COMPONENT ASSAY OF LX-09

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MASTER

QUALITY DIVISION

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ABSTRACT

A liquid chromatographic method was developed for analysis of FEFO and PDNPA in LX-09. The method is more accurate and rapid than previous analytical techniques.

INTRODUCTION

The explosive LX-09 is utilized in an existing weapon system. A complete characterization of the LX-09 is therefore vital to an evaluation of the entire system. The first step of the characterization is the basic component assay of LX-09 for HMX, FEFO, and PDNPA. At present, HMX is determined gravimetrically after extraction of the LX-09 with 1,2-dichloroethane. The FEFO is determined by a titration of the fluoride (produced by combustion of LX-09 in a Parr Bomb) with thorium. This method is not only time consuming and tedious, but assumes all fluoride to be due to FEFO, which is not necessarily true. In particular, decomposition of FEFO to nonmigratory products or transesterification would not be detected by this combustion-titration technique. The PDNPA is calculated as the difference between 100 and the sum of all other measured components. This technique is subject to positive PDNPA bias, as all impurities are counted as PDNPA. Also, it is statistically subject to the collective errors of all other measurements. Therefore, a high speed liquid chromatographic technique was developed for the rapid determination of FEFO and PDNPA. This technique is not only a time savings, but also represents direct measurement of the two components. Because of some of the unique characteristics of liquid chromatography, including the facts that it does not enhance structural transformations of the components, it is rapid and precise, and it does not require heating the explosive, a separation of the major components was attempted chromatographically. However, the widely varying characteristics of the FEFO, PDNPA, and HMX made this technically unfeasible. Therefore, a preliminary extraction of FEFO from LX-09 was performed, followed by separate LC assays for FEFO and PDNPA.

In this technique, the FEFO is extracted from LX-09 with ethyl ether. The ether is evaporated and the residue taken up in tetrahydrofuran (THF). An aliquot is then injected into a chromatograph using a 1 m Corasil II column and THF carrier. From comparison with a calibration curve, the total FEFO is calculated. The residue from the ether extraction is treated with THF and an aliquot of this solution injected into the chromatograph. The PDNPA is then calculated from comparison with a calibration curve. All peaks are detected with a differential UV detector.

EXPERIMENTAL

APPARATUS

All chromatographic measurements were performed using a Perkin Elmer Model 601 High Speed Liquid Chromatograph. The column was fabricated from 0.3175 OD x 100 cm stainless steel tubing and was packed with Corasil II. The carrier was unstabilized (UV grade) tetrahydrofuran (THF), and flow rate was 2 mL/min. A differential UV detector at 220 nanometers was used to detect the separated components.

PROCEDURE

A 500 mg sample of LX-09 is extracted with 10 mL ethyl ether for one hour. The mixture is then filtered through a fine glass-fritted crucible. The residue is washed with a minimum of ethyl ether. The filtrate is then evaporated to dryness under vacuum and this residue taken up in 10 mL of UV grade THF.

An aliquot is then analyzed chromatographically for the FEFO. The residue from the ether extraction is leached with 10 mL THF, filtered through a glass-fritted crucible, and transferred to a 10 mL volumetric flask. An aliquot of this liquid is then analyzed chromatographically for PDNPA.

DISCUSSION

PRELIMINARY EXAMINATION OF LX-09

The possibility of simultaneous separation and measurement of FEFO and PDNPA by chromatography was examined closely. Only a few solvents, THF, dimethylformamide (DMF), methylene chloride, methylethyl ketone (MEK), p-dioxane, and acetone were found to be suitable for both PDNPA and FEFO. The liquid chromatograph which was available was equipped with a differential UV detector. To get the necessary sensitivity, detection had to be at 225 nm or lower. This effectively removed DMF, MEK, and acetone from the usable solvent list. Within this limited framework, several combinations of column packings and solvents were tested (Table I). However, anything which was sufficiently powerful to dissolve the PDNPA also was so strong a solvent as to bring all the components through the column at the solvent front. The chemicals which did dissolve the PDNPA were so nearly equal in polarity that no adjustments could be made in order to enhance separation. Therefore, it was decided to selectively extract the FEFO from LX-09 with ethyl ether. This extract was analyzed by IR spectroscopy and no PDNPA was found, indicating complete separation of the FEFO from the PDNPA. The residue was likewise examined and no FEFO was found, indicating complete extraction of the FEFO.

