Method number:	PV2032
Target concentration:	0.2 mg/m^3 (arbitrary). There is no OSHA PEL or ACGIH TLV for HMX.
Procedure:	Samples are collected by drawing air through glass fiber filters. Samples are extracted with acetone and analyzed by high performance liquid chromatography (HPLC) with a UV detector.
Recommended air volume and sampling rate:	500 minutes at 1 Lpm (500 L)
Detection limit of the analytical procedure:	10.5 ng/injection
Status of method:	Partially Validated method. This method has been only partially evaluated and is presented for information and trial use.

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Yihlin Chan

Carcinogen and Pesticide Branch
OSHA Salt Lake Technical Center
Salt Lake City UT 84115-1802

1. General Discussion

1.1 Background

1.1.1 History of procedure

The OSHA Analytical Laboratory received a set of samples with a request for the analysis of HMX. The samples had been collected on glass fiber filters. This report describes the analytical procedure developed.

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)

The oral LD_{50} of HMX is 1500 mg/kg in mice and 300 mg/kg in guinea pigs. The intravenous LD_{50} is 28 mg/kg in guinea pigs. (Ref. 5.1)

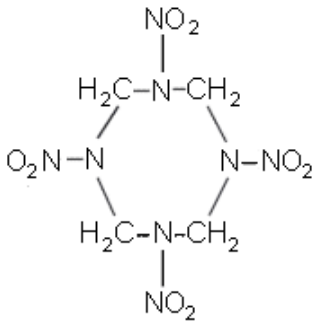
1.1.3 Potential workplace exposure

HMX is a high energy explosive. It is "much less toxic than TNT and may be handled with no physiological effect if appropriate precautions are taken to assure cleanliness of operations." (Ref. 5.2) No data on the extent of workplace exposure could be found.

1.1.4 Physical properties (Ref. 5.1, 5.2)

Chemical name:	Octahydro-1,3,5,7-tetranitro-1,3,5,7 tetrazocine
CAS #:	2691-41-0
Synonym:	Cyclotetramethylenetetranitramine; HMX; HW 4; LX 14-0; Octogen.
Mol. weight:	296.20
Mol. formula:	$C_4H_8N_8O_8$
Appearance:	White crystalline solid.
M.P.:	286 °C
Solubility:	Soluble in acetone.

Structure:



1.2 Detection limit of the analytical procedure

The detection limit of the analytical procedure is 10.5 ng per injection.

2 Sampling Procedure

2.1 Apparatus and reagents

2.1.1 A personal sampling pump that can be calibrated to within ±5% of the recommended flow rate with the sample filter attached.

2.1.2 Glass fiber filter, 37-mm diameter, Gelman Type A or equivalent.

2.1.3 Filter holder for 37-mm filters, Millipore M000037A0 or equivalent.

2.2 Sampling technique

Use standard air sampling procedure as specified in the OSHA Instruction CPL 2-2.20A, Chapter II: Standard Method for Sampling Air Contaminants.

2.3 Recommended air volume and sampling rate

2.3.1 The recommended air volume is 500 L.

2.3.2 The recommended sampling rate is 1 Lpm.

2.4 Extraction efficiency

Six glass fiber filters were each spiked with 23.44 ug of HMX. After overnight storage, two filters were extracted with 5 mL of acetone. The average recovery of HMX was 95.6%.

Table 2.4
Extraction Efficiency

sample #	HMX recovered	% recovered
1	22.8	97.3
2	22.0	93.9

average = 95.6%

2.5 Retention efficiency

Humid air (90% RH, 500 L) was drawn through the remaining four filters in Section 2.4. Two filters were analyzed. The average recovery of HMX was 93.7%.

Table 2.5
Retention Efficiency

sample #	HMX recovered	% recovered
3	21.4	96.0
4	20.5	91.3

average = 93.7%

2.6 Storage test (7 days)

Three glass fiber filters were each spiked with 23.44 ug of HMX. Humid air (RH 74%, 276 L at 1 Lpm) was pulled through the filters. The filters were stored at room temperature for 7 days, extracted, and analyzed. The average recovery of the HMX was 102.7%.

Table 2.6
Storage Test (7-days)

sample #	HMX recovered	% recovered
1	24.21	103.3
2	24.15	103.0
3	23.86	101.8

average = 102.7%

2.7 Interferences (Sampling)

There are no known interferences to the sampling procedure.

