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**SOME ANALYTICAL METHODS FOR
EXPLOSIVES AND EXPLOSIVE SIMULANTS**

Livermore, California

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Walter Selig

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PREFACE

This report is a compilation of methods for the analysis of explosives and explosive simulants. All of the methods with the exception of Section I were prepared for routine analysis by technicians and an attempt has therefore been made to keep them as simple as possible. Where possible, solvent extraction methods have been used. Section I presents a method for the estimation of the explosives RDX and HMX by means of nonaqueous titrimetry. Analytical methods for extrusible explosives are given in Sections II, III, and IV; Sections V, VI, and VII are concerned with plastic-bonded explosives; some explosive simulants are covered in Sections VIII, IX, and X.

W. Selig
May 1964

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SOME ANALYTICAL METHODS FOR EXPLOSIVES AND EXPLOSIVE SIMULANTS

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Lawrence Radiation Laboratory, University of California
Livermore, California

May 1964

I. THE ESTIMATION OF Sym-CYCLOTRIMETHYLENETRINITRAMINE (RDX) AND Sym-CYCLOTETRAMETHYLENETETRANITRAMINE (HMX) BY NONAQUEOUS TITRIMETRY*

Abstract

The nonaqueous titration of RDX and HMX as acids with tetrabutylammonium hydroxide (Bu_4NOH) is described. HMX is determined in dimethylformamide (DMF); RDX may be determined in either DMF, methylisobutyl ketone (MIBK), or cyclohexanone, although the latter two solvents are preferred. The total amount of RDX and HMX in mixtures may be estimated in DMF. Sample size is about 30 mg and a single determination takes about 25 minutes.

Introduction

A titrimetric method for the microdetermination of RDX and HMX by chromous chloride reduction has been used in this Laboratory.¹ The method, however, has a number of disadvantages. It requires: 1) complete absence of oxygen both during the titration and in storage of the titrants, 2) two titrants, 3) a large excess of chromous chloride and close control of the reaction temperature for the reduction of HMX, and 4) frequent blank determinations. In addition, any reducible impurities cause high results.

A rapid, simple titrimetric method for RDX has been described by Kaye² who titrated it as an acid in dimethylformamide (DMF), using sodium methoxide in benzene-methanol as the titrant and azo violet as the indicator. Disadvantages of Kaye's method are that sodium methoxide is somewhat

*General Chemistry Technical Note No. 65, dated November 7, 1961.

unstable and there is some difficulty in ascertaining the endpoint which is found by titrating to a green color persisting for 30 seconds. Also, a fairly large (300 mg) sample is required for each titration.

Sarson³ has described a method in which RDX is titrated as an acid in methylisobutyl ketone (MIBK) with tetrabutylammonium hydroxide (Bu_4NOH). When used as titrants for acids in nonaqueous media, tetraalkylammonium hydroxides have several advantages over previously used alkali metal bases.^{4,5} They are easily prepared and quite stable. The tetraalkyl ammonium salts are mostly soluble whereas precipitates are frequently formed when alkali alkoxides are used as titrants. Excellent potentiometric curves are obtained in a variety of solvents with the glass-calomel electrode system; with alkali metal bases the curves are not as reproducible.

While satisfactory for RDX, MIBK dissolves insufficient amounts of HMX to be of any use in its determination. Consequently, this work describes a modification of Sarson's method for the estimation of RDX, and the application of this modification to the estimation of HMX alone and HMX and RDX in mixtures.

Experimental

Apparatus

Beckman general-purpose glass electrode, No. 1190-80.

Beckman sleeve-type calomel electrode No. 1170-71, modified by replacing the aqueous potassium chloride solution with a saturated solution of potassium chloride in methanol.

Potentiometric titrator: Beckman Model G pH meter.

Buret, 10 ml Machlett, with 1000 ml reservoir, kept under nitrogen atmosphere.

Magnetic stirrer.

Titration cells: 200 ml tall-form electrolytic beakers without spouts covered with a No. 11 1/2 rubber stopper provided with a gas inlet tube and openings for two electrodes and the delivery tip of buret. The buret tip is inserted into the titration cell through a glass tube which provides space for exit of the sweeper gas.

Reagents

Tetrabutylammonium hydroxide. A 0.1 N solution in 10 to 1 benzene-methanol was prepared according to Cundiff and Markunas.⁴ Dissolve 40 grams tetrabutylammonium iodide in 90 ml absolute methanol. Add 20 grams finely ground purified silver oxide, stopper the flask, and agitate for one hour. Centrifuge several milliliters of the mixture and test the supernatant for iodide. If the test is positive, add two grams more of silver oxide and reagitate for 30 minutes. If the test for iodide is negative, filter the mixture through a fine porosity sintered-glass funnel. Rinse the reaction flask and funnel with three 50-ml portions of dry benzene and add to the filtrate. Dilute the filtrate to one liter with dry benzene. Transfer the solution to the reservoir of the Machlett buret and flush for five minutes with prepurified nitrogen. Keep the reservoir under a constant nitrogen blanket to protect from moisture and carbon dioxide. Standardize the titrant against benzoic acid.

Thymol blue indicator solution. Dissolve 0.3 gram of thymol blue in 100-ml isopropyl alcohol.

Benzoic acid. Primary standard (Baker Analyzed Reagent).

Nitrogen. Prepurified by running through Ascarite-magnesium perchlorate trap.

Methylisobutyl ketone. (4-methyl-2-pentanone) (Braun-Knecht-Heimann Co.).

Dimethylformamide. Reagent grade (Matheson, Coleman and Bell).

