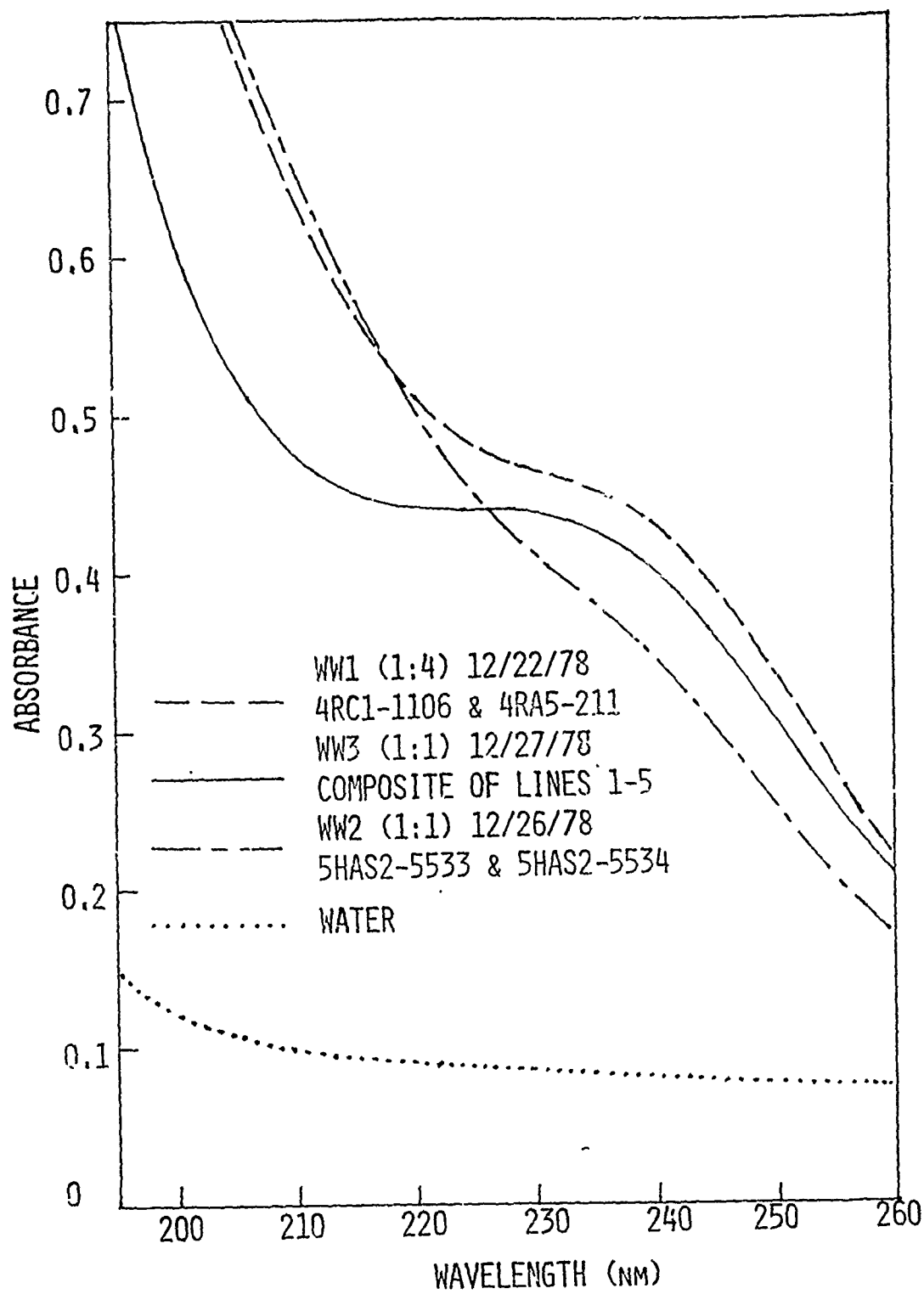| Ions	Date		Sample (ppb)			
			WW1	WW2	WW3	WW4
Cd	5/80	Avg (6)	0.866	0.320	0.210	0.338
		Std dev	0.019	0.023	0.024	0.019
		Rel std dev	2.2%	7.1%	11.2%	5.6%
		Rel error	+2.1%	–	-10%	-5.4%
Cu	5/80	Avg (6)	12.9	10.6	8.6	10.7
		Std dev	0.61	0.56	0.30	0.76
		Rel std dev	4.7%	5.2%	3.5%	7.1%
		Rel error	-3.1%	+11%	–	+11%
Cr	5/80	Avg (6)	0.019	0.021	0.015	0.017
		Std dev	0.00096	0.00076	0.00088	0.0011
		Rel std dev	5.1%	3.6%	5.9%	6.5%
		Rel error	–	–	–	–

16

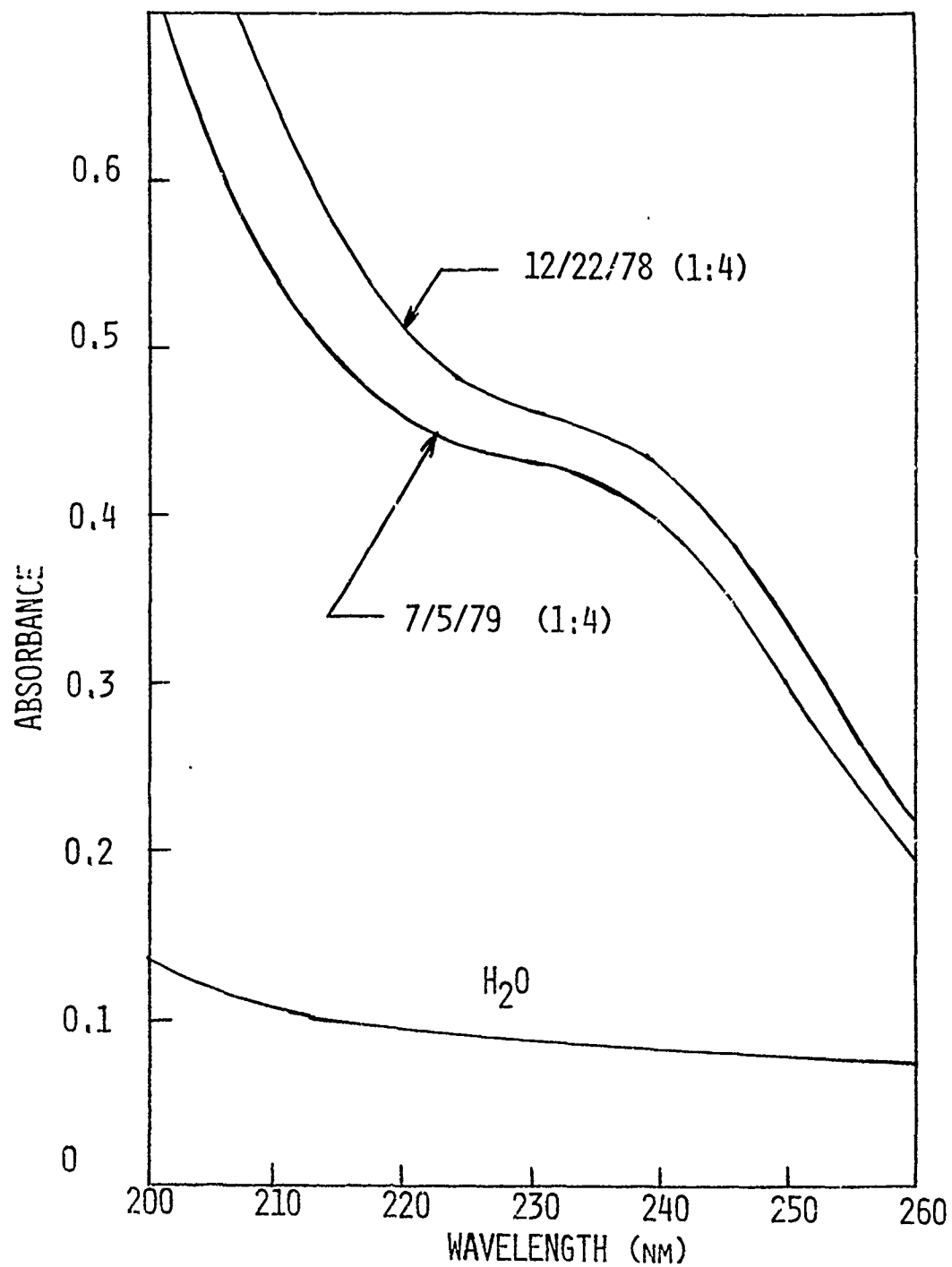Figure 1. Ultraviolet absorption spectra of HSAAP wastewaters

