MHSMP-80-55

Analysis of RDX and HMX in PBX 9404 by High Performance Liquid Chromatography

Benny R. Richardson

QUALITY DIVISION

November 1980

Process Engineering
28-6-82-11-004

Mason & Hanger-Silas Mason Co., Inc.
Pantex Plant

OPERATED FOR THE
Department of Energy
UNDER
U. S. GOVERNMENT CONTRACT DE-AC04-76DP-00487

P. O. BOX 30020
AMARILLO, TEXAS 79177
806-335-1581

NOTICE

ANALYSIS OF RDX AND HMX IN PBX 9404 BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

Benny R. Richardson

QUALITY DIVISION
(November 1980)

Process Engineering
28-6-82-11-004

ABSTRACT

An analysis for the HMX and RDX contents of PBX 9404 has been developed. Instrumental parameters, such as column type, solvent, flow rate, and method of detection are discussed. The calibration method is examined, and precision and accuracy investigated. The average percent recovery of HMX is 98.75% with a standard deviation of 0.82%; for RDX, the percent recovery is 98.66% with a standard deviation of 0.27%.

INTRODUCTION

The major component of PBX 9404 is 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX). It is the crystalline high explosive component, and comprises 94% of this composite material. However, 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) is an impurity present in HMX to varying degrees. RDX is also an explosive, but its explosive characteristics deviate dramatically from those of HMX. Therefore, a requirement has been placed on the permissible content of RDX in HMX to be used in PBX 9404.

In order to monitor the compositional analysis of PBX 9404 for surveillance purposes, an analysis was needed for the HMX and RDX contents. A method has been developed using high performance liquid chromatography(*1*). However, in order to more fully utilize the advances in liquid chromatography, another method has been developed. It offers several advantages over previous methods.

---

1. *C. S. MacDougall, "Liquid Chromatographic Determination of HMX and RDX in PBX 9404," MHSMP-75-40 (July - September 1975).*

EXPERIMENTAL

The HMX and RDX analyses utilize a Partisil 5/25 silica column. The analyses of these two compounds is not performed simultaneously because of the great difference in the relative concentrations of the two compounds. However, the same column can be used. The chromatograms of the two analyses are shown in Figs. 1 and 2. The calibrations for the two compounds are discussed in detail below. The mobile phase was UV-grade tetrahydrofuran with a UV-cutoff of about 210 nm. This solvent was filtered and degassed prior to its use; all dilutions of standards and samples were made with this same material. A Perkin-Elmer Model 601 liquid chromatograph, equipped with syringe-driven pumps and an LC-55 variable wavelength UV/VIS spectrophotometer detector, was used. The wavelength which was monitored for peak detection was 230 nm. It has been found that the sensitivity at 230 nm for both HMX and RDX is much greater than at other wavelengths, including 254 nm. The flow rate for the carrier was set at 1 ml/min. A fixed-loop injection system, using a Rheodyne 7010 injector valve with a 20-µl loop, was utilized.

Standards were prepared based on the relationship between absorbance and the amount of HMX or RDX injected. Typical calibration curves are shown in Figs. 3 and 4. A single calibration standard was used in both the HMX and RDX determinations; the concentration of standard material used was determined from the linear regions of the calibration curves. A convenient concentration was chosen from this region. Thus, a 0.5-g sample of HMX was dissolved and diluted with THF to a total volume of 1 litre. A 0.1-g sample of RDX as a standard was dissolved and diluted with THF to a total volume of 500 ml. The material used for the HMX standards contained a small amount of RDX. However, because of the dilute concentration of the HMX in the standard, there was no apparent RDX peak observed and the standard was assumed to be pure. This was not the case in the preparation of the RDX standard. The purest available RDX contained an appreciable amount of HMX, as seen by the chromatogram (Fig. IIB). In order to determine the purity of the RDX, it was reasoned that the sensitivity of both HMX and RDX at 230 nm wavelength was approximately equal, due to their very similar structures. Thus, a normalization based upon peak heights was performed. The weight fraction of RDX in the sample was determined by dividing the peak height of the RDX peak by the combined peak heights of both peaks of the chromatogram. The weight fraction, also called a purity factor, was multiplied by the standard's weight in order to determine the amount of RDX actually present in the standard.