Cyclohexanone. Reagent grade, purified.

Purification of Cyclohexanone⁷

Convert 50 grams of Dowex 1-X10, 100-200 mesh, to the hydroxyl form by stirring the resin for several hours with 10% NaOH. Wash the regenerated resin with distilled water until the washings are neutral, then with methanol. Air-dry the resin. Place the dry resin in an Erlenmeyer flask provided with a glass stopper, add 500 ml redistilled cyclohexanone, and stir for several hours. Decant the cyclohexanone and filter.

Analytical Procedure

Accurately weigh 20 to 40 mg sample into a 200-ml electrolytic tall-form beaker containing a Teflon-coated stirring bar. Add 20 ml of solvent and dissolve. Place the beaker into the titration assembly and sweep with nitrogen for five minutes while stirring. Add the titrant slowly under rapid agitation. After each addition of titrant, allow sufficient time to reach a steady potential. In the determination of HMX and RDX in DMF, add the titrant in 0.10-ml increments near the equivalence potential. In the determination of RDX in MIBK or cyclohexanone, add the titrant in 0.05-ml increments near the equivalence potential. Continue the titration until the cell potential reaches a maximum which remains relatively constant upon further addition of titrant. Maintain the nitrogen atmosphere throughout the titration. Perform a blank titration for each batch of solvent.

Determine the equivalence point from a titration curve of volume titrant versus emf, or by calculation⁷ (see appendix).

Calculations

$$\% \text{ RDX or HMX} = \frac{(V_1 - V_2)(\text{normality titrant})(100)(74.043)}{\text{mg sample}}$$

where V_1 = volume of titrant,

V_2 = volume of solvent blank, and

74.043 = equivalent weight of RDX and HMX.

Results and Discussion

Titration curves of RDX and HMX in DMF are shown in Fig. I-1. The titrant was Bu_4NOH . The potential breaks for the two compounds occur at voltages too close together to permit a differentiating titration; however, the total amount of RDX and HMX in a mixture may be estimated (Table I-1). Table I-2 gives results of the analysis of RDX using various solvents. The analysis of HMX in DMF gave the results shown in Table I-3.

Table I-1. Analysis of RDX plus HMX in DMF.

Taken			meq found	no. detns.	% recovery
meq RDX	meq HMX	meq total			
0.2851	0.3350	0.6201	0.6187	3	99.8
0.1504	0.4056	0.5560	0.5578	2	100.3
0.3995	0.1374	0.5369	0.5457	4	101.6

Table I-2. Analysis of RDX (Wabash).

Solvent	Number of determinations	meq taken	meq found	% recovery
DMF	4	0.4898	0.4922	100.5
Cyclohexanone	4	0.4740	0.4760	100.4
MIBK	3	0.4788	0.4777	99.8

Table I-3. Analysis of HMX* in DMF (HMX, class A, HOL-SR-204-60, purified on J. O. 2072).

Number of determinations	meq taken	meq found	% recovery
4	0.5304	0.5185	97.8

*Material contained impurities as determined by paper chromatography.

RDX

HMX

As shown above, the basic unit of RDX and HMX is $-\text{CH}_2\text{NNO}_2-$, formula weight 74.043. RDX consists of three, and HMX of four such units. One equivalent of RDX requires three equivalents of base for neutralization; one equivalent of HMX requires four equivalents of base for neutralization. The equivalent weight of the two explosives is identical.

The neutralization reaction of RDX and HMX is quite slow, hence sufficient time must be allowed for attainment of a steady potential after each addition of titrant.

Addition of several drops of thymol blue helps in anticipating the equivalence point. The color change is from yellow through green to blue. Before the equivalence point, when titrant is added the color will change immediately to blue; this color, however, will gradually change back to yellow. Simultaneously, a slow decrease in emf is observed. At the equivalence point the potential becomes steadier and the blue color will not change.

In MIBK the potential break at the equivalence point is greater than in DMF (Fig. I-2). In this solvent, therefore, the titrant should be added in 0.05-ml increments near the equivalence point.

RDX and HMX are fairly soluble in cyclohexanone and γ -butyrolactone. The latter solvent cannot be used in nonaqueous titrimetry since it reacts with the base, apparently being slowly saponified. RDX can be titrated in cyclohexanone, with a potential break even greater than in MIBK. The titrant should be added in 0.05-ml increments near the equivalence point. HMX, although soluble, could not be determined in this solvent.

Since the solvent blank for cyclohexanone was fairly large (0.35 ml/20 ml solvent) an attempt was made to purify this solvent. Redistillation plus ion exchange by the method of Mostalyk, Chatten, and Pernarowski⁶ reduced the blank to an acceptable level. (Table I-4.)

Table I-4. Blank titration of 20 ml cyclohexanone.

Treatment of solvent	Titration, ml
Reagent grade, as received	0.35
Redistilled	0.25
Ion exchange	0.15
Redistilled + ion exchange	0.03

Since the coefficient of expansion of nonaqueous solvents is considerably greater than for water, for precise results the titrant should be kept and used at constant temperature. It is believed that the results reported in Tables I-1, I-2 and I-3 could be improved by making use of constant temperature facilities.

The use of a well-ventilated hood is mandatory for this work.

Appendix Calculation of Equivalence Point⁷

The equivalence point is that point where $\Delta E/\Delta V$ is maximum. (E = emf, V = volume of titrant.) Equal increments of titrant are to be added near the endpoint. Compute the maximum slope $\Delta E/\Delta V$ at the point where the second derivative $\Delta^2 E/\Delta V^2$ (slope of $\Delta E/\Delta V$ versus the V curve) becomes 0.