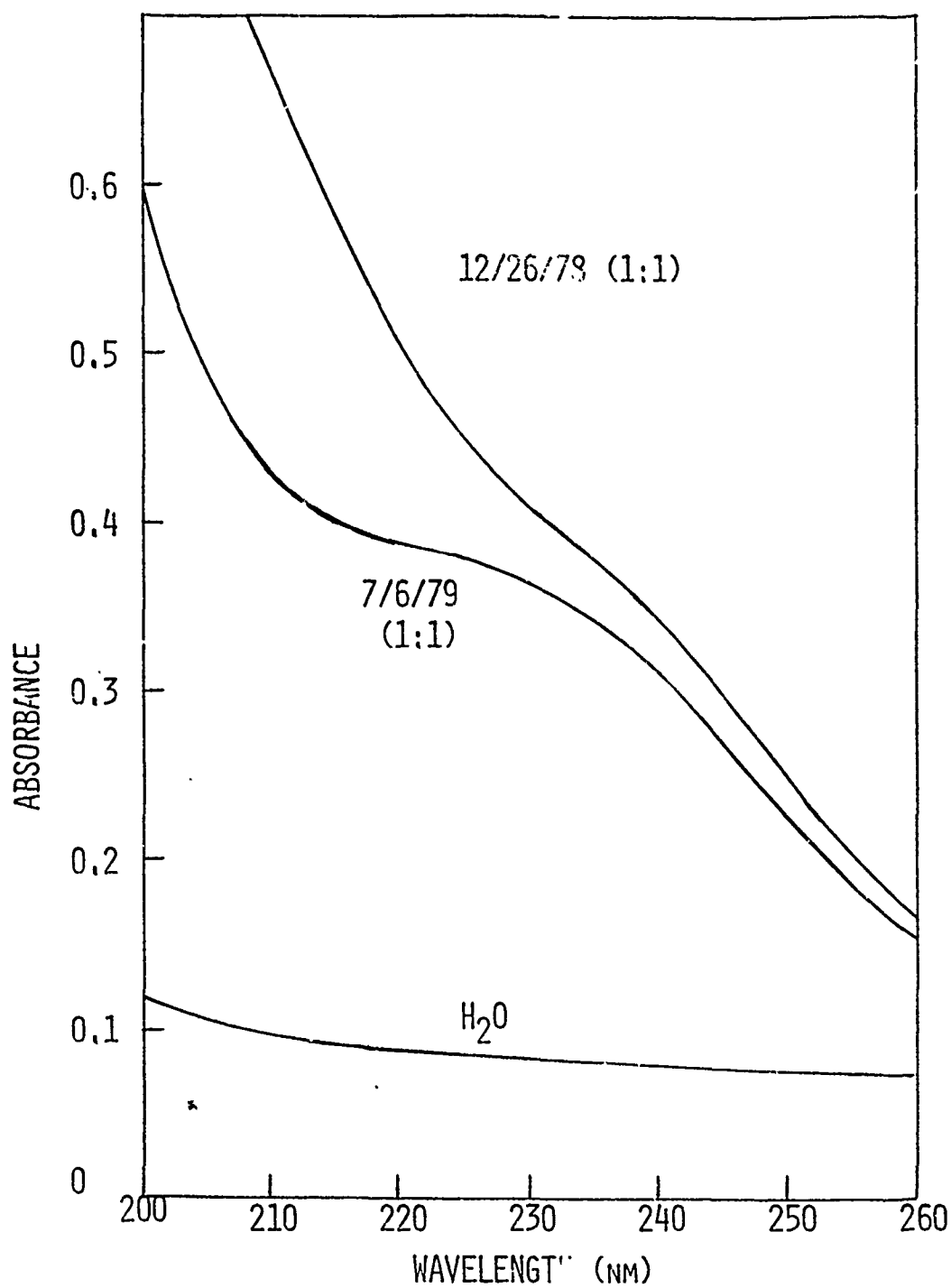Figure 2. Degradation ot HSAAP WW1 wastewater
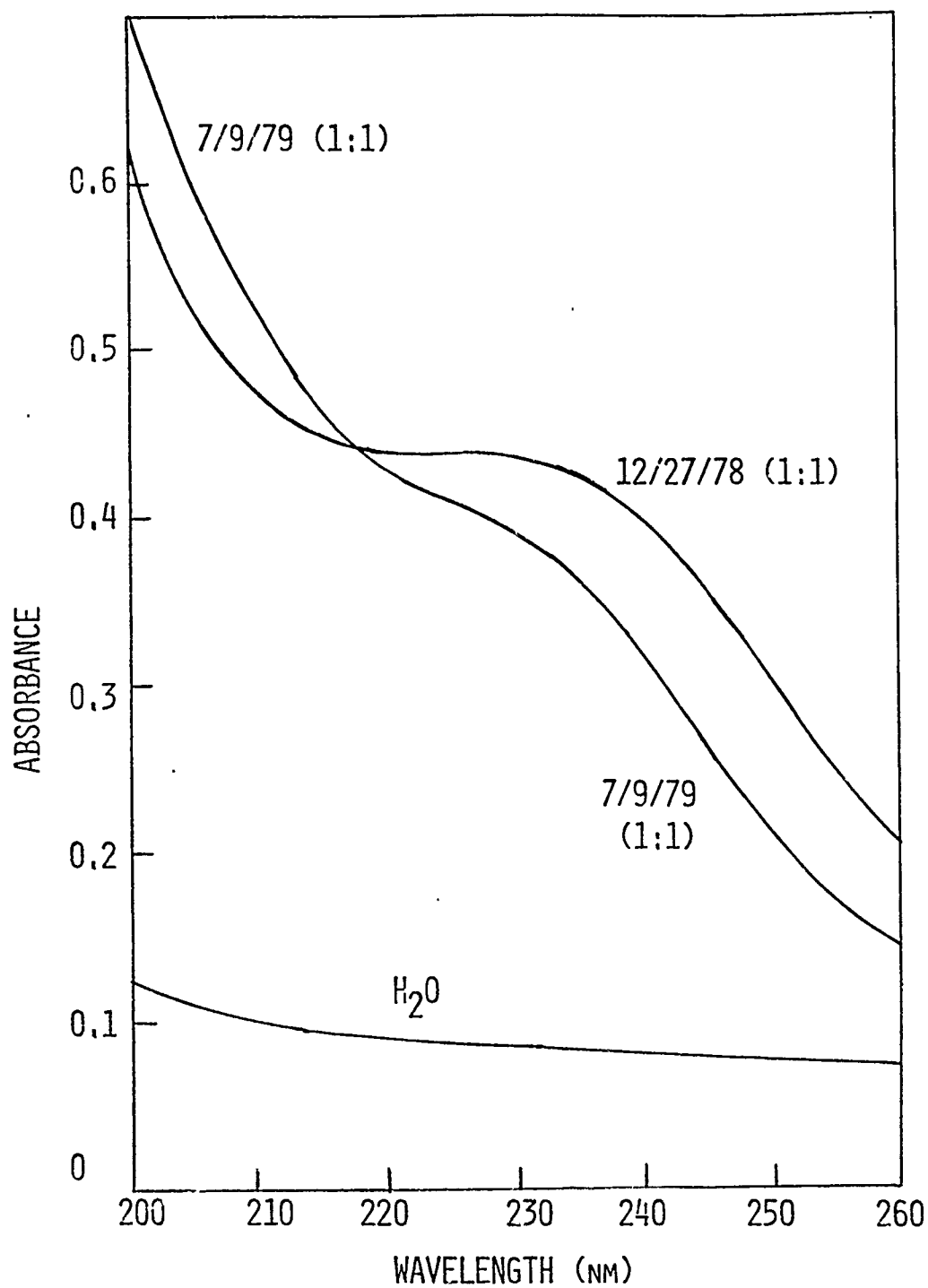
18

