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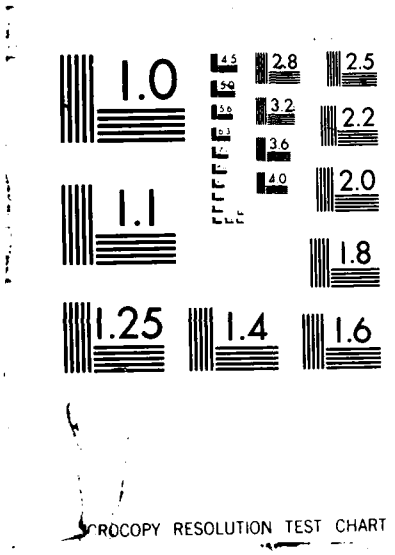
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DEVELOPMENT OF ASSAY METHODS FOR LIQUID PROPELLANTS

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Chromatogram
Dionex ion chromatography

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

A feasibility study conducted by Southwest Research Institute determined that mobile phase ion chromatography (MPIC) and high performance ion chromatography (HPIC) can identify and quantify the components of a liquid propellant. MPIC used a Dionex ion chromatograph equipped with a cation fiber suppressor and electrochemical and conductivity detectors in series. Sharp peaks were detected for the hydroxylamine and triethanolamine in LP 1845. In this sample, 252.7 ppm hydroxylammonium nitrate (86.9 ppm as free hydroxylamine) and 79.8 ppm (cont)

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20. ABSTRACT (cont)

triethanolammonium nitrate (56.1 ppm as free triethanolamine), were detected. Hexanesulfonic acid was used as the eluent in this MPIC separation. Two different mobile phase systems were found suitable for the liquid propellant separation of NOS-365 and LP 1845 by HPIC. For NOS-365, an acetonitrile/water (5:95), 0.01M in octanesulfonic acid at a pH 3.1 and a flow rate of 2.0 ml/min. eluted hydroxylammonium nitrate (HAN) at 4.8 minutes and isopropylammonium nitrate (IPAN) at 7.0 min. An acetonitrile/water (10:90), 0.005M in octanesulfonic acid at a flow rate of 2.0 ml/min. was used for LP 1845 to elute HAN at 5.3 min., triethanolammonium nitrate (TEAN) at 4.8 min., and IPAN at 14.0 min. Before quantification of these separations can be meaningful, optimization of the systems and creation of standard curves will have to be established.

CONTENTS

INTRODUCTION

The Ballistics Research Laboratory has sought to develop an accurate, reliable method for the analysis of the constituent components in a liquid propellant formulation. This is essential to ensure reproducible ballistic performance of liquid propellants. Variations in any one of the formulation ingredients can result in a loss in desired ballistics. Different analytical test methods have been attempted in an effort to establish a viable method of analysis for liquid propellants. The use of the ASTM 31-78 test method to determine carbon, hydrogen, nitrogen, and oxygen proved inaccurate. Erratic test data were obtained with gas chromatography because the liquid propellants decomposed and the column deteriorated.[1] Potentiometric titrations[2] and Fourier Transform Infrared Spectroscopy (FTIR)[3] are presently under investigation. Although these methods appear attractive, accuracy in quantification by these techniques has not been fully established. In general, chromatographic methods provide complementary information to these other techniques.

High Performance Ion Chromatography (HPIC) and Mobile Phase Ion Chromatography (MPIC) have been used successfully in the past as a separation mechanism to quantify components which are very polar, multiply ionized, and/or strongly basic. In each of these methods, the analyte ions are "paired" with a surfactant-like ion which contains a hydrophilic and hydrophobic moiety. The ion pairs formed between the analyte ions and the pairing reagent are different in hydrophobic character which provides the basis for their separation on a hydrophobic column. The HPIC columns are silica based; while the MPIC columns are polystyrene-divinyl benzene. These different column materials affect the eluent system and pH range which each column can accommodate. The availability of different detection modes and column materials increases the probability of developing a fast, accurate, and precise assay method for liquid propellants.