Example:

<u>Volume</u>	<u>emf.</u>	<u>$\Delta E/\Delta V$</u>	<u>$\Delta^2 E/\Delta V^2$</u>
10.90	294	>	6
11.00	300		+ 4
11.10	310	>	10
11.20	340		+20
11.30	430	>	30
11.40	500		+60
11.50	560	>	90
			-20
		>	70
			-10
		>	60

$$V_{\text{endpoint}} = 11.20 + (0.10) \left(\frac{60}{60 + 20} \right) = 11.275$$

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- ⁷J. J. Lingane, Electroanalytical Chemistry (Interscience Publishers, N. Y., 1958), 2nd ed., pp. 91-3.

Fig. I-1. Titration of RDX and HMX in DMF.

Fig. I-2. Titration of RDX in various solvents.

II. THE ANALYSIS OF HMX, POLY-2, 2-DINITROPROPYLACRYLATE, SILICA, AND ETHYL- AND METHYL-4, 4-DINITROPENTANOATE IN EXPLOSIVES*

Abstract

Procedures for the analysis of explosives containing HMX, poly-2, 2-dinitropropylacrylate (D_a), mixtures of ethyl- and methyl-4, 4-dinitropentanoate (E_dM_p), and silica are presented. The dinitropentanoates are extracted with carbon tetrachloride. In the absence of silica, D_a is extracted with ethylene dichloride leaving a residue of HMX which may be removed by dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), or γ -butyrolactone.

In the presence of silica, HMX and D_a are extracted with DMF. The D_a is determined photometrically in the presence of sodium hydroxide at 375 m μ . HMX is determined by difference.

The methods presented are general and may be applied over wide ranges of composition. They supersede procedures given previously for specific compositions.

Introduction

A method for the analysis of an extrusible explosive containing HMX, silica, poly-2, 2-dinitropropylacrylate (D_a), and a mixture of ethyl- and methyl-4, 4-dinitropentanoate (E_dM_p) was reported previously.¹ This method, however, was found to be not applicable for a solid high-energy explosive containing the same ingredients (with the exception of silica) in different proportions. The approximate compositions of the two explosives are:

<u>Component</u>	<u>Extrusible Explosive</u>	<u>Solid Explosive</u>
HMX	74%	92%
E_dM_p	24%	2%
D_a	1%	6%
SiO_2	1%	-

This note describes methods for the analysis of mixtures containing any or all of the following ingredients: HMX, SiO_2 (Cab-O-Sil), and mixtures of methyl- and ethyl-4, 4-dinitropentanoate (E_dM_p) and poly-2, 2-dinitropropylacrylate (D_a).

*General Chemistry Technical Note No. 130, dated October 3, 1963.

Experimental

Materials and Equipment

Analytical balance, Ainsworth, Type S.

Beckman Model DK-2 Spectrophotometer or equivalent instrument,
with 1 cm silica cells.

Sintered-glass crucibles, medium porosity, 50 ml capacity.

Vacuum oven, 60-70°C.

Suction filtration equipment (Fisher Filtrator).

Volumetric glassware.

Carbon tetrachloride, reagent grade.

Acetone.

N,N-dimethylformamide (DMF).

1,2-dichloroethane, technical grade.

Dimethylsulfoxide (DMSO).

γ -butyrolactone.

Sodium hydroxide, 0.2 M aqueous.

HMX.

Silica, Cab-O-Sil.

Poly-2,2-dinitropropylacrylate (D_a).

$E_d M_p$, consisting of 85% by weight ethyl-4,4-dinitropentanoate and
15% methyl-4,4-dinitropentanoate.

Procedures

1. Determination of HMX, $E_d M_p$, and SiO_2 . If the material is solid, grind it up by a remote-control mortar and pestle. Weigh 1 to 1.5 g into a tared 100 ml beaker containing a stirring rod flattened out at the end into a disc of approximately 5 mm diameter. Add 20 ml carbon tetrachloride, cover with a watch glass, and bring cautiously (danger of bumping) to boil on a hot plate. Remove occasionally from the hot plate and macerate any conglomerates with the stirring rod; this is particularly required for extrusible explosives. Let cool to room temperature and filter by suction through a tared medium-porosity 50 ml sintered-glass crucible. Wash beaker and crucible with four 5 ml portions of CCl_4 and filter. Dry beaker and crucible in a vacuum oven at 60-70°C for one hour. Cool to room temperature and weigh.

Transfer most of the precipitate quantitatively into the previously used 100 ml beaker. Add about 25 ml hot DMSO and warm on hot plate until most of the precipitate is dissolved. Filter by suction through the corresponding previously used crucible. Rinse beaker and crucible with several portions of warm DMSO and filter. Finally, wash beaker and crucible with several portions of acetone and filter. Dry beaker and crucible in a vacuum oven at 60-70°C for one hour. Cool to room temperature and weigh.

Carry out all extractions in a well-ventilated hood. Discard the DMSO extract in a waste explosives container.

Calculations:

- 1) Weight loss after CCl_4 extraction = amount of $E_d M_p$
- 2) Weight loss after DMSO extraction = amount of HMX
- 3) Residue = amount of SiO_2

2. Determination of HMX, $E_d M_p$, and D_a . Determine the $E_d M_p$ as described above. Transfer most of the precipitate quantitatively into the previously used 100 ml beaker. Add 20 ml ethylene dichloride, cover with a watch glass, and cautiously (danger of bumping) bring to boil on a hot plate. Cool to room temperature and filter by suction through the previously used sintered-glass crucible. Wash beaker and crucible with four 5 ml portions of ethylene dichloride and filter. Dry beaker and crucible in a vacuum oven for one hour, cool to room temperature, and weigh.