Figure 3. Degradation of HSAAP WW2 wastewater

Figure 4. Degradation of HSAAP WW3 wastewater

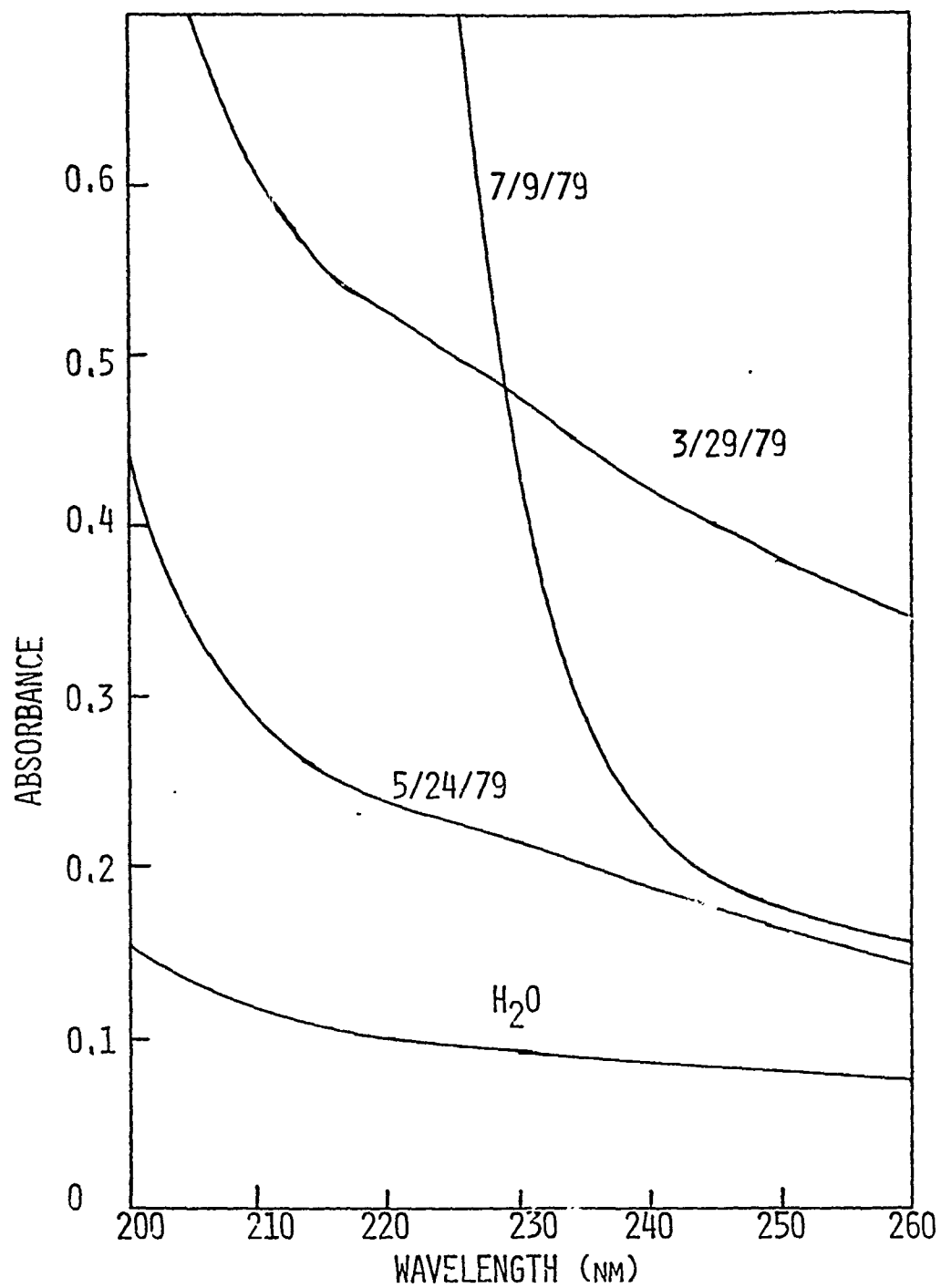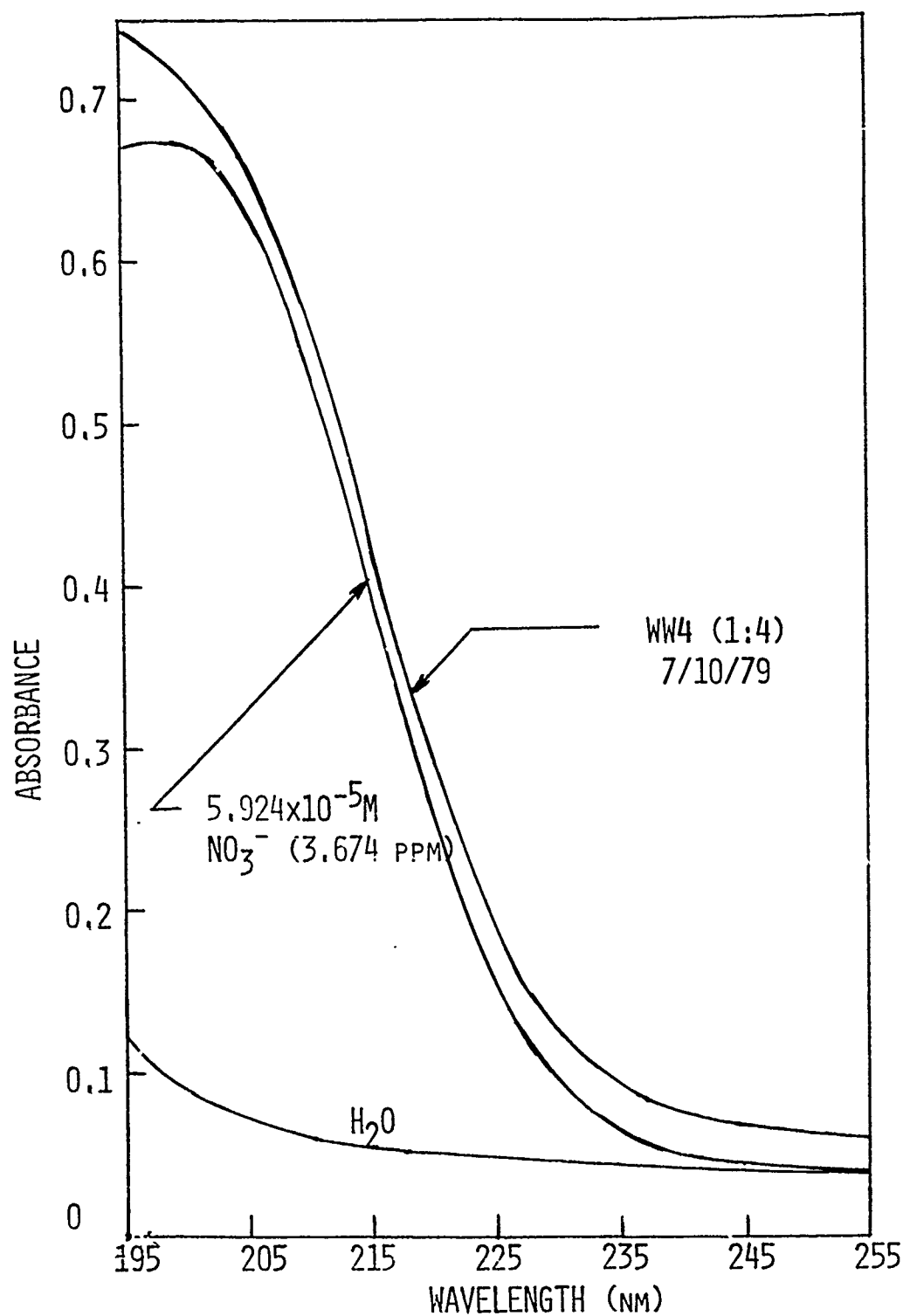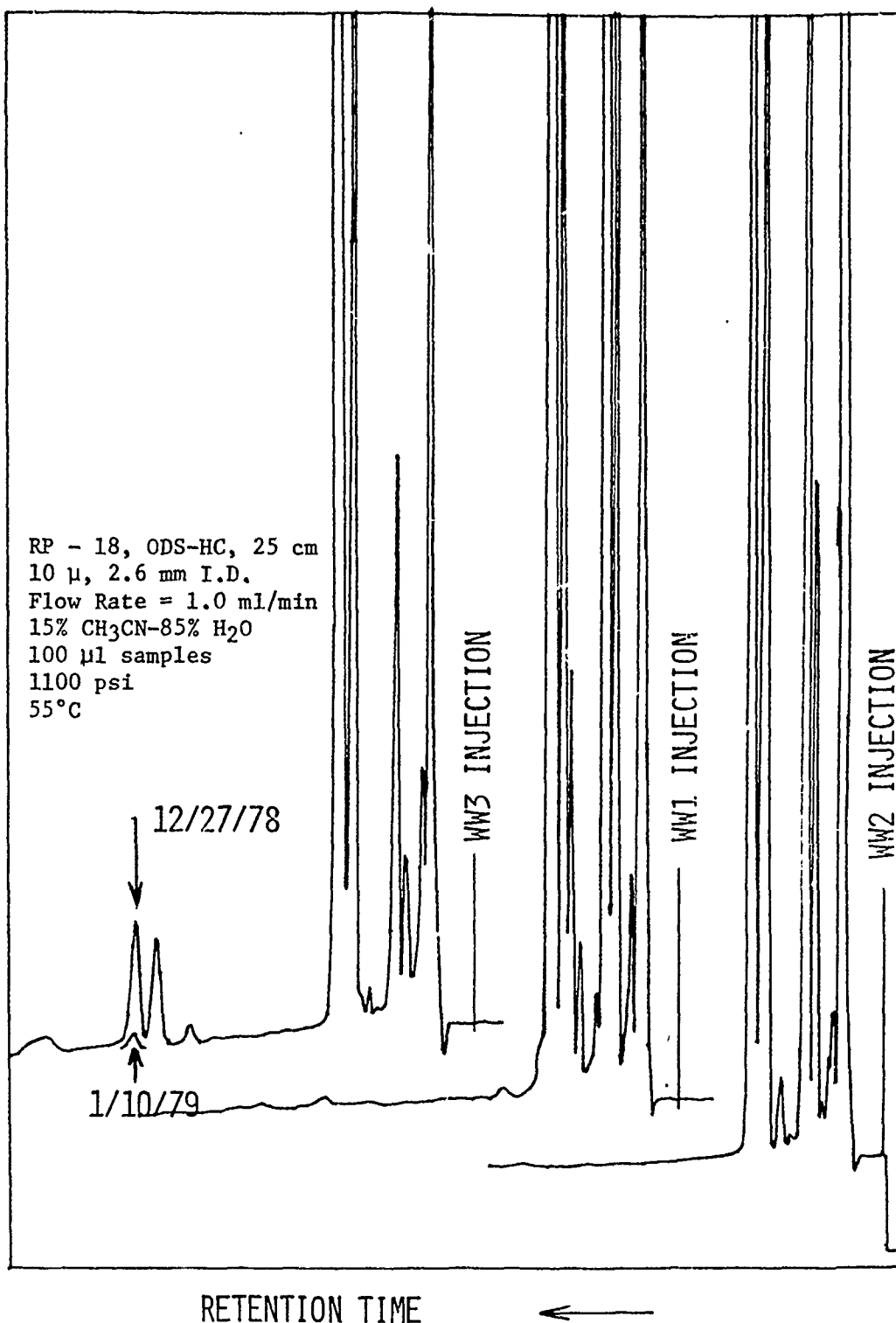Figure 5. Degradation of HSAAP WW4 wastewater

