Thin-Layer Chromatographic Analysis of HMX in Water

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INTRODUCTION

Since HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane) may be considered a contaminant in waste waters arising from various explosives operations, it is desirable to have a reliable method for its detection and/or analysis at low concentrations (ppm, parts per million) in water.

The following procedure is based on a method previously used for the analysis of 1,3-diamino-2,4,6-trinitrobenzene and 2,2',4,4',6,6'-hexanitrostilbene (Hoffsommer,et al. 1968).

Procedure for the Determination of HMX in Water

One hundred milliliters of aqueous solution saturated with HMX was extracted with four 25 ml portions of benzene. The combined benzene extracts were evaporated under reduced pressure (17 mm/20^{o}C) with a water aspirator to dryness. The residue was taken up in 1.0 ml of acetone. A total of 20 ul (0.020 ml) were spotted in four 5 ul portions as one spot with drying between spottings onto a 0.3 mm silica gel HF-254 thin-layer glass plate. Standard solutions of HMX were similarly spotted to the right and to the left of the unknown, and the thin-layer plate was developed in an ascending manner with benzene/acetone, 4:1, as eluent. Under these conditions HMX has an $R_f = 0.6$ while RDX (if present) has an $R_f = 0.8$. These R_f values are based on two developments of 10 cm each with air drying between developments. After the final air drying, the TLC plate was placed in a ultraviolet cabinet, and zones for HMX were located as dark spots under 254 nm radiation.

In order to determine the HMX present, the dark areas were marked with a needle and photographed with a model 95 Polaroid camera with 146 L transparency film. The developed film was projected by means

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of a lantern slide projector onto a sheet of white paper 3 to 4 feet away, and the areas for the HMX spots traced with a pencil. The standard and sample areas were measured by means of a precision planimeter. The weight of HMX in the unknown spot was calculated from the following:

$$\log \mathrm{wgt}_{\mathrm{HMX}} = m\,(A^{1/2}_{\mathrm{HMX}} - A^{1/2}_{\mathrm{STD-1}}) + \log \mathrm{wgt}_{\mathrm{STD-2}}$$

where m = slope of the straight line between the points for the standards and is equal to

$$(\log \mathrm{wgt}_{\mathrm{STD-1}} - \log \mathrm{wgt}_{\mathrm{STD-2}})/(A^{1/2}_{\mathrm{STD-1}} - A^{1/2}_{\mathrm{STD-2}}$$

and A = the area of the respective spots.

Results and Discussion

The results are as follows for the solubility of HMX in water (stirred for 11 days at 22° ± 2°C, then filtered from solid HMX):

TABLE

Solubility of HMX in Water by Thin-Layer Chromatographic Analysis

Solution[a]	Concentration g/ul x 10^{-7}	Grams/ spot x 10^{-6}	Spot Area[b]	ppm (aqueous) solution)
Std-1	8.99	18.0	17	-
HMX Unknown	5.0 calc.	10.0 calc.	10	5.0
Std-2	4.49	9.0	9	-

(a) Acetone solvent.
(b) for 20 ul/spot: four 5 ul spotting.
R_f (HMX) = 0.6

By this combination of extraction, concentration, and thin-layer chromatography, we estimate that HMX may be detected at a lower limit of 0.02 ppm in water. This estimate is based on dissolving all of the residue from the extraction in 10 ul of acetone and spotting the total volume to give a planimeter count of 2. We also estimate that HMX may be determined with the following accuracies in the ranges: (a) 0.05 to 0.1 ppm; 15% (b) 0.1 to 1.0 ppm; 10%, and (c) greater than 1.0 ppm; 5%

Summary

HMX may be determined in concentrations down to 0.05 ppm in water by a combination of extraction, concentration, and thin-layer chromatography. The solubility of HMX in water was determined to be 5.0 ppm at $22^{\circ} \pm 2^{\circ}C$.

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References

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