If desired, the residue may be dissolved in DMSO as described above to check the results obtained for HMX by difference.

Calculations:

- 1) Weight loss after CCl_4 extraction = amount of $E_d M_p$
- 2) Weight loss after ethylene dichloride extraction = amount of D_a
- 3) Residue (or loss after DMSO extraction) = amount of HMX

3. Determination of HMX, $E_d M_p$, D_a , and SiO_2 . Determine $E_d M_p$ as described previously. Transfer most of the residue quantitatively into the previously used 100 ml beaker, add about 25 ml warm DMF, and heat on a hot plate until most of the precipitate is dissolved. Filter by suction through the corresponding previously used filter crucible, collecting the filtrate quantitatively in a 100 ml volumetric flask. Wash beaker and

crucible with several portions of warm DMF. Remove the volumetric flask, and wash beaker and crucible with several portions of acetone. Dry beaker and crucible in a vacuum oven at 60-70°C for one hour, cool to room temperature, and weigh.

Dilute the volumetric flask to volume with DMF and mix. Pipet an aliquot not to exceed 0.4 mg D_a into a 50 ml volumetric flask, add 1.0 ml 0.2 M aqueous sodium hydroxide, and dilute to volume with DMF. Determine the absorbance at 375 m μ versus a DMF reference. At this wavelength the molar absorbance of D_a is 18,600. The solution is stable for at least 3 hours. Calculations:

1) Weight loss after CCl_4 extraction	= amount of $E_d M_p$
2) Residue after DMF extraction	= amount of SiO_2
3) Spectrophotometric determination	= amount of D_a
4) Calculated by difference	= amount of HMX

Results and Discussions

The method reported previously¹ for the analysis of an extrusible explosive did not work when the amount of dinitropropylacrylate polymer was increased from 1 to 6%. Although the $E_d M_p$ was completely extracted, the amount of 1,2-dichloroethane specified (10 ml) was insufficient to extract the increased amount of D_a in a reasonable length of time.

Two methods were investigated in this work. In the first, increasing amounts of cold solvent were used to extract the polymer. The results are presented in Table II-1, and illustrated in Fig. II-1. With 60 ml of ethylene dichloride, 98.6% of the polymer is extracted on the average. This procedure is limited to a polymer content of 5-8%. If the composition is changed beyond this range the optimum amount of ethylene dichloride must be redetermined.

The second method investigated is that outlined in procedure 2. Rather than extracting the D_a with several portions of cold solvent, the explosive mixture is brought to boiling with the solvent, cooled to room temperature, filtered, and washed. This procedure is more time consuming because of additional weighing and the necessity of cooling before filtering (HMX being more soluble in the hot solvent). However, the total solvent required for extraction of D_a is less, and the procedure is valid over a wide range of D_a concentrations. It was tried successfully on mixtures containing up to 28% D_a .

An attempt to substitute ethanol for carbon tetrachloride in the extraction of $E_d M_p$ was unsuccessful.

An attempt was made to apply the hot extraction method also to mixtures containing HMX, $E_d M_p$, and SiO_2 and HMX, $E_d M_p$, D_a , and SiO_2 . This succeeded for the former; for the latter, however, the extraction of D_a by dichloroethane was not quantitative. Table II-2 shows that as the amount of Cab-O-Sil increases in a mixture the recovery of D_a by extraction with ethylene dichloride decreases. In the presence of Cab-O-Sil D_a must, therefore, be determined photometrically in DMF.³

Recoveries of the components of known mixtures are presented in Tables II-3, II-4, II-5, and II-6. Analyses of some explosives are given in Table II-7. Where available, results using the cold extraction technique previously used are shown.

Adoption of the hot extraction method described here is recommended for materials containing two or more of the components described.

Acknowledgment

The writer is indebted to Guy Lopez for running the extractions reported in Table II-1.

Table II-1. Recovery of D_a by cold extraction with 1,2-dichloroethane.

mg taken	mg recovered	% recovery	ml dichloroethane
139.9	130.1	93.0	20
102.0	92.0	90.2	"
90.2	79.5	88.1	"
104.5	100.2	95.9	40
103.1	96.7	93.8	"
120.0	116.2	96.8	"
178.0	174.0	97.8	"
110.2	109.9	99.7	60
98.8	97.2	98.4	"
105.0	103.0	98.1	"
97.7	96.2	98.5	"
94.7	93.3	98.5	"
90.0	88.6	98.4	"
Average recovery with 60 ml solvent:			98.6%
Standard deviation:			0.56

Table II-2. Recovery of D_a in presence of SiO_2 by procedure 2.

mg taken	mg recovered	% recovery	mg SiO_2 present
12.9	12.3	95.4	11.0
23.7	21.6	91.1	11.2
11.7	7.9	67.5	23.5
201.9	190.5	94.4	11.4
204.5	191.0	93.4	22.6
195.2	168.5	86.3	42.4
66.8	63.5	95.1	21.6
128.3	117.8	91.8	21.4
62.1	44.2	71.2	41.9

Table II-3. Recovery of D_a by procedure 2.

mg taken	mg recovered	% recovery
127.4	126.5	99.3
119.2	118.4	99.3
129.6	132.0	101.9
110.3	111.1	100.7
176.5	176.6	100.1
Average recovery		100.3%
Standard deviation		1.09