Figure 6.   Degradation of HSAAP WW4 wastewater

22

Figure 7. Liquid chromatograms of HSAAP wastewaters
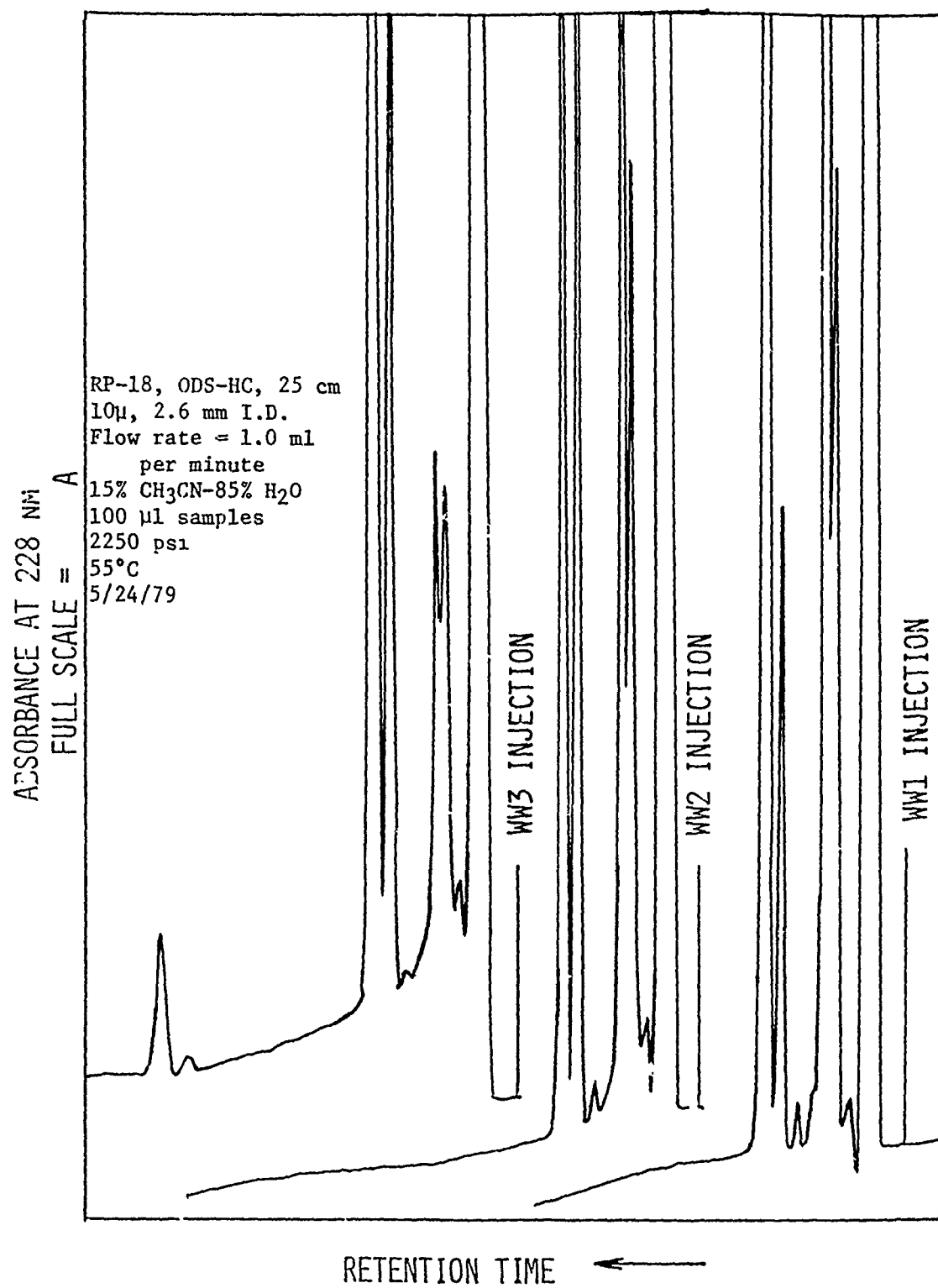
Figure 8. Liquid chromatograms of HSAAP wastewaters

The figure contains the following labels and annotations:

ABSORBANCE AT 228 NM

FULL SCALE = A

RP-18, ODS-HC, 25 cm
10μ, 2.6 mm I.D.
Flow rate = 1.0 ml
    per minute
15% CH_3CN-85% H_2O
100 μl samples
2250 psi
55°C
5/24/79