CALIBRATION OF EQUIPMENT

Calibration curves were prepared with solutions of neat FEFO or PDNPA in THF. Fig. 1 shows typical calibration curves for each material. It is to be noted that the relation between total FEFO and detector response is not linear. However, this does not affect accuracy of the measurements, as sufficient calibration points are used to clearly delineate the curve. The PDNPA calibration exhibits standard linear response throughout the concentration ranges studied.

ANALYSIS OF SAMPLE

In order to establish the precision of the liquid chromatographic techniques for FEFO and PDNPA, one sample was repeatedly analyzed, and results are given in Table II. The FEFO is measured with a 2.5% relative standard deviation, which compares very well with the standard deviation of the older technique for FEFO (3.1% relative). The PDNPA is determined with a 1% relative standard deviation, which is a big improvement over the difference technique. The difference method for PDNPA is not only an indirect method of measurement, but also includes the cumulative errors of FEFO and HMX determinations (3.5% relative). The accuracy of the HPLC methods for FEFO and PDNPA was determined by (1) comparing the values obtained by LC with those determined classically (Table III), and (2) adding total components, all measured separately, and comparing with the total value of 100% (Table IV). In both cases, accuracy is excellent, and the new techniques are direct assays.

From the foregoing discussion, it is evident that the new techniques are more accurate than the classical methods, as well as more precise.

In addition, liquid chromatography is much quicker than the older methods. By LC measurement, six samples in duplicate can be analyzed for both FEFO and PDNPA in an 8 hour day. Previously, only 6 samples for FEFO alone were assayed in this time.

CONCLUSION

A new method for determining FEFO and PDNPA in LX-09 has been developed. It is more rapid than previous techniques, and is quantitative and precise. This method does not involve other measurements for calculation of data.

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Table I. Packing and Solvent Combinations

<u>Packing</u>	<u>Solvents</u>
Amino-Silex	THF Me Cl ₂ p-dioxane THF - Me Cl ₂ THF - Hexane p-dioxane-Hexane
Cyano - Silex	Same as above
Corasil II	THF THF - Hexane THF - IPA p-dioxane p-dioxane-Hexane
C ₁₈ - Corasil	THF - H ₂ O

Table II. Replicate Analysis for Precision Determination

<u>Run No.</u>	<u>FEFO (%)</u>	<u>PDNPA (%)</u>
1	2.08	4.60
2	2.08	4.58
3	2.15	4.65
4	2.01	4.55
5	2.11	4.62
6	2.01	4.54
7	2.00	4.54
8	2.08	4.61
9	2.00	4.54
10	<u>1.98</u>	<u>4.50</u>
	2.05 ± 0.05	4.57 ± 0.05

Table III. Comparison of New Technique with Conventional Methods

<u>Sample No.</u>	<u>FEFO HPLC (%)</u>	<u>FEFO Titration (%)</u>	<u>PDNPA HPLC (%)</u>	<u>PDNPA Difference (%)</u>
1	2.05	2.37	4.57	4.28
2	1.95	2.07	4.28	4.27
3	2.37	2.27	4.05	4.24

Table IV. Total Component Analysis of LX-09

<u>Sample No.</u>	<u>FEFO (%)</u>	<u>PDNPA (%)</u>	<u>HMX (%)</u>	<u>Total (%)</u>
1	2.05	4.57	93.35	99.96
2	1.95	4.28	93.66	99.89
3	2.37	4.05	93.49	99.91

Fig. 1. Calibration Curves