Table II-4. Recovery of HMX by procedures 1 and 2.

mg taken	mg recovered	% recovery
839.3	839.1	100.0
800.2	800.8	100.1
835.9	832.2	99.7
894.0	893.2	99.9
840.8	840.7	100.0
728.0	727.9	100.0
731.6	731.8	100.0
755.2	755.5	100.0
Average recovery		99.96%
Standard deviation		0.14

Table II-5. Recovery of E_dM_p by procedures 1, 2, and 3.

mg taken	mg recovered	% recovery
85.5	86.6	101.3
140.2	140.4	100.1
77.9	78.2	100.4
407.8	408.0	100.1
201.7	201.7	100.0
153.2	152.4	99.5
229.8	229.7	100.0
220.8	220.9	100.1
248.5	247.9	99.8
Average recovery		100.14%
Standard deviation		0.50

Table II-6. Recovery of silica.

mg taken	mg recovered	% recovery	Procedure
65.8	67.6	102.7	2.3.
76.4	77.5	101.4	2.3.
73.7	76.4	103.7	2.3.
82.7	85.8	103.7	2.3.
86.5	89.5	103.5	2.3.
78.7	81.9	104.1	2.3.
24.9	25.1	100.8	2.1.
39.1	38.8	99.2	2.1.
82.3	82.6	100.4	2.1.
Average recovery procedure 3			103.2%
Standard deviation			0.99
Average recovery procedure 1			100.13%
Standard deviation			0.83

Table II-7. Analysis of explosive compositions.

Sample	% HMX	% E _d M _p	% D _a	% SiO ₂
RX-06-AC	68.23	29.68	--	2.08
(J. O. 1095-1)	67.75	30.14	--	2.11
	68.18	29.69	--	2.13
Average	68.05	29.84		2.11
By Ref. 4,	Average	67.87		1.94
RX-06-AF	73.90	24.49	--	1.61
(J. O. 1115)	73.95	24.42	--	1.63
	74.22	24.17	--	1.61
Average	74.02	24.36		1.62
By Ref. 4,	Average	73.71		1.48
RX-06-AF	73.93	24.64	--	1.43
(43612B)	74.00	24.55	--	1.45
	74.47	24.14	--	1.39
Average	74.13	24.44		1.42
By Ref. 4,	Average	73.86		1.51
RX-06-AA	69.79	27.64	2.56	--
(Sn 1065-2)	69.66	27.79	2.55	--
	69.84	27.55	2.61	--
Average	69.76	27.66	2.57	
RX-09-AA	93.23	0.74	6.03	--
(5K110)	93.52	0.69	5.79	--

References

¹G. L. Crossman and W. Selig, "The Analysis of Extrusible Explosives. II. The Determination of Ethyl- and Methyl-4,4-dinitropentanoate, Poly-2, 2-dinitropropylacrylate, Silica, and HMX," Lawrence Radiation Laboratory (Livermore) Internal Document GCTN-78 (July 10, 1962).

²W. Selig, "The Spectrophotometric Determination of Ethyl- and Methyl-4,4-Dinitropentanoate Mixtures in an Extrusible Explosive," Lawrence Radiation Laboratory (Livermore) Internal Document GCTN-77 (June 18, 1962).

³W. Selig, "The Spectrophotometric Determination of Some gem-Dinitro Compounds in N,N-Dimethylformamide," UCRL-7116 (October 23, 1962).

⁴W. Selig and G. L. Crossman, "The Determination of the Components of an Extrusible Explosive," Lawrence Radiation Laboratory (Livermore) Internal Document GCTN-75 (May 17, 1962).

Fig. II-1. Recovery of poly-2,2-dinitropropylacrylate versus volume of 1,2-dichloroethane.

III. THE DETERMINATION OF PETN AND SILICA IN LX-02-1*

Abstract

A method is presented for the analysis of an extrusible explosive containing PETN, silica, butyl rubber, and acetyltributyl citrate. The rubber and plasticizer are extracted with carbon tetrachloride; PETN is extracted with acetone, leaving a residue of silica.

Introduction

This work describes the analysis of an extrusible explosive of the approximate composition

PETN	73%
SiO ₂	2%
Butyl rubber + acetyltributyl citrate	25%

The procedure given is a modification of one suggested by du Pont.

Experimental

Experiment and Materials

Analytical balance, Ainsworth, Type S.

Sintered glass crucibles, medium porosity, 50 ml capacity.

Vacuum oven, maintained at room temperature.

Steam bath.

Suction filtration equipment (Fisher Filtrator).

Carbon tetrachloride, reagent grade, saturated with PETN.

Acetone, reagent grade.

PETN.

Cab-O-Sil (SiO₂).

du Pont 4600-D Adhesive, Lot 12-61, 48.5% in hexane.

Citroflex A-4, Pfizer & Company (acetyltributyl citrate).

Procedure

Weigh approximately 2 g material into a tared 100 ml beaker containing a glass stirring rod. Add 50 ml carbon tetrachloride and cover with watch glass. Keep on a steam bath for 30-45 minutes and break up

*General Chemistry Technical Note No. 88, dated September 20, 1962.

lumps with the stirring rod. Let cool to room temperature and filter by suction through a tared medium-porosity, 50 ml, sintered glass crucible. Wash beaker, stirring rod, and crucible with three successive 5 ml portions of carbon tetrachloride. Dry the beaker with stirring rod and crucible in a vacuum oven at room temperature for one hour and weigh.