WW3 INJECTION

WW2 INJECTION

WW1 INJECTION

RETENTION TIME ←

ABSORBANCE AT 228 NM

INJECTION

INJECTION

INJECTION

HMX
RDX

4.30 MIN.
4.83 MIN.

4.15
4.66

2/7/79

5/24/79

7/10/79

RP- 18, ODS–HC, 25 cm
10μ, 2.6 mm I.D.
Flow rate = 1.0 ml/min
15% CH₃CN – 85 % H₂O
100μl samples
55°C
Pressure psi   1200 (2/7)
2250 (5/24), 1200 (7/10)
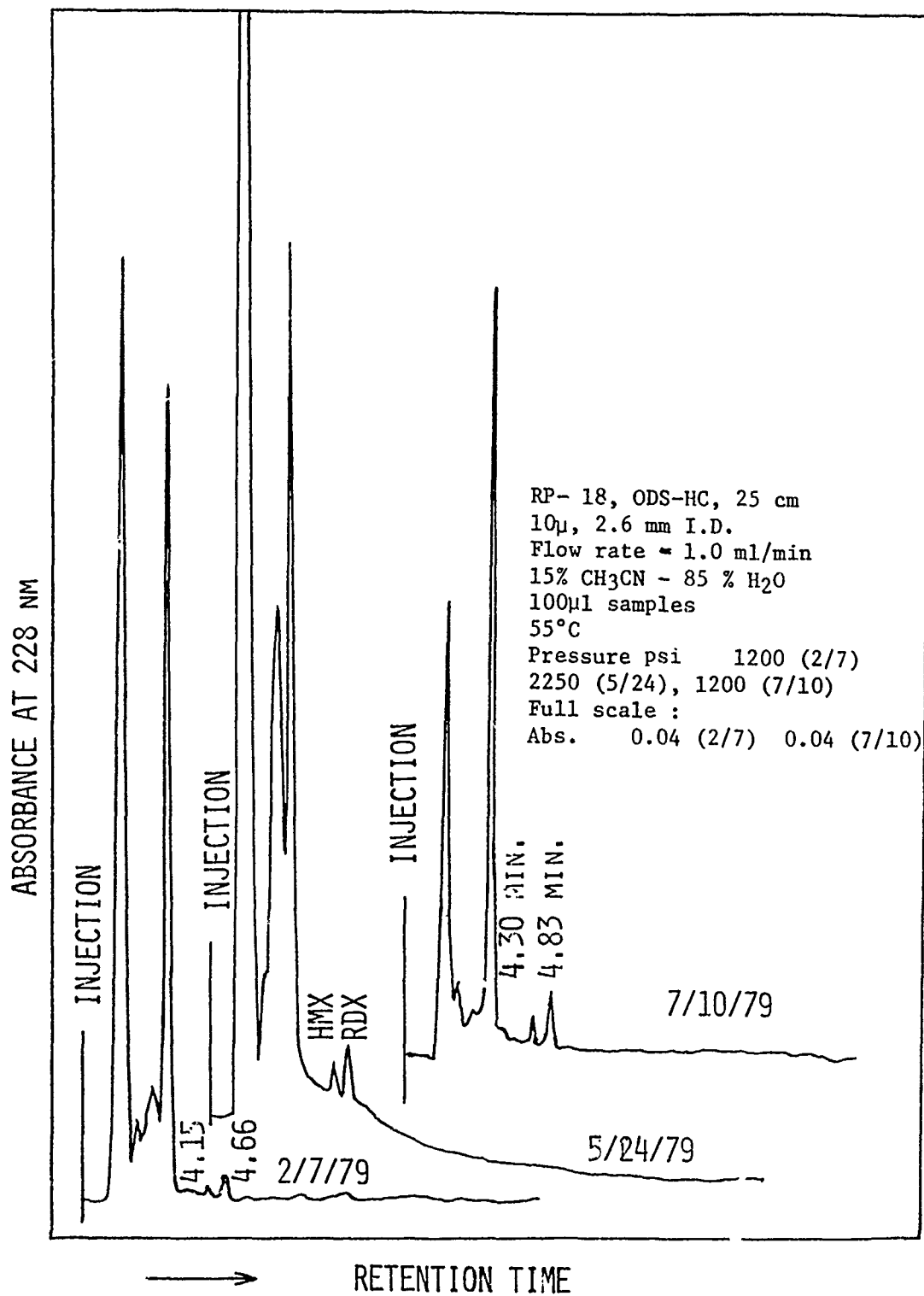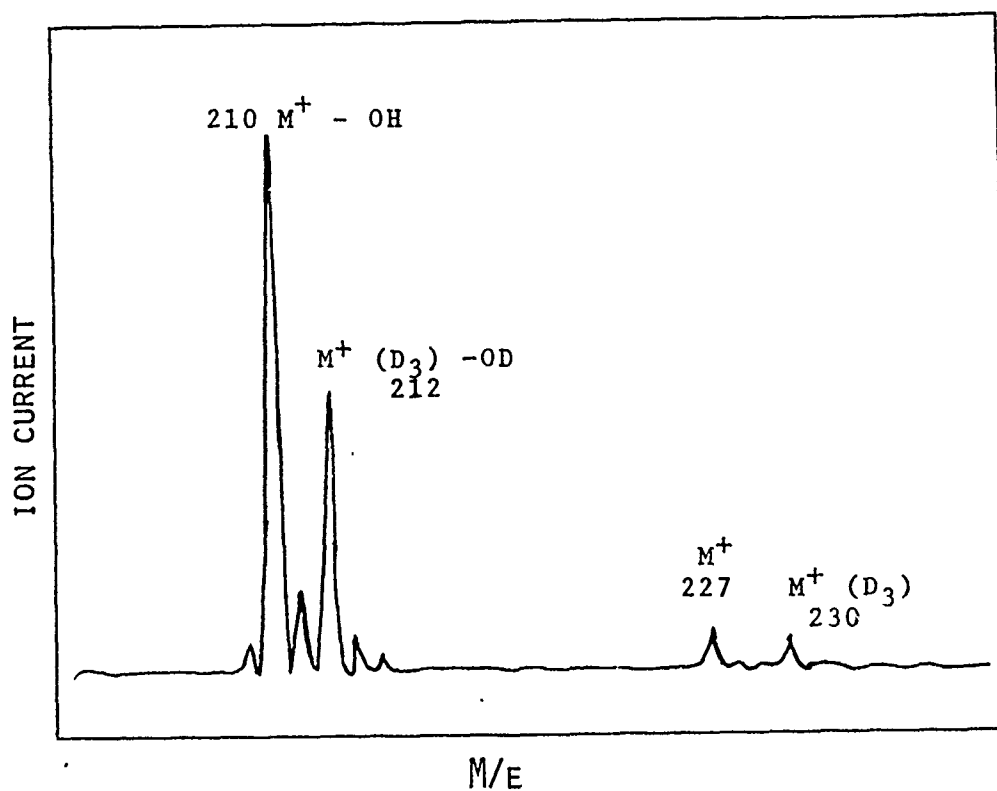Full scale :
Abs.   0.04 (2/7)   0.04 (7/10)

RETENTION TIME

Figure 9. Liquid chromatograms of HSAAP WW4 wastewater

25

Figure 10. Partial mass spectrum (EI, 70 ev) of a mixture of deuterated and undeuterated alpha-TNT (58.83% : 41.17%)
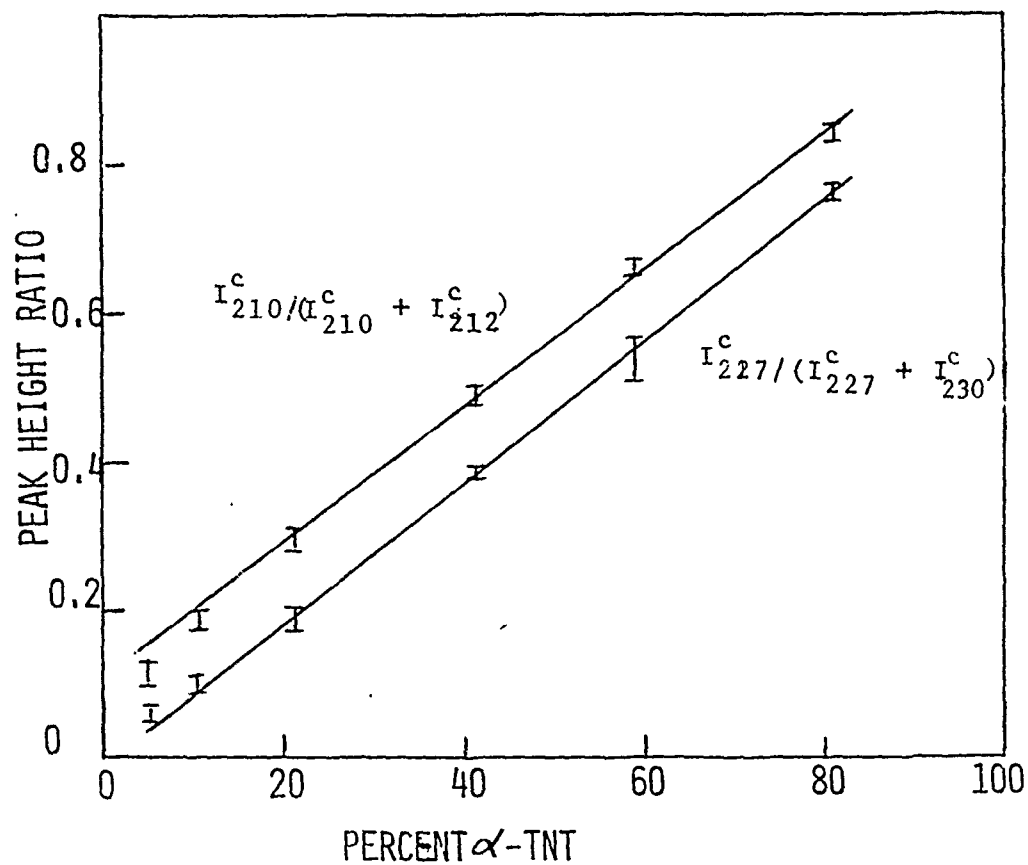
Figure 11. Linearity plot for quantitative determination of alpha-TNT by isotope dilution technique
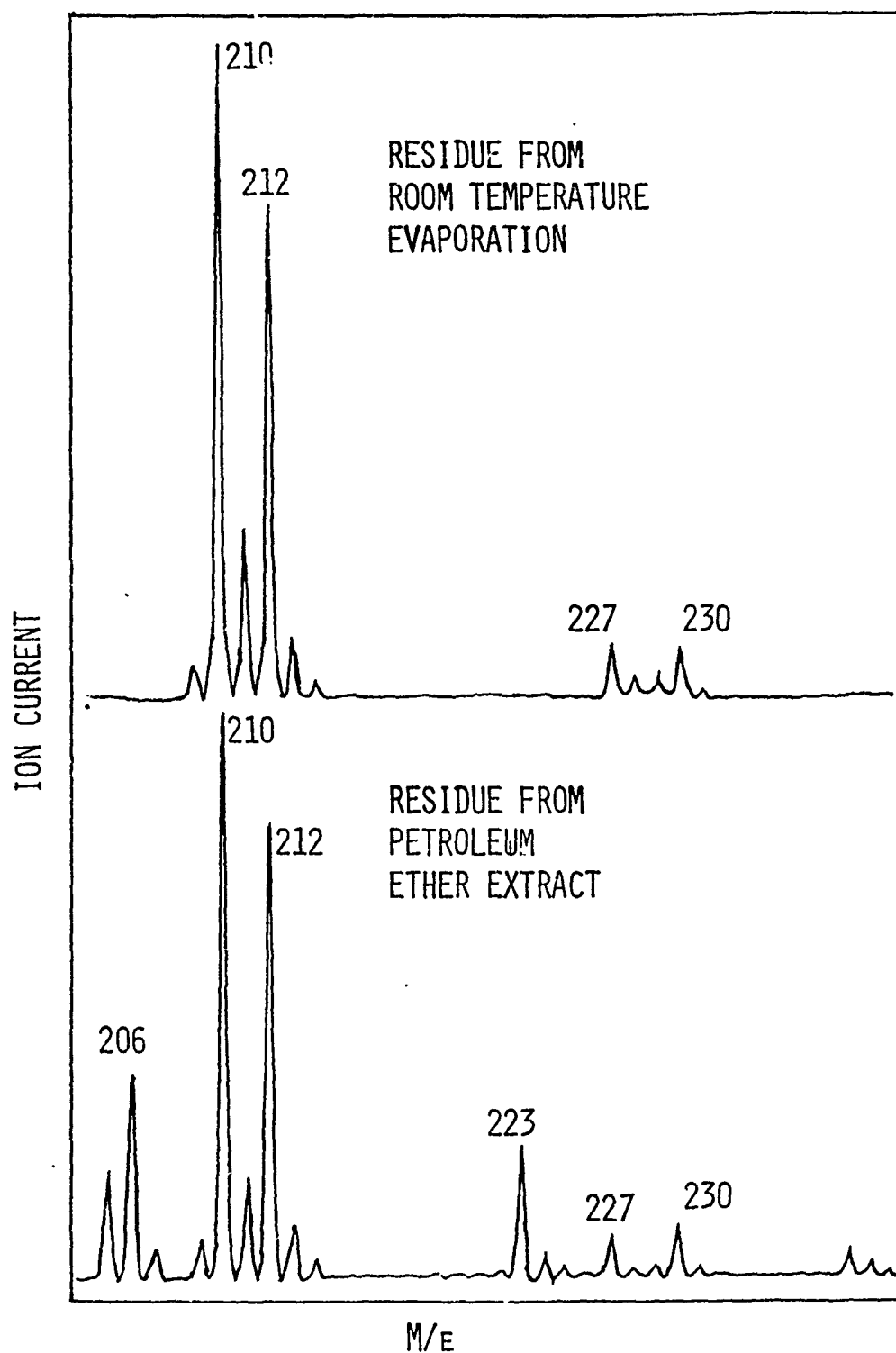
Figure 12. Partial mass spectra (EI, 70 ev) of a mixture of deuterated and undeuterated alpha-TNT (47.6 ppm : 45.7 ppm)
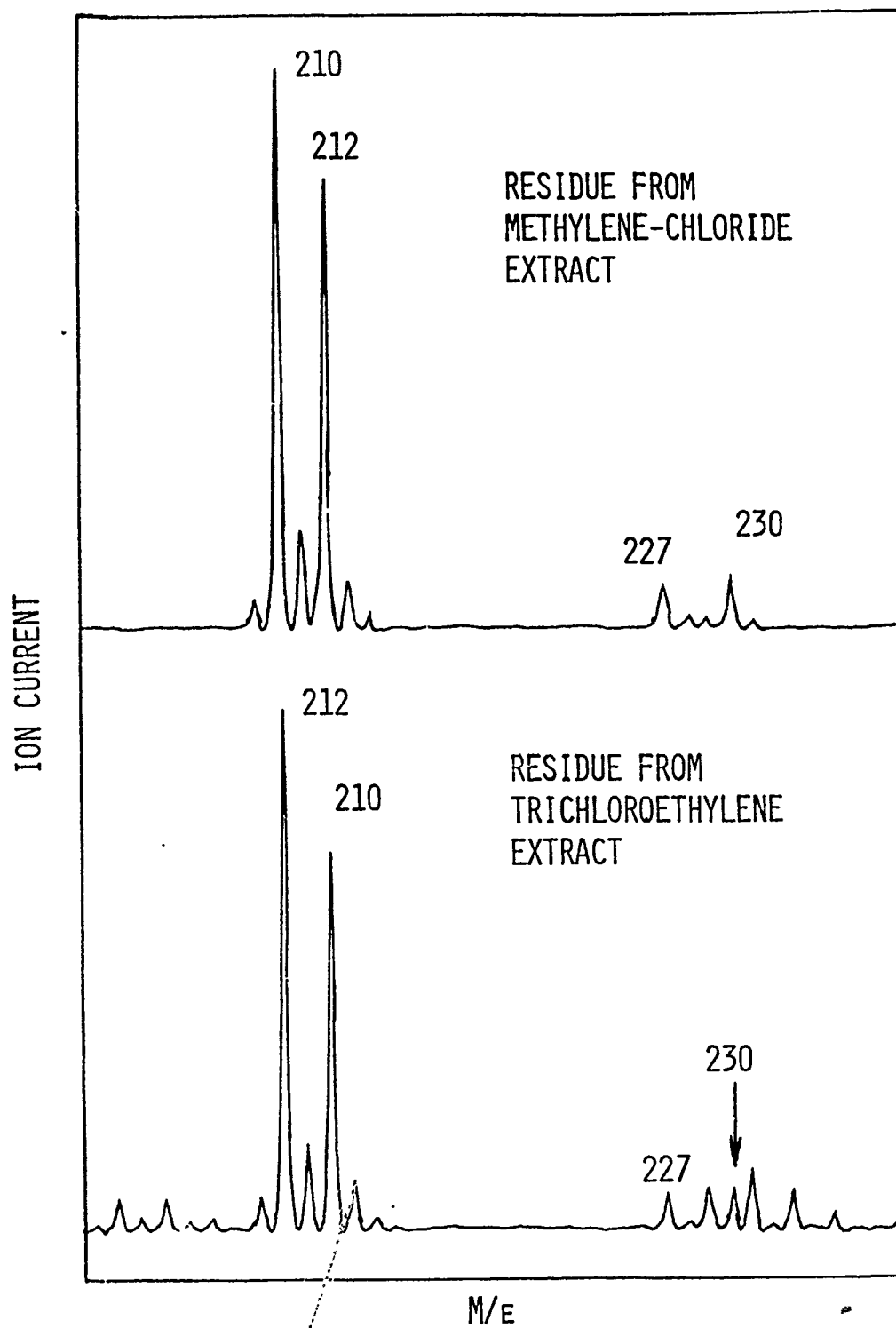
28