Samples were prepared separately for each analysis. For the HMX determinations a 50-mg sample of the PBX 9404 to be tested was diluted with 100 ml of THF. For the RDX determination, a 1-g portion of PBX 9404 was diluted with 5 ml of THF.

The method of calibration and sample analysis in the case of both RDX and HMX consisted of injecting a standard before and after duplicate runs of a sample. A sensitivity for each of the compounds was determined from the calibration runs in the following manner:

$$S_{RDX} = \frac{\text{peak height of RDX peak measured in A.U. or counts}}{\left(\frac{\text{weight of RDX standard, grams}}{500 \text{ ml final volume}}\right)\left(\frac{1000 \text{ mg}}{1 \text{ g}}\right)\left(\frac{1000 \text{ µg}}{1 \text{ mg}}\right)\left(\frac{1 \text{ ml}}{1000 \text{ µl}}\right)\left(20 \text{ µl}\right)\left(\text{purity factor}\right)}$$

Column: Partisil 5/25, 4.8 mm x 25 cm
#1A1186

Solvent: UV Grade THF; Cutoff: 210 nm

Sample Volume: 20 µl

Pressure: 1000 psi

Flow Rate: 1 ml/min

Detector: UV; λ = 230 nm

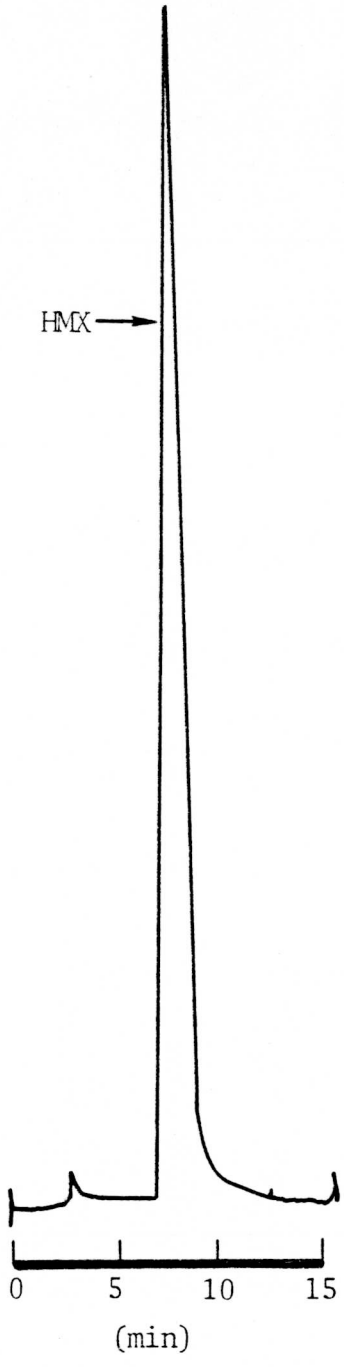

Fig. 1. Chromatogram of HMX

Column: Partisil 5/25, 4.8 mm x 25 cm #1A1186

Solvent: UV grade THF, Cutoff: 210 nm

Sample Volume: 20 µl

Pressure: 1000 psi

Flow Rate: 1 ml/min

Detector: UV; λ = 230 nm

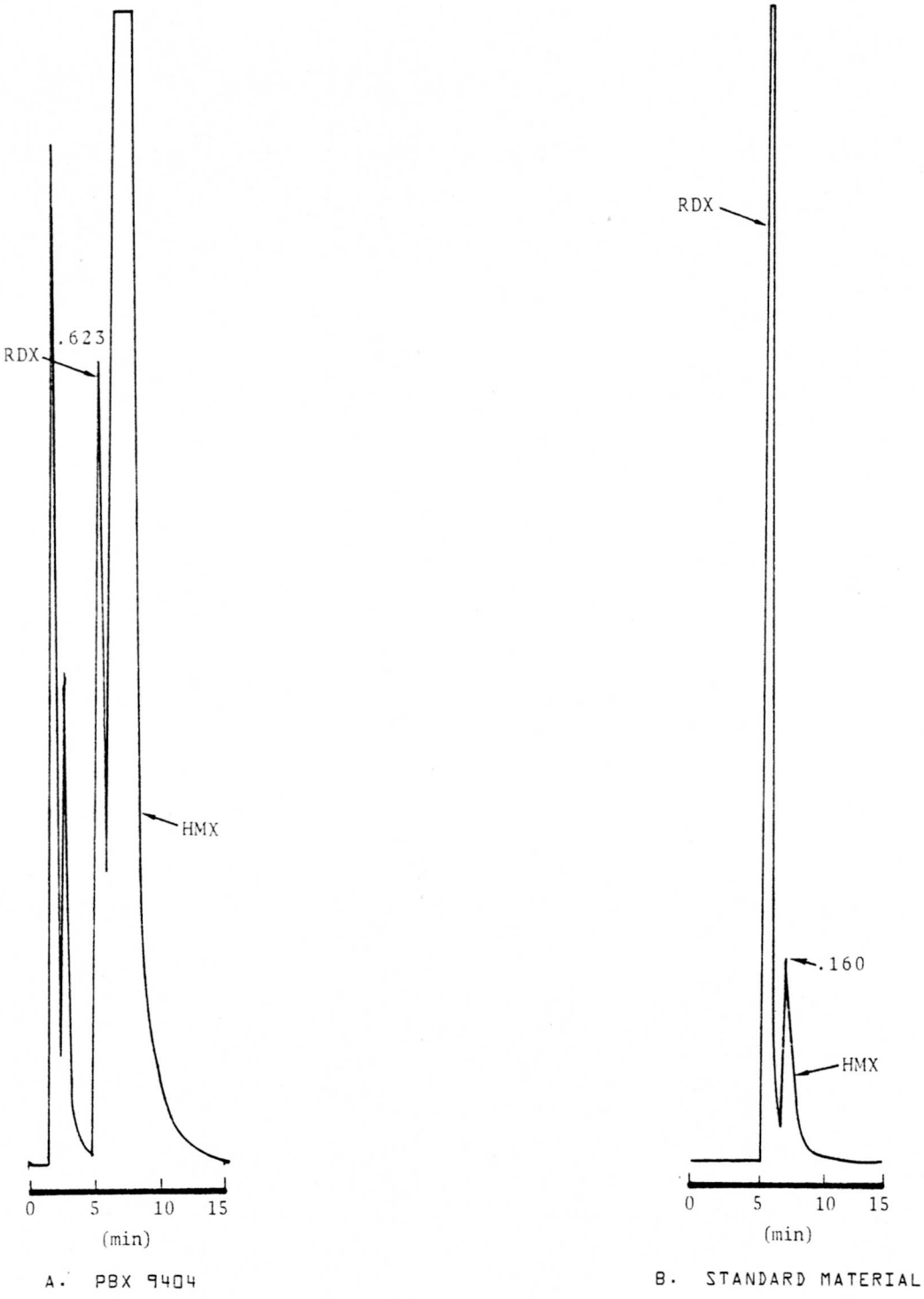

Fig. 2. Chromatograms of RDX

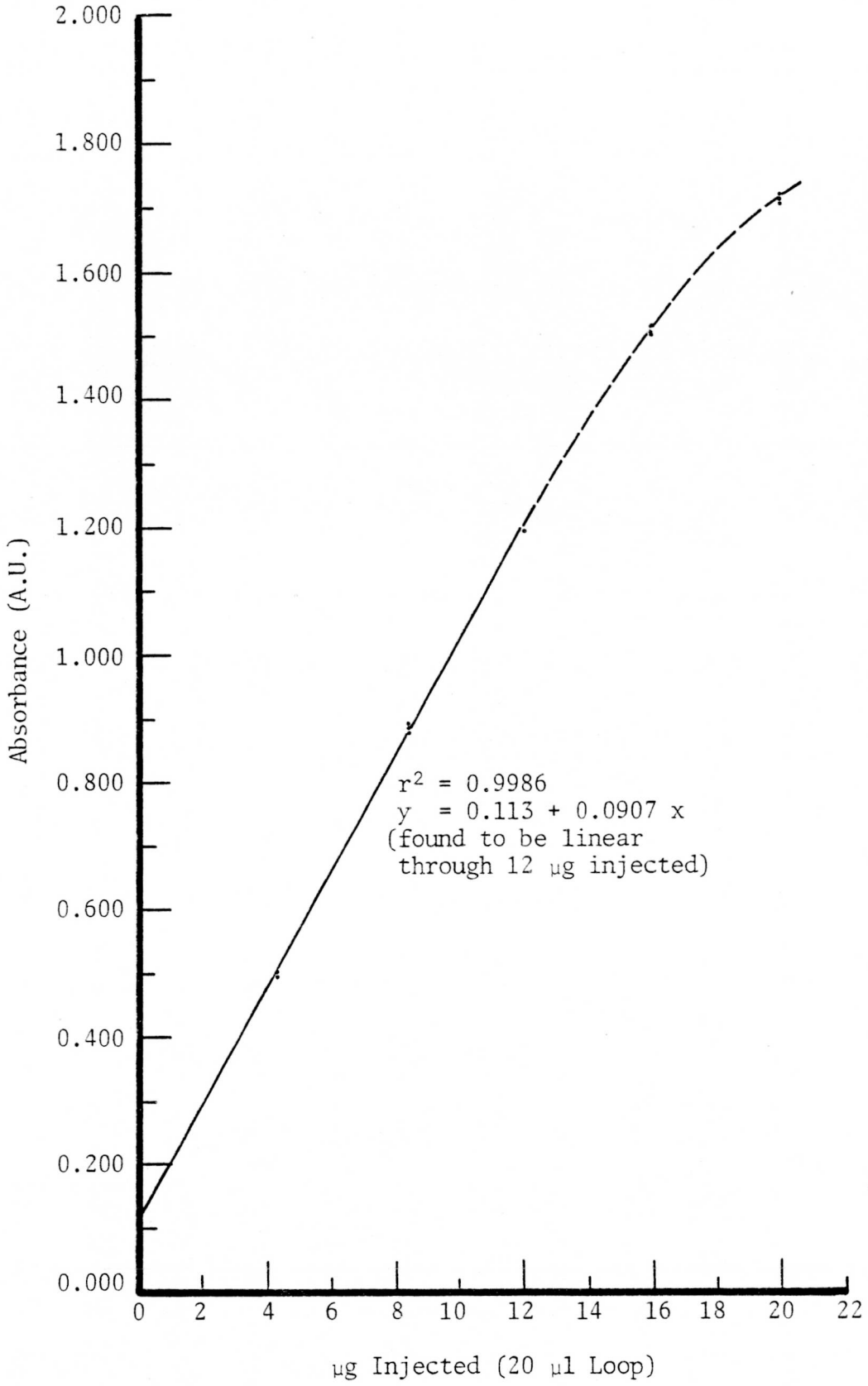

Fig. 3. Calibration Curve for HMX

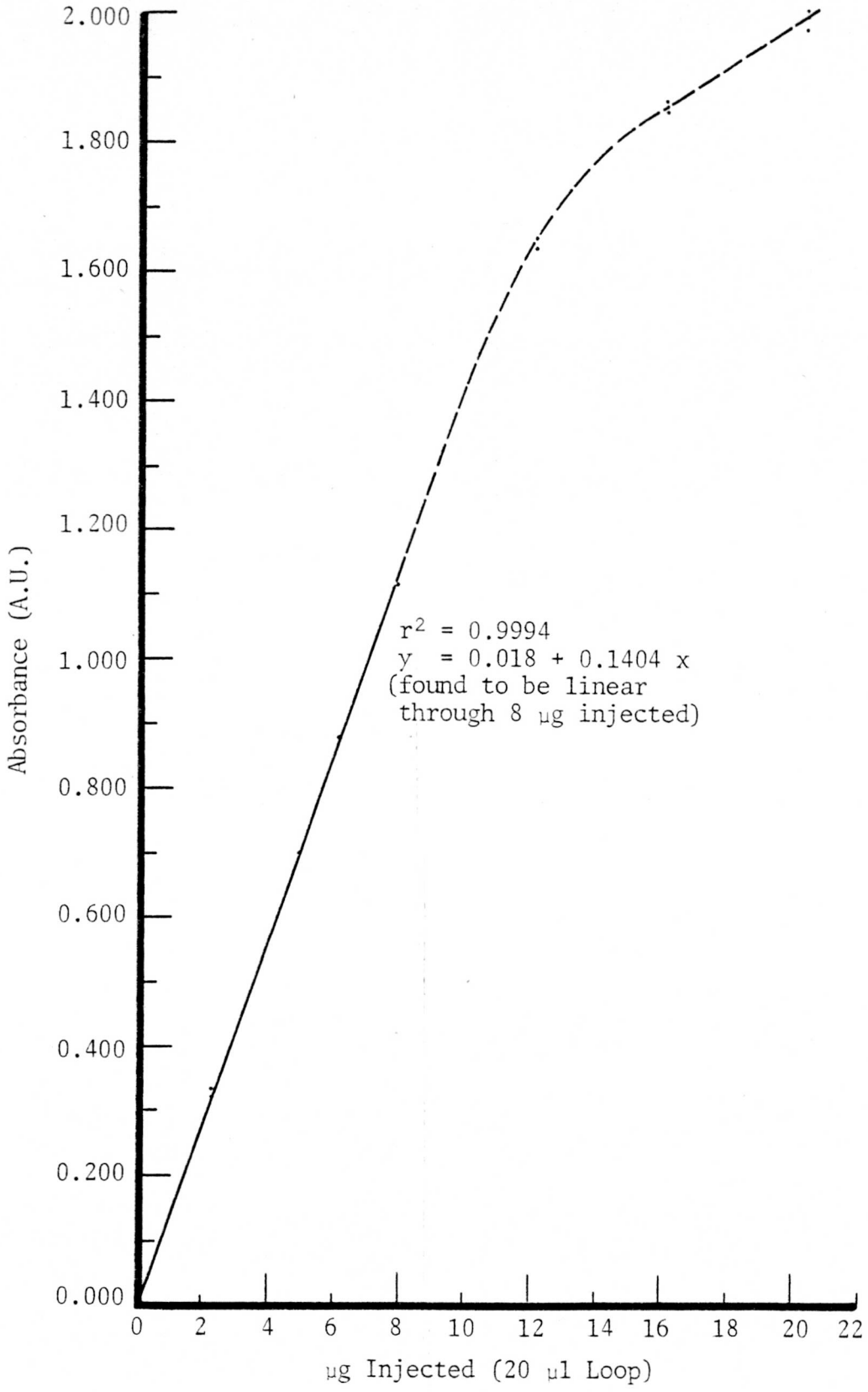

Fig. 4. Calibration Curve for RDX

In this equation, S_{RDX} stands for the sensitivity of RDX and A.U. stands for absorbance units. Likewise, the sensitivity for HMX (S_{HMX}) was determined as follows:

$$S_{HMX} = \frac{\text{peak height of HMX peak measured in A.U. or counts}}{\left(\frac{\text{weight of HMX standard, grams}}{1000 \text{ ml final volume}}\right)\left(\frac{1000 \text{ mg}}{1 \text{ g}}\right)\left(\frac{1000 \text{ µg}}{1 \text{ mg}}\right)\left(\frac{1 \text{ ml}}{1000 \text{ µl}}\right)\left(20 \text{ µl}\right)}$$

As mentioned earlier, no purity factor was involved in the HMX standardization since no RDX peak was seen. However, if one became apparent, the peak heights could be easily normalized to obtain a purity factor.

An average sensitivity can be calculated from the duplicate runs of the standard and applied to the calculation of the RDX or HMX content, as shown in the equations below:

$$\% \text{ RDX} = \frac{\left[\frac{\left(\frac{\text{peak height of RDX in sample in A.U. or counts}}{\text{average sensitivity for RDX in A.U./µg or counts/µg}}\right)}{20 \text{ µl total volume}}\right]\left(\frac{1 \text{ mg}}{1000 \text{ µg}}\right)\left(\frac{1 \text{ g}}{1000 \text{ mg}}\right)\left(\frac{1000 \text{ µl}}{1 \text{ ml}}\right)\left(5 \text{ ml}\right)}{\text{sample weight in grams}} \text{ X } 100$$

$$\% \text{ HMX} = \frac{\left[\frac{\left(\frac{\text{peak height of HMX in sample in A.U. or counts}}{\text{average sensitivity for HMX in A.U./µg or counts/µg}}\right)}{20 \text{ µl total volume}}\right]\left(\frac{1 \text{ mg}}{1000 \text{ µg}}\right)\left(\frac{1 \text{ g}}{1000 \text{ mg}}\right)\left(\frac{1000 \text{ µl}}{1 \text{ ml}}\right)\left(100 \text{ ml}\right)}{\text{sample weight in grams}} \text{ X } 100$$