Dissolve the PETN in the beaker and crucible with successive portions of a total of 50 ml acetone at room temperature. Wash with several 5 ml portions of acetone. Discard the filtrate in the explosives waste container. Dry the beaker with stirring rod and crucible in a vacuum oven at room temperature for one hour and weigh.

Calculations

1. Weight loss after carbon tetrachloride extraction = amount of adhesive
2. Weight loss after acetone extraction = amount of PETN
3. Residue = amount of silica

Results and Discussion

The extraction scheme given in the procedure is based on the solubility of the adhesive (butyl rubber + acetyltributyl citrate), in carbon tetrachloride which does not dissolve the PETN and silica. The PETN is then extracted with acetone, leaving a residue of silica.

Tables III-1 and III-2 present results obtained with known samples prepared by weighing the components into a beaker. The data were obtained by the procedure suggested by du Pont, using vacuum drying at 60°C. Under these conditions the average recovery rate for PETN was 99.64%. If vacuum drying at room temperature, as outlined in the procedure given here, is used, the recovery rate for PETN will be closer to 100%.

Table III-3 shows results for some extrusible explosives.

The use of an ultrasonic generator is suggested for the carbon tetrachloride extraction. This will probably speed up the disintegration of the rubber-like sample material and may eliminate the use of steam bath.

Table III-1. Recovery of PETN from extrusible explosive.

mg taken	mg recovered	% recovery
1506.5	1501.6	99.67
1500.7	1496.3	99.71
1268.5	1262.7	99.54
Average recovery		99.64%
Average deviation		0.07

Table III-2. Recovery of silica from extrusible explosive.

mg taken	mg recovered	% recovery
99.8	99.9	100.10
103.8	103.6	99.81
94.9	95.4	100.53
Average recovery		100.15%
Average deviation		0.26

Table III-3. Analysis of extrusible explosives.

Sample No.	% PETN	% SiO ₂
HE 107, A5	72.86	1.81
	72.89	1.84
HE 107, 0	72.96	1.84
	72.92	1.82
HE 107, 03	72.68	1.51
	72.75	1.60
HE 121	73.07	2.05
	73.10	2.05

IV. THE SPECTROPHOTOMETRIC DETERMINATION
OF ACETYLTRIBUTYL CITRATE
IN AN EXTRUSIBLE EXPLOSIVE, LX-02-1*

Abstract

A spectrophotometric method for the analysis of acetyltributyl citrate (ATBC) in an extrusible explosive (LX-02-1) containing pentaerythritol tetranitrate (PETN), silica, butyl rubber, and ATBC is presented. ATBC is extracted with anhydrous ethanol. The ester is converted to the hydroxamic acid with basic hydroxylamine and the purple complex developed with ferric ion is determined photometrically. (A correction for the absorbance of PETN is necessary.)

Introduction

The analysis of an extrusible explosive, LX-02-1, of the approximate composition

PETN	73%
Silica	2%
Butyl rubber + acetyltributyl citrate (ATBC) plasticizer	25%

is reported in Section III. In this method the rubber and plasticizer are extracted with carbon tetrachloride and PETN is then extracted with acetone, leaving a residue of silica.

The determination of the plasticizer, by saponification or by the ferric hydroxamate method, requires the presence of sodium hydroxide. Therefore, carbon tetrachloride, which is attacked by caustic, is unsatisfactory as an extractant. No selective solvent for the differential extraction of ATBC is available.

Many recent papers report on the photometric determination of esters by the ferric hydroxamate method; of these, the most promising are by Goddu, LeBlanc, and Wright,¹ Pilz,² and Gutnikov and Schenk.³

Organic esters form hydroxamic acids by the reaction shown in Eq. (1). The hydroxamic acid then reacts with ferric ion to form a purple complex [as shown in Eq. (2)] which can be determined photometrically.

*General Chemistry Technical Note No. 127, dated September 5, 1963.

The above procedures were tried for acetyltributyl citrate and only the method of Gutnikov and Schenk³ was found applicable with minor modifications.

This paper presents a procedure for the determination of ATBC in LX-02-1 using this method.

Experimental

Reagents and Equipment

1.4 M Hydroxylammonium perchlorate. This solution is prepared according to the procedure of Gutnikov and Schenk.³ Dissolve 195 g sodium perchlorate monohydrate in 450 ml absolute methanol with heating. Dissolve 105 g reagent grade hydroxylamine hydrochloride in 550 ml absolute methanol with heating. Add the sodium perchlorate solution slowly to the hydroxylamine solution with stirring. Add 50 ml benzene and let cool to room temperature. Chill solution and precipitate for one hour in an ice bath and filter the sodium chloride on a sintered glass filter with suction. Store the hydroxylammonium perchlorate solution in a polyethylene bottle.

2.5 M Sodium hydroxide. Reflux 100 g sodium hydroxide with 1000 ml absolute methanol. Store the solution in a polyethylene bottle.

Stock ferric perchlorate solution. Weigh 3.1534 g iron wire into a 150 ml beaker. Add 36 ml 70% perchloric acid and heat at low heat on a hot plate until the iron dissolves. (Caution: The iron dissolves quite rapidly when the acid is hot.) Cool the beaker and transfer the contents to a 200 ml volumetric flask with absolute ethanol. Dilute to volume with absolute ethanol, cooling under a tap as the alcohol is added.

Ferric perchlorate reagent. To about 1.5 liters of absolute ethanol add 100 ml of the ferric perchlorate stock solution. Slowly add 130 ml 70% perchloric acid while cooling under a tap. Allow to cool and dilute to 2 liters with absolute ethanol.