Figure 13. Partial mass spectra (EI, 70 Ev) of a mixture of deuterated and undeuterated alpha-TNT (47.6 ppm : 45.7 ppm)

Figure 14. Liquid chromatogram of HSAAP WW1 wastewater
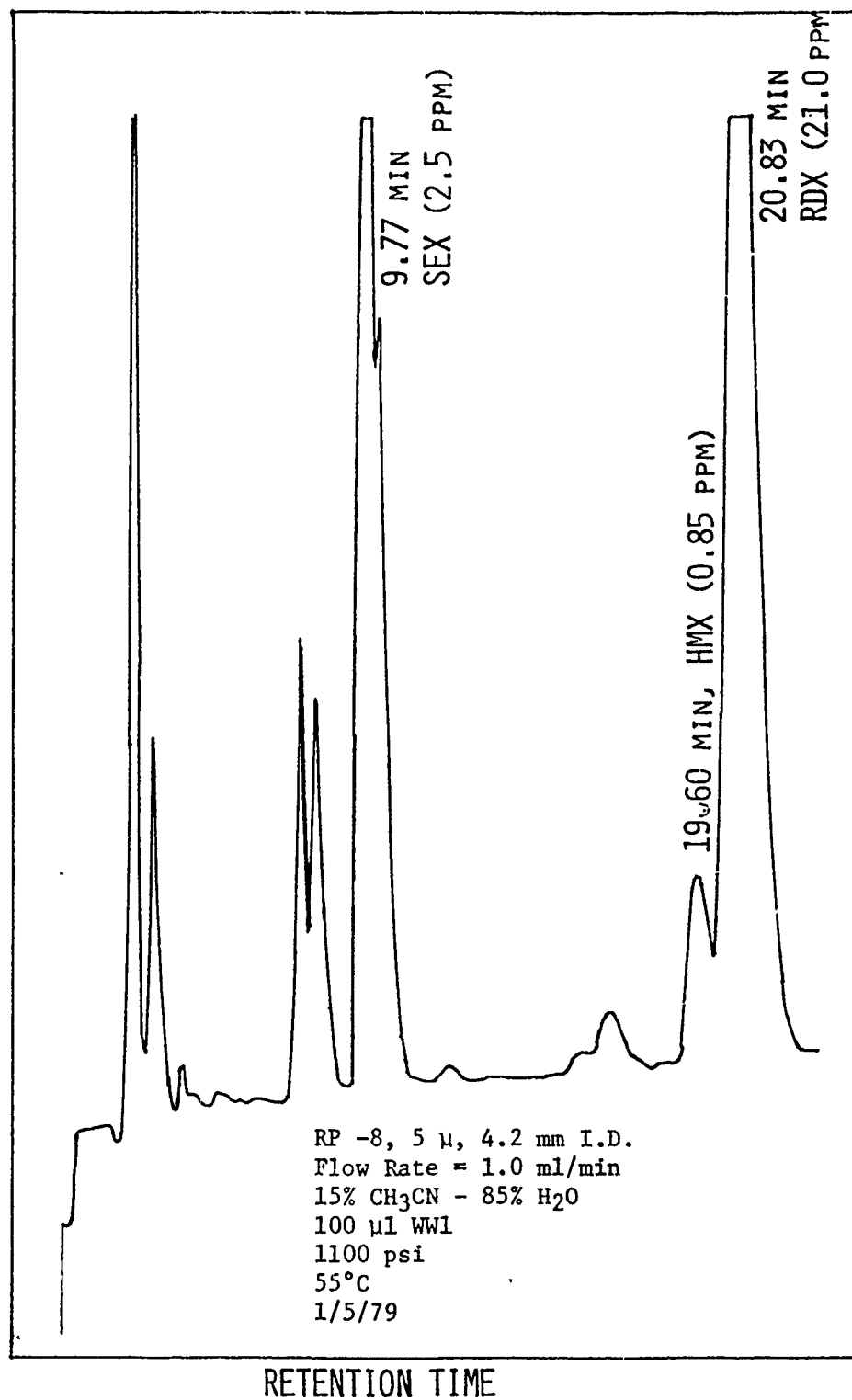
30