OBJECTIVE

The objectives of this feasibility study were to explore the application of two distinct, but closely related analytical techniques as potential viable analytical methods of analyses for liquid propellants.

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[1]Work conducted under BRL contract DAAD05-83-M-M082 at Southwest Research Institute, San Antonio, Texas.

[2]Work conducted under BRL Contract DAA 629-81-D-0100 at the University of Maryland.

[3]Fifer, R.A.; Cronin, J.T.; Determination of Liquid Propellant Compositions by A Fourier Transform Infrared-Cylindrical Internal Reflection (TIR-CIR) technique; Paper 1984 JANNAF Propellant Characterizating Sub-Committee Meeting, Colorado Springs, September 1984.

MOBILE PHASE ION CHROMATOGRAPHY

The work effort for the mobile phase ion chromatography program was conducted on a Dionex Ion Chromatograph equipped with electrochemical and conductivity detectors in series. A listing of the specific equipment items used in the system can be found in Table 1. In the initial efforts to separate the components hydroxylammonium nitrate (HAN) and triethanolammonium nitrate of a liquid propellant, LP 1845 Lot 244, a cation fiber suppressor column was used. The advantage of this fiber suppressor is its ability to regenerate continuously while the analysis is being conducted. An aqueous hexanesulfonic acid eluent was prepared in-house by ion exchanging aqueous sodium hexanesulfonate with an acid form cation exchange resin. A very erratic performance of the chromatographic system was obtained with this eluent and column. It was suspected that the in-house eluent was not sufficiently pure for a stable system operation. A certified, chemically pure hexanesulfonic acid was obtained from Dionex and the cation fiber suppressor was replaced with a fixed bed cation suppressor in the borate form. The change resulted in a significantly improved system stability.

It was anticipated that the impurities monoethanolammonium nitrate and diethanolammonium nitrate would be present. Under chromatographic conditions cited in Table 2, a near baseline separation of mono-, di- and triethanolamines with very symmetrical peak shapes was obtained. This separation, shown in Figure 1, was achieved with an aqueous sample that contained 50 ppm hydroxylammonium chloride (HACL), 25 ppm monethanolammonium chloride (EACL), 50 ppm diethanolammonium hydrochloride (DEACL), and 100 ppm triethanolammonium hydrochloride (TEACL). An electrical conductivity detector with a sensitivity of 3 microsiemens (uS) was used for the detection. The retention times for EACL, DEACL, and TEACL were 12.0, 16.5, and 20.7 minutes, respectively. There was a very small peak occuring at 9.7 minutes that was concluded to be HACL. This very small peak could indicate insufficient sensitivity of the conductivity detector for this compound or problems associated with the chemical aspects of mobile phase ion chromatography. The post column suppressor functions by removing excess pairing reagent, hexanesulfonic acid, or more specifically, the hexanesulfonate ion from the eluent. This provides for low background conductivity. If the ion-pair formed between the hydroxylamine and hexanesulfonic is sufficiently weak to allow removal of the hexanesulfonate ion from the ion pair in the suppressor, the free hydroxylamine generated would be expected to decompose.

An electrochemical detector was placed in the system ahead of the suppressor. The detector was fitted with a platinum electrode set at a potential of +1.0 volt relative to a silver-silver chloride reference electrode. As shown in the left hand chromatogram of Figure 2A, HACl (50 ppm as free amine) afforded a single peak with a retention time of 9.7 minutes. Some tailing of the peak can be observed which is indicative of less than optimal chromatographic conditions. No peaks were observed at retention times that correspond to alkanol amines. This indicates that the alkanol amines were oxidatively stable at these detector conditions.