The results of an RDX analysis of PBX 9404 Lot 620-12 are shown below:

Run Number	% RDX
1	0.182
2	0.181
3	0.182
4	0.179
5	0.178
Avg. ± Standard Deviation	0.180 ± 0.002%

The procedure was thus shown to be quite precise. It displayed a coefficient of variation of 1.11%. The accuracy of the procedure is proven by the data shown below. On injection of 4.12 µg of RDX, the following recoveries were obtained:

Run Number	µg RDX Injected	µg RDX Found	% Recovery
1	4.12	4.04	98.06
2	4.12	4.08	99.03
3	4.12	4.07	98.79
4	4.12	4.07	98.79
5	4.12	4.07	98.79
6	4.12	4.08	99.03
7	4.12	4.06	98.54
8	4.12	4.06	98.54
9	4.12	4.06	98.54
10	4.12	4.06	98.54
	Avg. ± Standard Deviation	4.06 ± 0.01	98.66 ± 0.27

The standard deviation between the ten runs was 0.01 µg, with a percent error(2) of -1.46%. The average recovery was 98.66%.

The results of the duplicate analysis of the HMX content of Lot 620-12 were 95.3% and 94.4%, respectively, for an average of 94.9%. In order to further study the accuracy and precision of the technique, the following test was devised: 10.35 µg of HMX was injected and the amount of HMX recovered and the percent recovery was calculated from the resulting chromatogram. These data are shown below:

Run Number	µg HMX Injected	µg HMX Found	% Recovery
1	10.35	10.20	98.55
2	10.35	10.10	97.58
3	10.35	10.34	99.90
4	10.35	10.24	98.94
5	10.35	10.30	99.52
6	10.35	10.34	99.90
7	10.35	10.25	99.03
8	10.35	10.15	98.07
9	10.35	10.19	98.45
10	10.35	10.10	97.58
	Avg. ± Standard Deviation	10.22 ± 0.08	98.75 ± 0.82

---

2. *Percent Error (P.E.) is defined as follows:*

$$P.E. = \frac{\textit{Amount found - known amount injected}}{\textit{known amount injected}} \times 100$$

The percent error between the mean result and the actual amount injected was -1.26%. The standard deviation between the ten runs is 0.08 µg. The average recovery was 98.75%.

This procedure is now being implemented for the routine testing of PBX 9404 for its HMX and RDX contents. By this analysis, evaluation of stockpiled materials by its chemical composition can be successfully continued.

ACKNOWLEDGMENT

We are indebted to M. D. Payne, G. Tung, and L. M. Boyles for their technical assistance.

DISTRIBUTION

Department of Energy - Washington, D.C.

Caudle, R. E.
  Attn: Clough, R. E.

Department of Energy - ALO

Weber, H. A.
Fredlund, R. R., Jr.

Department of Energy - AAO

Johnson, G. W.

Lawrence Livermore National Laboratory

Brockett, C. T.
Clarkson, J. E.
Root, G. S.
  Attn: van Dyk, A. C. (18)

Los Alamos National Scientific Laboratory

Daly, R. J.
Flaugh, H. L.
Fuller, J. C.
Mortenson, G. F.
Wechsler, J. J.
Yasuda, S. K.
Report Library - ISD-4

Mason & Hanger - Pantex

Bailey, R. E.
Carr, B. H.
Ihne, R. J.
Johnson, M. S.
Myers, L. C.
Poynor, E. D.
Slape, R. J.
Taylor, R. E.

Circulation Copy:

1. Plant Manager, PX
2. M&H, Lexington, KY

Technical Library

File (5)
Technical Information Center (27)

Mound Facility

Braun, R. J.

Sandia National Laboratories - Albuquerque

Arthur, B. E.
Central Technical Files
Crawford, J. C./
  Anderson, D. H.
Garner, W. L. (3)

Sandia National Laboratories - Livermore

Aas, E. A.
Cozine, R. D.

United Kingdom

Long, W. S., British Embassy
  For: Kirkham, J.