Figure 15. Liquid chromatogram of HSAAP WW2 wastewater

ABSORBANCE AT 228 NM
FULL SCALE = 0.04 A

9.80 MIN
SEX (2.5 PPM)

19.41 MIN, HMX (1.7 PPM)
20.64 MIN, RDX (5.1 PPM)

RP-8,5µ, 4.2 mm I.D.
Flow rate = 1.0 ml/min
15% CH$_3$CN - 85% H$_2$O
100 µl WW2
1100 psi
55°C
1/5/79

RETENTION TIME
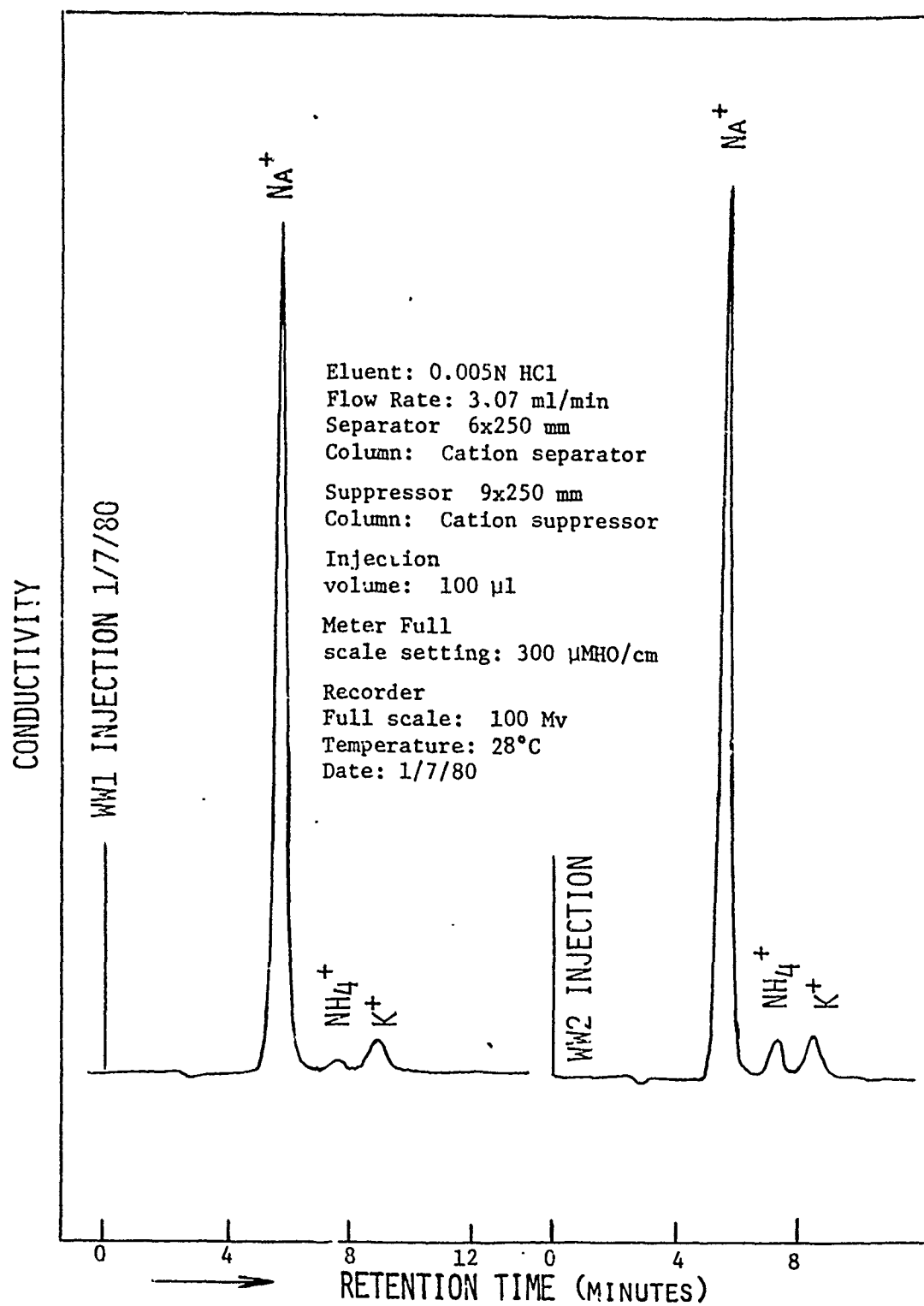
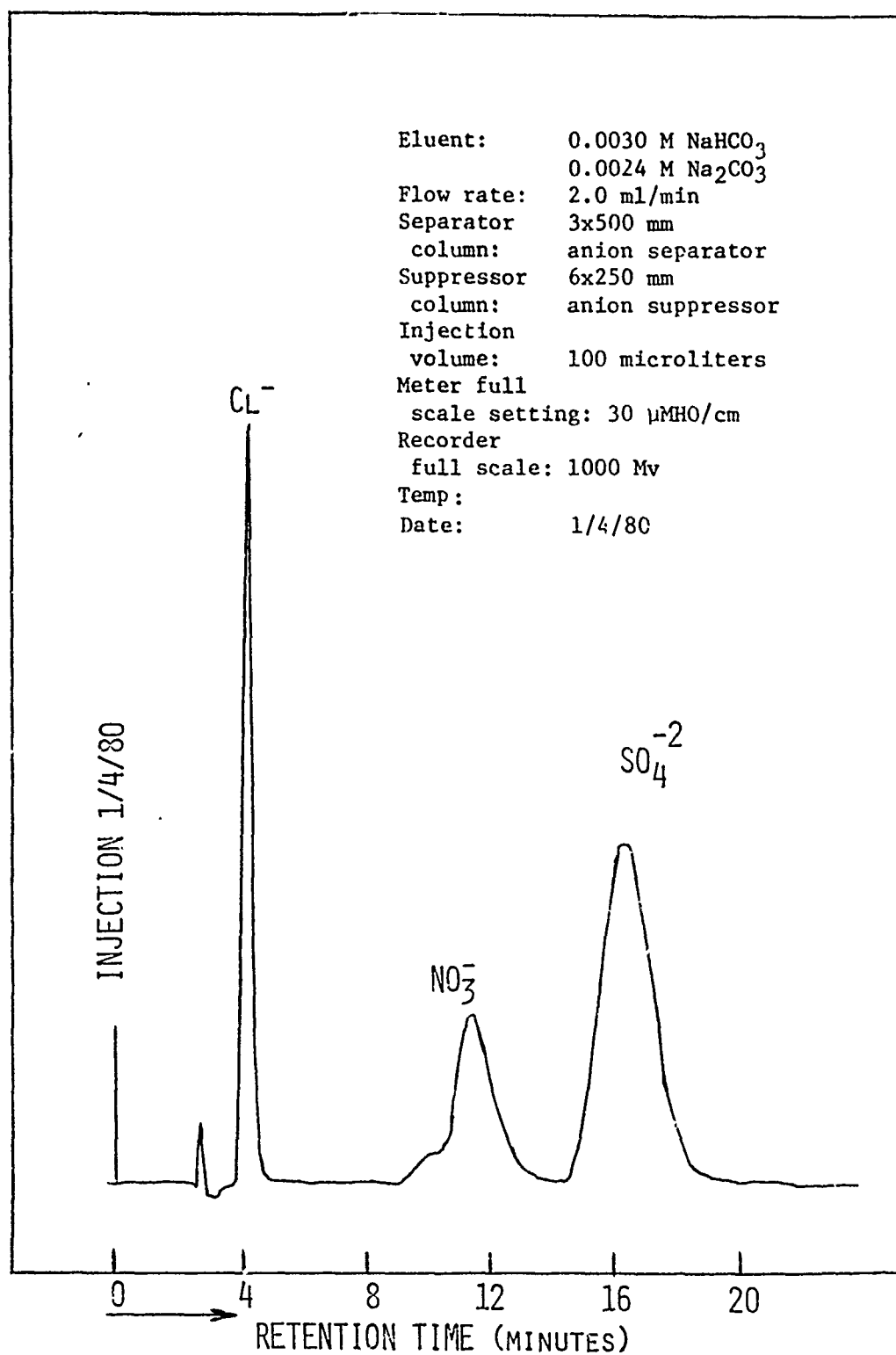Figure 16. Ion chromatogram of HSAAP WW2 wastewater