A sample of LP 1845 Lot 244 was diluted 1:2500 with deionized water to give a solution containing 252.7 ppm HAN (86.9 ppm as free hydroxylamine) and 79.8 ppm TEAN (56.1 ppm as free triethanolamine). This solution was then analyzed using electrochemical and conductivity detectors in series. The electrochemical response is seen in Figure 2B. Again, the detector showed one peak at a retention time of 9.7 minutes. The trailing was more pronounced in this chromatogram. This was probably due to the higher column loading. Figure 3 shows the chromatogram of hydroxylamine. HNO_3 in LP 1845 Lot 244 using a conductivity detector. There are two peaks of interest. The peak 3B is seen at 9.7 minutes with a second unresolved shoulder at 10.3 minutes. This shoulder is suggestive of hydroxylamine, although the response was significantly greater than the one obtained from hydroxylamine hydrochloride (Figure 1). The shoulder could be attributed to an impurity. It does not appear to be monoethanolamine which was found to elute at 12.0 minutes. The hydroxylamine concentration in the solution of hydrochlorides was 50 ppm, while the hydroxylamine in the LP 1845 sample was 86.9 ppm (as the free amine). The limited level of effort available for this feasibility study did not permit the resolution of this discrepancy. Peak 3C is triethanolamine HNO_3 and eluted at 20.8 minutes.

It should be noted that on the chromatograms there is a detector response of varying size at 2.3 minutes. This peak is characteristic of most ion chromatograms for it represents the detection of trace quantities of ionic material which have a zero interaction with the separation column. The peak always elutes at the time required to pump the materials through the pore (or free void) volume of the column. This peak is called the void volume peak. For a given volume, the elution time of the peak is a function of the free volume and eluent flow rate.

REVERSE PHASE HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC) USING ION-PAIR TECHNIQUES

Samples of liquid propellants NOS 365 (HAN, isopropylammonium nitrate (IPAN), and water) and LP 1845 (HAN, TEAN, and water) were analyzed under the ion-pairing chromatographic systems described in Tables 3 and 4. Two different mobile phases were required for the component separations, one for NOS 365 and one for LP 1845. For the NOS 365, a mixture of acetonitrile/water, (5:95), 0.01M in octanesulfonic acid at a 3.1 pH and a flow rate of 2.0 mL/min eluted HAN in 4.8 min. and IPAN in 7.9 min. A peak of unknown origin was observed to elute in 4.3 min. under these conditions when any of the LP's or their component salts were injected. This peak may be ascribed to a nitrate in some form.

In the LP 1845 analysis, the HAN and TEAN were not well separated under these conditions. A modification to the mobile phase allowed the HAN and TEAN to be separated. This mobile phase was acetonitrile/water (10:90), 0.005M in octanesulfonic acid at a flow rate of 2.0 mL/min. With this system HAN eluted at 5.3 min. and TEAN at 4.8 min. When NOS 365 was analyzed by this system, IPAN eluted at approximately 14 min. as a broad, tailing peak. It should be noted that small changes in the pH (2.5-3.5) had no observable effect on the chromatography in either mobile phase system.

CONCLUSIONS

1. Hydroxylammonium nitrate, triethanolammonium nitrate, monoethanolammonium nitrate, and diethanolammonium nitrate can be cleanly separated in LP 1845 by MPIC with a combination of conductivity and electrochemical detectors.

2. High purity hexanesulfonic acid is essential for the MPIC system to insure stability of the system.

3. Separation of the major components of NOS 365 and LP 1845 was achieved with HPLC.

4. The differential refractive index detector, used in the HPLC system, proved to be non-ideal for quantifying the peak separations. A state-of-the-art conductivity detector may be more suitable for this application.

RECOMMENDATIONS

1. Optimization of the mobile phase and/or separation column and detection system for either chromatographic technique should follow directly from this feasibility work.

2. The general techniques of mobile phase ion chromatography and ion paired chromatography should be developed as simple, rapid, and precise analytical methods for the assay of liquid propellants.

