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LIQUID CHROMATOGRAPHIC DETERMINATION OF HMX AND RDX IN PBX 9404

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QUALITY DIVISION

JULY - SEPTEMBER 1975

Normal Process Development
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SUMMARY

A high speed liquid chromatographic method for determining HMX and RDX in PBX 9404 has been developed. A 300 mg sample of explosive is dissolved in 100 mℓ acetone, and a 40 μℓ aliquot of the solution is then injected into an LC system using a 2 m Corasil II column and a 30% paradioxane - 70% cyclohexane carrier at 0.7 mℓ/min flow rate. The separated HMX and RDX components are measured with a differential UV-detector. The amounts of HMX and RDX are then calculated from measured peak areas. Analyses of standards show recovery of HMX to be 99.7 ± 0.4 percent and RDX is 99.7 ± 0.9 percent recovered. Binder and plasticizer components do not interfere in the analysis.

INTRODUCTION

As PBX 9404 is utilized in several weapons systems, a simple, accurate and precise assay for HE components is critical for production and stockpile laboratory evaluations (SLT). One method currently used for HMX assay consists of determining the binder materials and assuming the difference to be HMX. This technique is subject to positive HMX bias, as all impurities are counted as HMX. Another method in use is an IR spectrophotometric determination that is specific for the nitro group in HMX. In the absence of RDX the method is specific for HMX. The RDX interference is not important in analyses of recent batches of PBX 9404 (materials made after 1964), but is significant in the analysis of older preparations.

Therefore, a high speed liquid chromatographic technique was developed for the rapid and simultaneous determination of HMX and RDX. This method is specific for both HMX and RDX, and does not depend upon other analyses for calculation of data. In this technique a sample of PBX 9404 is dissolved in acetone. An aliquot is then injected into a 30% paradioxane - 70% cyclohexane carrier. A 2 m Corasil II column separates the HMX and RDX. Peak areas, as measured with a differential UV detector, are directly proportional to quantities of the respective components.

EXPERIMENTAL

APPARATUS

All separations were performed using a Waters Associates Model ALC 202 Liquid Chromatograph. The column was fabricated from 0.3175 cm OD x 200 cm length stainless steel tubing and was packed with Corasil II. The carrier was a 30% paradioxane/70% cyclohexane mixture, and flow rate was maintained at 0.7 mℓ/min. A differential UV detector at 254 nanometers was used to detect the separated components.

PROCEDURE

A 300 mg sample of PBX 9404 is weighed into a 100 mℓ volumetric flask and acetone is added to the mark. A 40 μℓ aliquot of the solution is injected into the liquid chromatograph and the HMX and RDX are separated, detected, and quantitatively measured from their peak areas.

DISCUSSION

CALIBRATION OF EQUIPMENT

Identification of the species separated by the liquid chromatograph necessitated calibration of retention times. Accordingly, the major components of PBX 9404 were chromatographed in the same manner as samples. Retention times are recorded in Fig. 1. The CEF was eluted at the same time as the acetone, and nitrocellulose did not come through the column. Calibration curves were prepared with solutions of purified RDX and HMX in acetone. Fig. 2 shows typical calibration curves for each material.

INHERENT ACCURACY OF ANALYSIS

A synthetic standard was prepared to contain 5 μg/μℓ HMX, 0.5 μg/μℓ RDX, 0.5 μg/μℓ CEF and 0.5 μg/μℓ NC. This standard was analyzed repeatedly for HMX and RDX and results are given in Table I. HMX recovery is 99.7 ± 0.4 percent and RDX recovery is 99.7 ± 0.9 percent. Analysis of this synthetic standard gives the maximum accuracy and precision which may be attained by use of this method. Sample heterogeneity would decrease precision but would not affect accuracy of measurement.

ANALYSIS OF SAMPLE

In order to establish the accuracy of the LC method, as compared with the alternate methods described previously, several library samples were assayed for HMX and RDX. The results are shown in Table II. The values obtained by the new LC method agree very well with the older techniques, and precision is excellent. Special note should be taken of samples 219-58, 37-62 and 93-140. The older techniques measure RDX as HMX. When the LC values for HMX and RDX are totaled, the values agree very well with the other methods.

CONCLUSIONS

A new method for determining HMX and RDX in PBX 9404 has been developed. It is more rapid than previous techniques, and is quantitative and precise. In addition, the capability for simultaneous determination of RDX has been added. This technique does not involve empirical data or outside analyses.