3 Analytical procedure

3.1 Apparatus

3.1.1 High performance liquid chromatograph

3.1.2 Zorbax ODS HPLC column

3.1.3 UV detector. Waters 490 Programmable Multiwavelength Detector was used in this study.

3.1.4 Strip chart recorder

3.2 Reagents

3.2.1 HMX standard

3.2.2 Acetonitrile, HPLC grade

3.2.3 Water, HPLC grade

3.2.4 Acetone, reagent grade

3.3 Standard preparation

Weigh 3 to 5 mg of HMX in a 10-mL volumetric flask. Add acetone to the mark. Dilute standards to a working range of 0.7 to 20 ug/mL.

3.4 Sample preparation

Place glass fiber filter in a scintillation vial. Add 5 mL of acetone. Shake on a mechanical shaker for 30 minutes.

3.5 Analysis

3.5.1 Instrument conditions

Column:	Zorbax ODS column
Eluent:	40% acetonitrile/60% water
Flow rate:	1.0 mL/min
Detector:	235 nm (primary), 225 nm
Retention time:	11.1 min

3.5.2 Chromatogram (see Figure 1)

3.6 Interferences

3.6.1 Any compound that has the same retention time as the HMX and absorbs at 235 nm and 225 nm is interference.

3.6.2 Most interference can be circumvented by altering the chromatographic conditions.

3.6.3 Retention time alone is not proof of a chemical identity. Confirmation by other means should be sought when possible.

3.7 Calculations

3.7.1 A calibration curve is constructed by plotting concentration versus detector response.

3.7.2 The concentration of a sample is determined from the calibration curve.

3.7.3 The concentration of HMX is given by:

$$mg / m^3 = \frac{(\mu g / mL,\ blank\ corrected)(5\ mL)}{(air\ volume,\ L)(desorption\ efficiency,\ decimal)}$$

4 Recommendations for further study

The method should be fully validated.

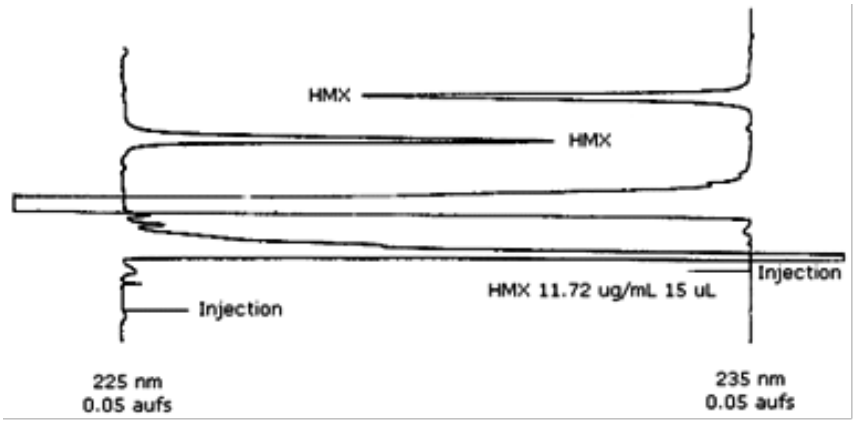


Figure 1 HPLC Chromatogram of HMX

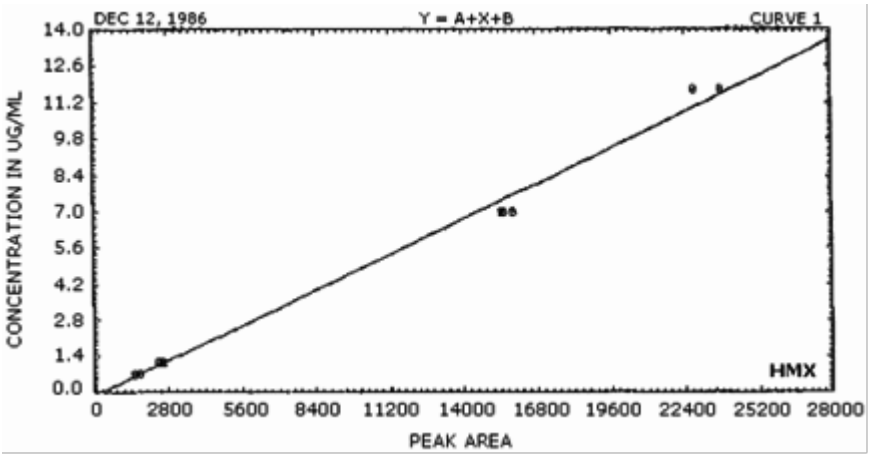


Figure 2 Calibration Curve of HMX

5 References

5.1 Registry of Toxic Effects of Chemical Substances 1983-84, DHHS (NIOSH) Publication No. 86-103.

5.2 Grayson, Martin, ed., Kirk-Othmer Encyclopedia of Chemical Technology, Volume 9, New York: John Wiley & Sons, 1980.