Table 1. Ion chromatography (MPIC) system

Dionex Model 2020i Dual Channel Instrument

Percolumn	MPIC-NG1	4x50 mm
Separator Column	MPIC-NS1	4x200 mm
Suppressor Column	CSC-1 cation suppressor in forate form	6x60 mm
Detectors	Ion Chrom/Cond electrical conductivity detector Ion Chrom/Amp amperometric electrochemical detector	

Table 2. MPIC chromatography conditions

Eluent	0.002 M aqueous hexanesulfonic acid
Eluent Flow Rate	1.0 mL/min
Sample Loop Volume	60 µL
Conductivity Detector	3.0 µS or 10.0 µS full scale
Electrochemical Detector	3.0 µA/V or 10.0 µA/V full scale

Table 3. Ion-pairing chromatography (HPLC) system

Pump:	Waters Associates M-6000A
Injector:	Rheodyne Model 7125
Sample Loop Volume	20 µL
Column:	Waters Associates Radial Compression Module fitted with either a C-8 or C-18 10 um cartridge
Detector:	Waters Associates R401 Differential Refractometer

Table 4. List of ion-pairing chromatographic conditions examined

Column	Mobile Phase	Ion-Pairing Agent (Concentration, M)	pH	Flow, mL/min	Comments
C-8[a]	MeOH/H_2O (30:70)	PSA[b] (0.005)	3.0	2.0	No separation
C-8[a]	MeOH/H_2O (40:60)	PSA[b] (0.005)	3.0	2.0	No separation
C-8[a]	MeOH/H_2O (50:50)	OSA[c] (0.005)	3.0	2.0	No separation
C-8[a]	MeOH/H_2O (40:60)	OSA[c] (0.005)	3.0	2.0	No separation
C-18[d]	MeOH/H_2O (40/80)	OSA (0.005)	3.5	2.0	HAN, TEAN not separated
C-18[d]	MeOH/H_2O (30/70)	OSA (0.005)	3.5	2.0	HAN, TEAN not separated
C-18[d]	MeOH/H_2O (30/70)	OSA (0.005)	3.5	1.0	IPAN had poor peak shape
C-18[d]	MeOH/H_2O (30/70)	OSA (0.005)	3.5	2.0	HAN, TEAN not separated
C-18[d]	MeOH/H_2O (30/70)	OSA (0.005)	3.5	2.0	HAN, TEAN not separated
C-18[d]	CH_3CN/H_2O (20/80)	OSA (0.005)	3.5	2.0	HAN, TEAN not separated
C-18[d]	CH_3CCN/H_2O (10/90)	OSA (0.005)	3.5	2.0	HAN, TEAN not separated
C-18[d]	CH_3CN/H_2O (5/95)	OSA (0.005)	3.5	2.0	HAN, TEAN separated; IPAN had poor peak shape
C-18[d]	CH_3CN/H_2O (5/95)	OSA (0.01)	3.5	2.0	HAN, TEAN poorly separated, IPAN peak tailed
C-18[d]	H_2O	PSA (0.005)	2.8	1.0	No peaks eluted <15 min

a. Waters Associates10 µm C-8 Radial Compression Cartridge, 8x100 mm
b. Pentanesulfonic acid
c. Octanesulfonic acid
d. Waters Associates10 µm C-18 Radial Compression Cartridge, 8x100 mm