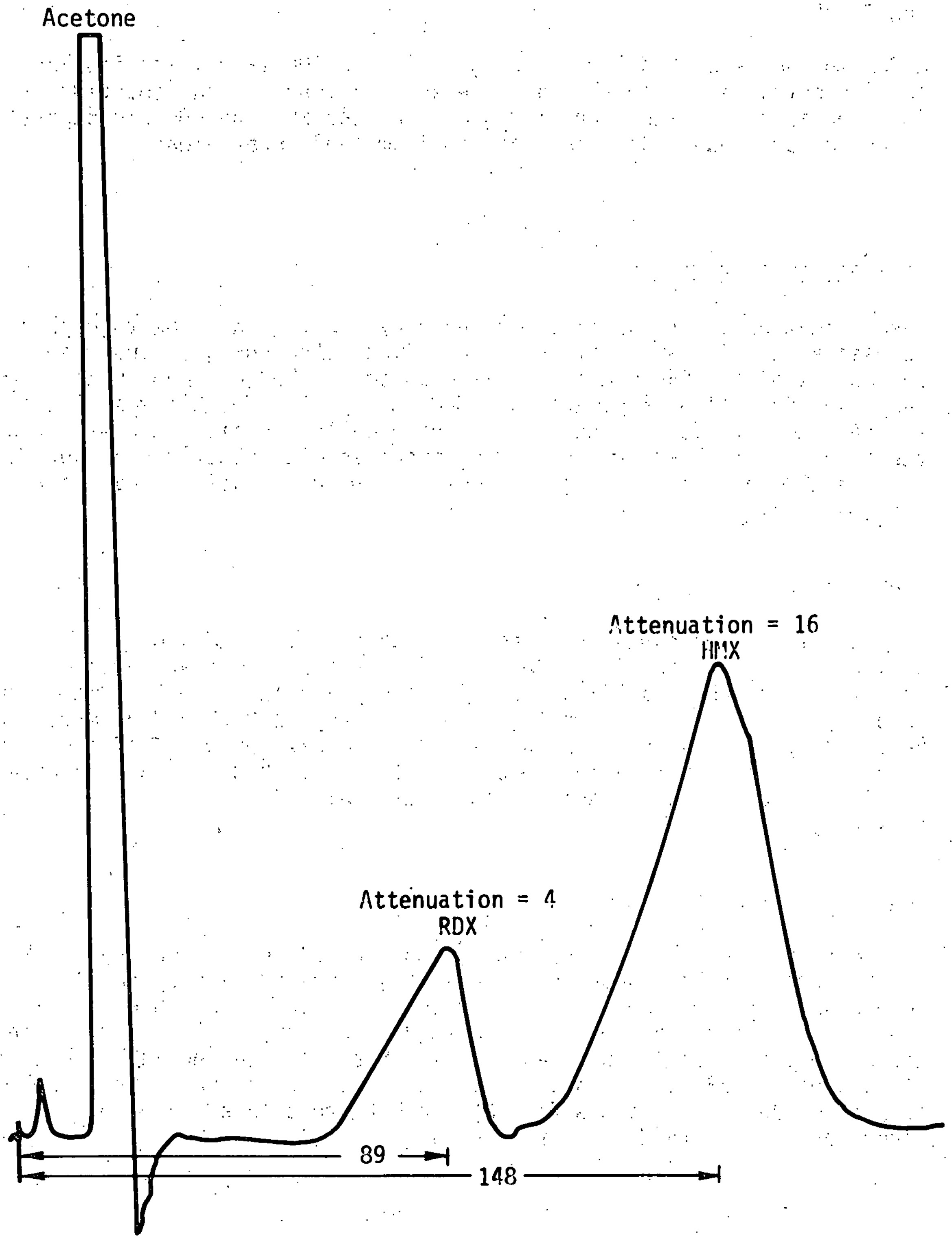

Fig. 1. Chromatogram of HMX and RDX

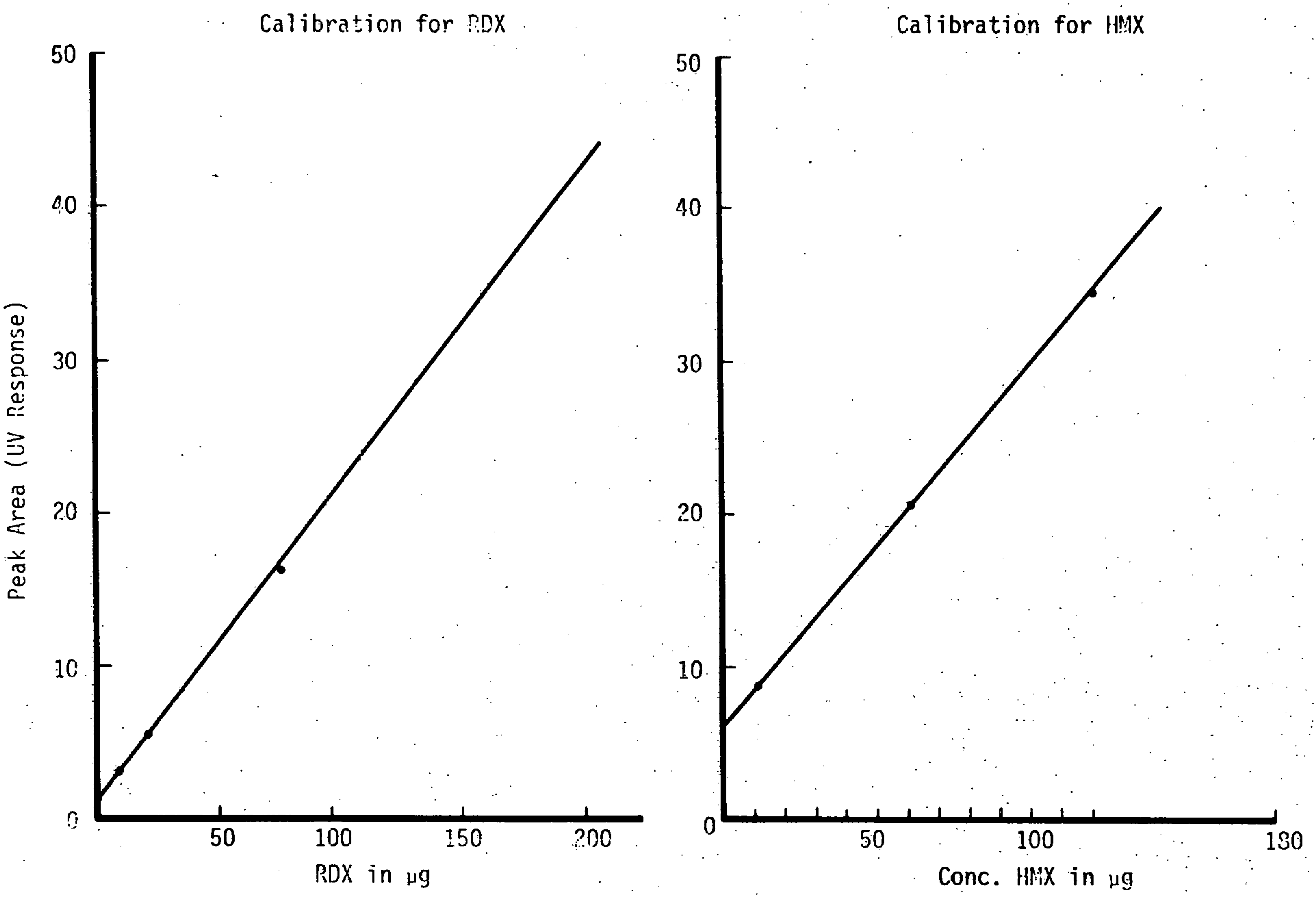

Fig. 2. Sample Calibration Curves for HMX and RDX

Table I. Reproducibility of Measuring HMX and RDX

Sample	HMX Added (μg)	HMX Found (μg)	Recovery (%)	RDX Added (μg)	RDX Found (μg)	Recovery (%)
Std	200	198	99.00	20	19.7	98.50
		199	99.50		19.9	99.50
		199	99.50		19.8	99.00
		200	100.00		20.0	100.00
		198	99.00		20.1	100.50
		200	100.00		20.0	100.50
		200	100.00		20.2	101.00
		199	99.50		19.7	98.50
		200	100.00		19.9	99.50
		200	100.00		20.0	100.00
		Avg =	99.65 ± 0.41		Avg =	99.70 ± 0.86

Table II. Comparison of Liquid Chromatographic Determination of HMX and RDX with Alternate Methods

Sample	% HMX (IR)	% HMX (Physical)	% HMX (LC)	% RDX (LC)
219-58	92.59	92.33	87.46	4.85
37-62	93.79	93.95	93.33	0.50
93-90	93.87	93.68	93.88	0
93-110	94.07	-	94.16	0
93-140	93.29	93.26	93.12	0.13
620-4	93.80	93.75	93.75	0