Figure 17.   Ion chromatogram of HSAAP WW4 wastewater
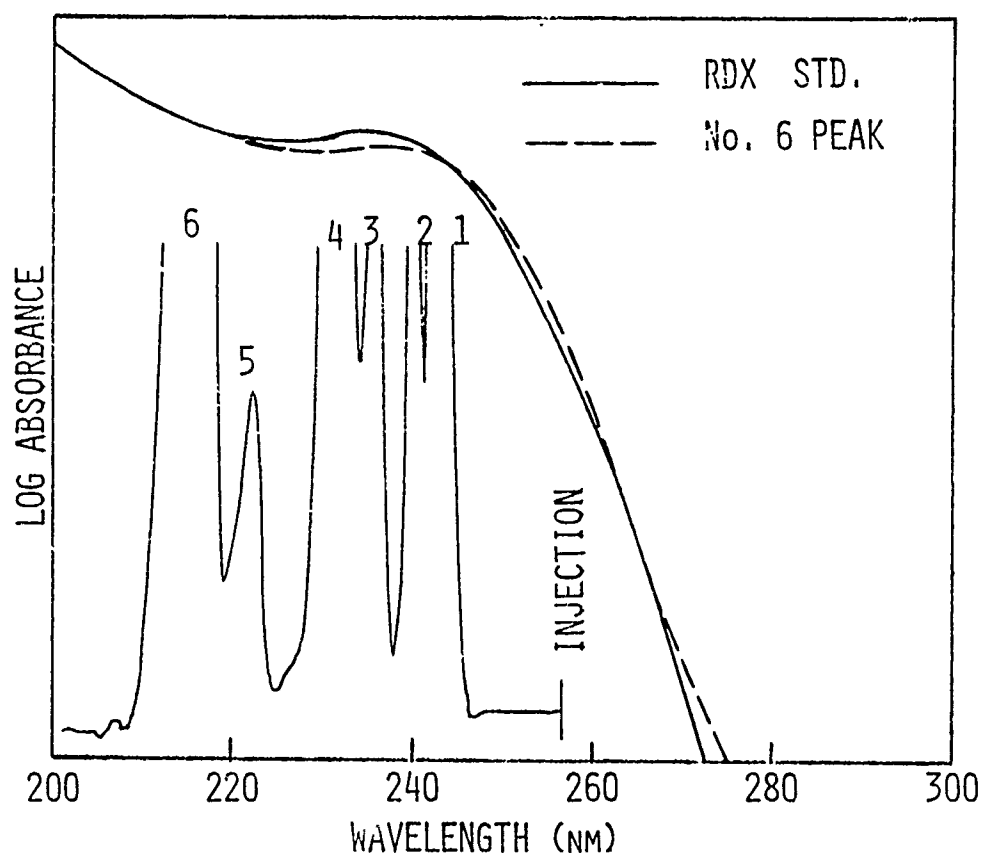
Figure 18.   Full spectrum scanning of No. 6 peak in the HPLC chromatogram of HₒₐP WW1 wastewater by stopped-flow technique

	Metals		
	Cd	Cu	Cr
λ, nm	228.8	324.7	357.9
Slit, mm	1.0	1.0	1.0
Drying Temp. °C/Time, Sec	110/40	110/30	110/40
Charring Temp. °C/Time, Sec	350/10	950/10	1300/10
Atomizing Temp., °C,/Time, Sec	1500/15	2500/15	2700/15
Recorder Range, mv	5	5	2
Chart Speed, mm/min	60	60	60
Conc. of Std., ppb	31.3	106	0.5, 1.0
Vol. of Std., µl	1.0, 2.0	2.0, 5.0	1.0

HGA 2100 Graphite Furnace
Model 56 Recorder

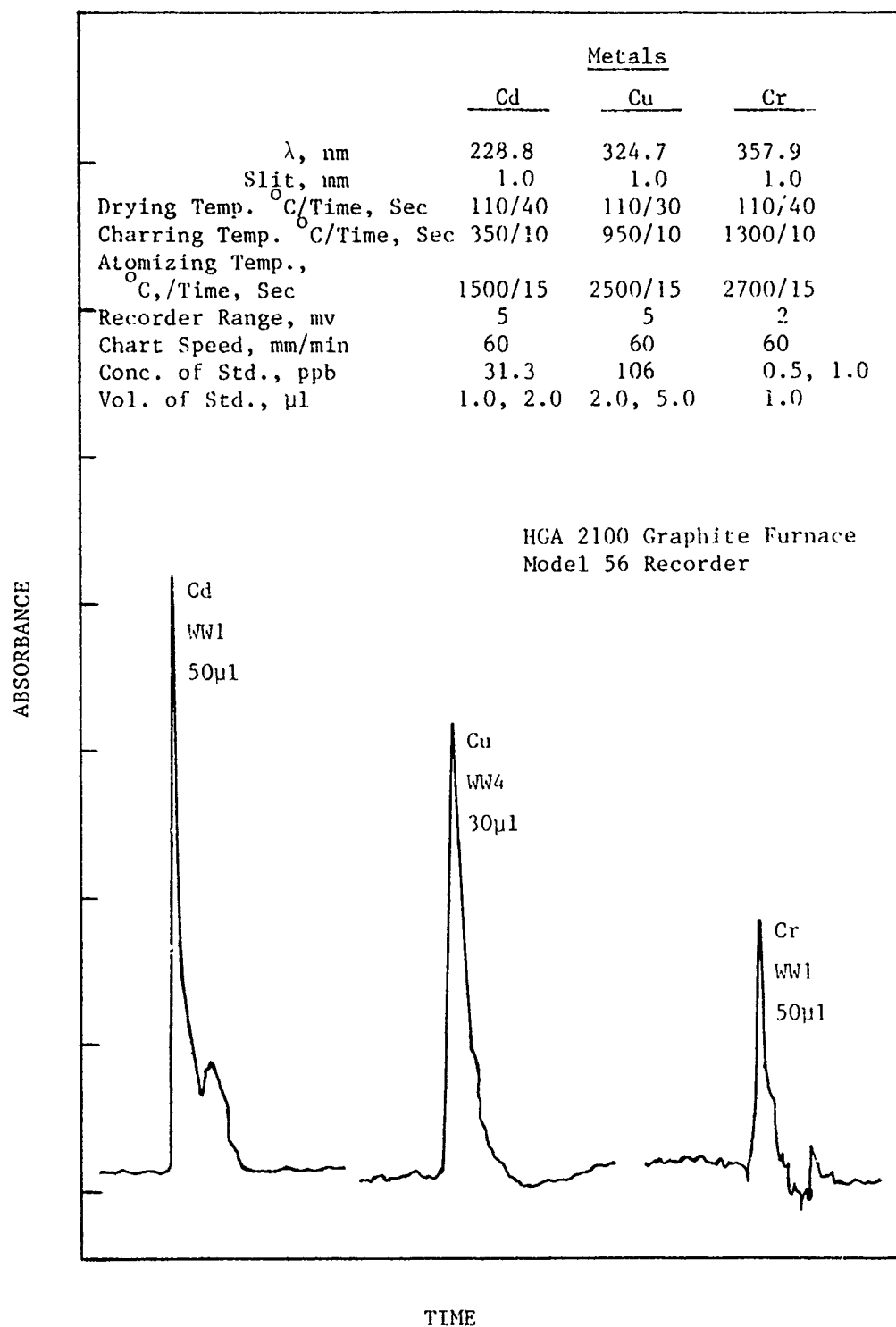ABSORBANCE

Cd
WW1
50µl

Cu
WW4
30µl

Cr
WW1
50µl

TIME

Figure 19. Atomic absorption signals of cadmium, copper, and chromium in HSAAP wastewaters

DISTRIBUTION LIST

Commander
U.S. Army Armament Research and
    Development Command
ATTN: DRDAR-GCL
        DRDAR-LCE (3)
        DRDAR-LCE-C (20)
        DRDAR-TSS (5)
Dover, NJ   07801

Administrator
Defense Technical Information Center
ATTN: Accessions Division (12)
Cameron Station
Alexandria, VA   22314

Director
U.S. Army Materiel Systems Analysis Activity
ATTN: DRXSY-MP
Aberdeen Proving Ground, MD   21005

Commander/Director
Chemical Systems Laboratory
U.S. Army Armament Research and
    Development Command
ATTN: DRDAR-CLB-PA
        DRDAR-CLJ-L
APG, Edgewood Area, MD   21010

Director
Ballistics Research Laboratory
U.S. Army Armament Research and
    Development Command
ATTN: DRDAR-TSB-S
Aberdeen Proving Ground, MD   21005

Chief
Benet Weapons Laboratory, LCWSL
U.S. Army Armament Research and
    Development Command
ATTN: DRDAR-LCB-TL
Watervliet, NY   12189

Commander
U.S. Army Armament Materiel
    Readiness Command
ATTN: DRSAR-LEP-L
Rock Island, IL   61299

37

Director
U.S. Army TRADOC Systems
   Analysis Activity
ATTN: ATAA-SL
White Sands Missile Range, NM 88002

Mr. David E. Renard
USATHAMA
Aberdeen Proving Ground, MD 21010

Commander
Holston Army Ammunition Plant
ATTN: Mr. Mike Mills
       SARHO-EN
Kingsport, TN 37662

Dr. John Glaser
Environmental Research Center
Cincinnati, OH 45268