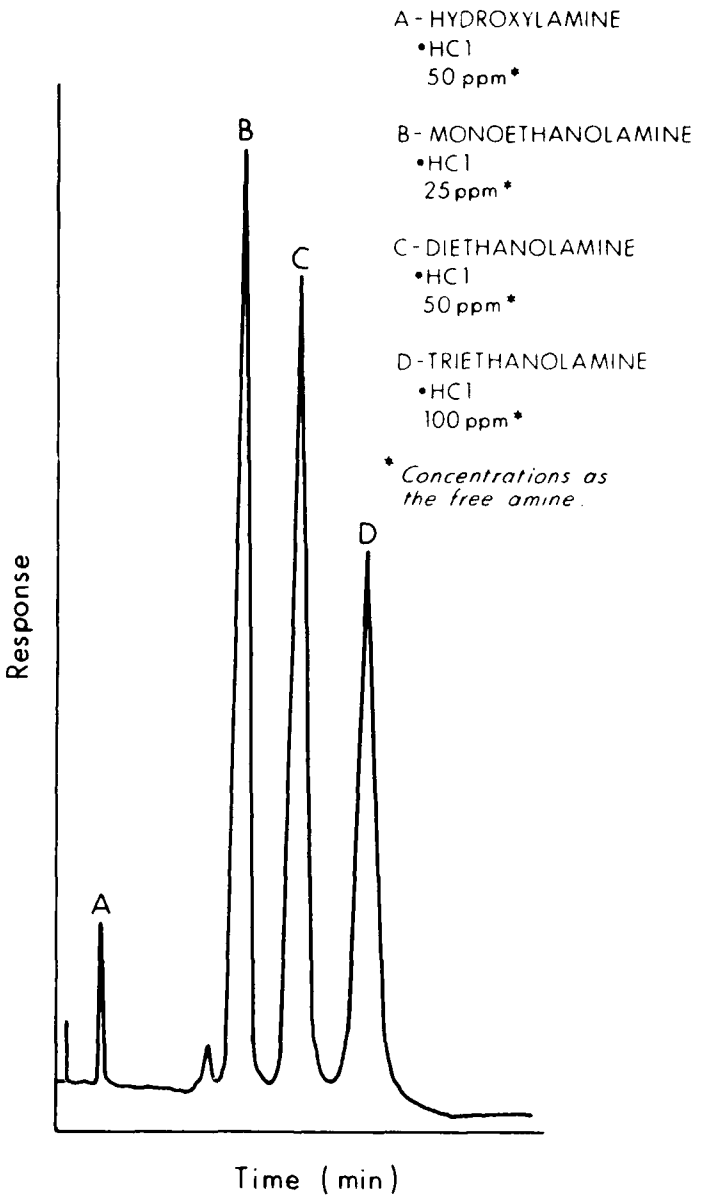

Figure 1. Separation of alkanolamines by MPIC conductivity detection

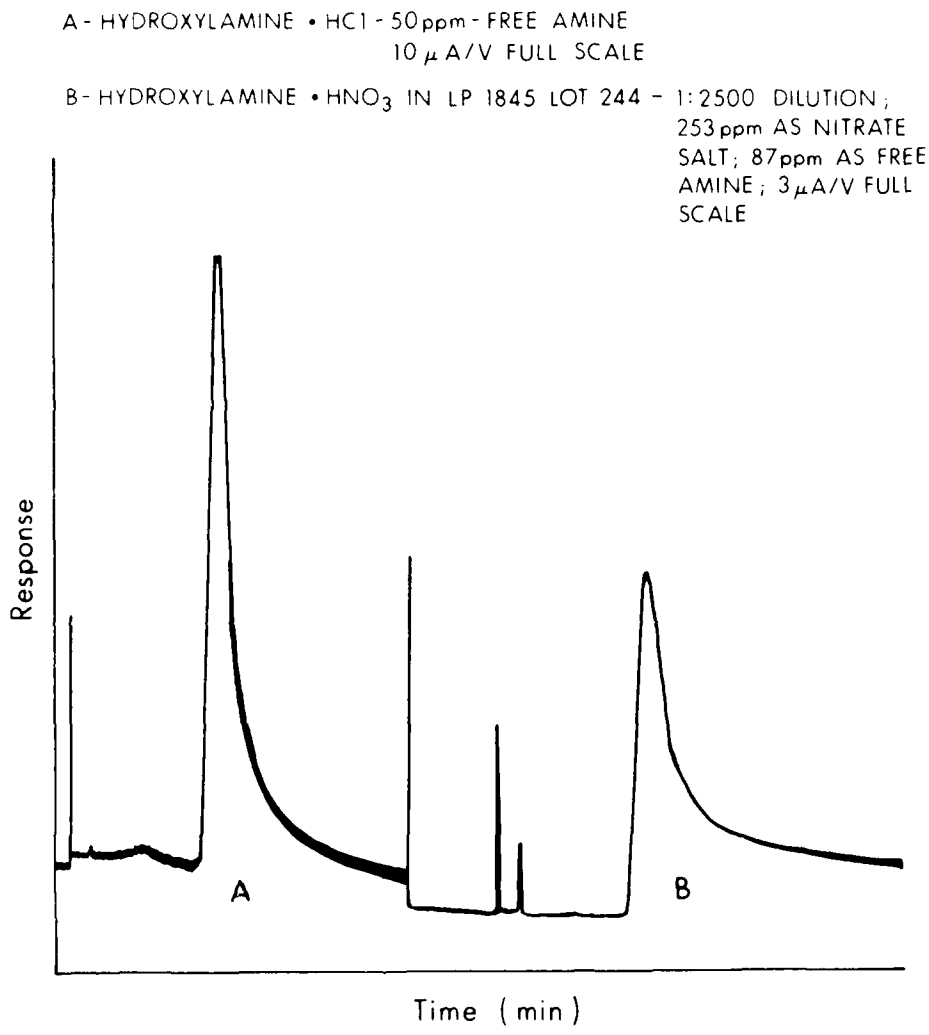