Ethanol, anhydrous, Rossville Gold Shield.

Acetyltributyl citrate, Pfizer Citroflex A-4.

Acetyltriethyl citrate, Pfizer Citroflex A-2.

Tributyl citrate, Pfizer Citroflex 4.

Triethyl citrate, Pfizer Citroflex 2.

Beckman Model DK-2 recording spectrophotometer or equivalent instrument, with 1 cm cells.

Preparation of Calibration Curve

Weigh several samples of ATBC (or other citrate esters) covering the range of 0.5 to 8 mg into 50 ml volumetric flasks and add 5 ml of anhydrous ethanol, or prepare stock solutions so that aliquots of 5 ml result in the desired amounts. Pipet in 3 ml of 1.4 M hydroxylammonium perchlorate and then 10 ml of 2.5 M methanolic sodium hydroxide. Let stand for 20 minutes and add 22 to 23 ml of a ferric perchlorate-acetone mixture made by mixing, for each sample, 35 ml ferric perchlorate reagent and 2.5 ml acetone. Allow to stand for 5 minutes, then dilute to volume with the same acetone-ferric perchlorate mixture. Mix thoroughly, let stand for one hour, and read the absorbance versus a reagent blank at 517-522 m μ . Plot absorbance versus mg ATBC. (The absorbance of a sample containing ATBC may be read up to 4 hours after sample preparation.)

PETN Blank Preparation

Weigh approximately 750 mg dry PETN into a 150 ml beaker, add 50 ml anhydrous ethanol, and heat gently until dissolved. Cover with a watch glass and let cool to room temperature. Filter by suction through a medium porosity sintered-glass crucible into a 100 ml volumetric flask. Wash crucible and funnel with several portions of ethanol; dilute to mark with ethanol. Use 5 ml of this solution as a blank for the determination of ATBC in LX-02. This solution, if well stoppered, may be kept indefinitely.

Determination of ATBC in LX-02-1

Accurately weigh approximately 500 mg of explosive sample into a 100 ml beaker. Add 25 ml anhydrous ethanol, place on a hot plate at low heat, and let boil gently for 15 to 30 minutes, stirring occasionally to break up large agglomerations. Let cool to room temperature. Filter by suction through a medium-porosity, sintered-glass crucible into a 50 ml volumetric flask. Wash crucible and funnel with several portions of ethanol and dilute

to mark with ethanol. Transfer an aliquot containing 2-7 mg ATBC into a 50 ml volumetric flask then follow the procedure for preparation of the calibration curve (see above).

Results and Discussion

The absorption spectrum of the ferric hydroxamate complex of ATBC is shown in Fig. IV-1. Maximum absorption for this compound and the other citrate esters investigated occurs between 517 and 522 mμ as a broad peak (same as previously reported for other esters^{1,4}). The molar absorbances for several citrate esters are given in Table IV-1. As shown in this table, the absorptivity per ester group is constant.

Table IV-1. Molar absorbances for some citrate esters at 517-522 mμ.

Citrate	$\epsilon \times 10^{-3}$ *	$\epsilon \times 10^{-3}$ per ester group
Acetyltributyl	3.52	0.88
Acetyltriethyl	3.43	0.86
Tributyl	2.54	0.85
Triethyl	2.49	0.83

* Average of 4 to 7 determinations.

The ferric hydroxamate complex of ATBC is stable up to four hours after sample preparation; the complexes of the other citrate esters are somewhat less stable as shown in Table IV-2. Therefore, determination of the absorbance of the complexes one hour after sample preparation is recommended.

Table IV-2. Fading rates in percent for ferric hydroxamate complexes of some citrate esters.

Citrate	Hours after initial reading	Percent Decrease in Absorbance					
		0.5	1	1.5	2	3	4
Acetyltributyl						0.6	
Acetyltriethyl				1.1	1.3	2.8	4.1
Triethyl			0.6		2.1	3.6	5.2
Tributyl	0.5		2.3		3.4	5.3	

Beer's Law applies up to 8 mg ester per 50 ml. A calibration curve for ATBC is shown in Fig. IV-2. The results of some analyses of ATBC in LX-02-1 are presented in Table IV-3.

Table IV-3. Percent ATBC in LX-02-1.

Sample No.	% ATBC added	% ATBC found
1	3.4	3.4
2	5.1	5.0
3	6.8	7.0
4	6.8	7.0
5	6.8	6.7
6	5.6	5.4
7	5.6	5.6

A summary of the reaction conditions used by Goddu *et al.*,¹ Pilz,² and Gutnikov and Schenk³ is given in Table IV-4. Goddu's method could not be used for ATBC since the fading rate of the complex was 5% per hour and the results were not reproducible.

Pilz's procedure applied to ATBC produced a 4% decrease in absorbance during the first hour after the initial reading, decreasing thereafter at a slower rate; no reproducible results were obtained.

The method of Gutnikov and Schenk³ was found applicable to ATBC and other citrate esters. A slight modification was required, however. After dilution to volume and mixing, the sample was allowed to reach thermal equilibrium before the photometric determination. This required approximately one hour. Also, in preparation of the ferric perchlorate reagent, iron wire was found superior to anhydrous ferric perchlorate due to the hygroscopicity of the salt. In addition, a PETN blank was required since the absorbance of a saturated solution of PETN in ethanol at 25°C is 0.022 at 520 mμ.