Figure 2. Electrochemical detection of hydroxylamine

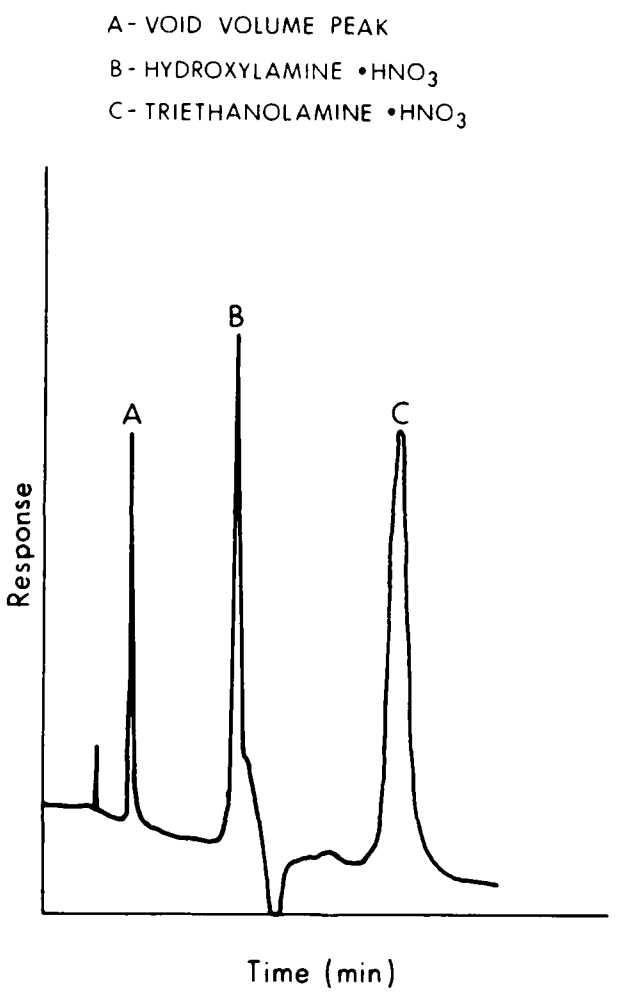

Figure 3. Separation of LP 1845 components

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