References

- ¹R. F. Goddu, N. F. LaBlanc, and C. M. Wright, *Anal. Chem.* 27, 1251 (1955).
- ²W. Pilz, *Z. Anal. Chem.* 162, 81 (1958).
- ³G. Gutnikov and G. H. Schenk, *Anal. Chem.* 34, 1316 (1962).
- ⁴G. Norwitz, *Anal. Chem.* 31, 2012 (1959).

Table IV-4. Experimental conditions for some methods for ester determination in the recent literature.

	Goddu et al. ¹	Pilz ²	Gutnikov and Schenk ³
mg Fe/ml	0.27	5.05 - 11.2	0.51
Acidity (molar)	0.1	0.004 - 0.04	0.07 - 0.08
NH ₂ OH (mmol)	2.7	2.5	4.2
NaOH (mmol)	4.7	6.25	25
Removal of excess hydroxylamine	None	KNO ₃	Acetone
Solution	Ethanol	Water	Ethanol
λ_{max} (m μ)	520 - 550	490	524
Color stability (hours)	0 to "several"	1/2 - 4	0 - 3

Fig. IV-1 Absorption spectrum of the ferric hydroxamate complex of acetyltributyl citrate (3.97 mg ATBC/50 ml).

Fig. IV-2. Calibration curve for acetyltributyl citrate at 520 mμ.

V. THE ANALYSIS OF MIXTURES OF HMX, VITON, AND OXAMIDE*

Abstract

A method for the analysis of a plastic-bonded explosive containing HMX, Viton, and oxamide is presented. Viton is determined by a nitric acid Soxhlet extraction. HMX plus Viton is determined by hot-water extraction and the oxamide calculated by difference. The oxamide may also be determined by γ -butyrolactone extraction and the HMX calculated by difference.

Introduction

This note describes a method for the analysis of a plastic-bonded explosive of the approximate composition:

HMX	80%
Viton	15%
Oxamide	5%

The Viton is determined by a nitric acid Soxhlet extraction which is also used for the determination of Viton in LX-04.¹ An attempt to find specific solvents for the other components, HMX and oxamide, did not succeed. Hence the methods presented require corrections for partial solubility of the components in the solvents used. These methods are a hot-water extraction for oxamide and a γ -butyrolactone extraction for HMX.

In the hot-water extraction oxamide is removed leaving a residue of HMX and Viton. The HMX usually contains a small amount of RDX which is appreciably soluble in hot water. It is, therefore, necessary to establish the water solubility of each batch of HMX used in making the plastic-bonded explosive, and to correct for it in the determination of HMX plus Viton.

The alternate procedure uses γ -butyrolactone to extract HMX and Viton, leaving a residue of oxamide. Since oxamide is somewhat soluble in butyrolactone, a correction must be applied.

*General Chemistry Technical Note No. 108, dated March 20, 1963.

Experimental

Materials and Equipment

Analytical balance, Ainsworth, Type S.

Sintered glass crucibles, medium porosity, 50 ml capacity.

Vacuum oven, at 60-70°C.

Suction filtration equipment (Fisher Filtrator).

Soxhlet extraction apparatus consisting of:

Soxhlet tube, 70 ml capacity,

Round-bottom flask, 250 ml capacity,

Tall-form fritted glass extraction thimble, coarse porosity,
25 mm diameter, 85 mm high,

Condenser,

Anti-bump rod,

Heating mantle with Variac.

Nitric acid, reagent grade.

γ -Butyrolactone, Matheson, Coleman, and Bell.

Carbon tetrachloride, reagent grade.

HMX, Lot A134.

Oxamide, Matheson, Coleman, and Bell.

Viton A.

Explosive sample.

Procedures

1. Soxhlet extraction for determination of Viton. Weigh a sample of approximately 1 gram accurately into an extraction thimble. Place the thimble into a Soxhlet tube. Connect the extraction tube to a water-cooled condenser and a round-bottom 250 ml flask. The latter contains an anti-bump rod and is two-thirds filled with concentrated nitric acid. Fill the thimble containing the sample about one-half full with concentrated nitric acid. Place a heating mantle under the flask and heat to refluxing (Variac setting of approximately 110 volts). Allow to reflux for about 4 hours. Let the apparatus cool and remove thimble from extraction tube. Wash the thimble with distilled water and filter by suction (Fisher Filtrator). Inspect the Viton residue which should be a clear translucent film. If inclusions of HMX and/or oxamide are found, break up the film with a porcelaine spatula.

and re-extract for several hours. Dry the thimble in a vacuum oven at 60-70°C for at least one hour. Cool to room temperature and weigh.

2. Water extraction for the determination of HMX and Viton. Weigh a ground sample of approximately 1 gram accurately into a tared 100 ml beaker containing a stirring rod. Add 50 ml hot water and boil gently on a hot plate for about 10 minutes, stirring meanwhile to wet all particles and to prevent spattering. Filter by suction (Fisher Filtrator) while hot through a tared 50 ml medium porosity sintered glass crucible. Wash beaker, stirring rod, and crucible with several portions of hot water. Dry beaker with stirring rod and crucible in a vacuum oven at 60-70°C for one hour. Cool to room temperature and weigh.

3. Butyrolactone extraction for the determination of oxamide. Weigh approximately 1 g ground sample accurately into a tared 50 ml medium porosity sintered glass crucible containing a stirring rod. Add 10 ml γ -butyrolactone and stir thoroughly to break up the material. The stirring may require about 15 minutes, and may be facilitated by first introducing the crucible into a beaker containing butyrolactone suspended in an ultrasonic transducer unit. Filter by suction and repeat with three additional 5 ml portions of butyrolactone. Wash crucible and stirring rod with two successive 5 ml portions of carbon tetrachloride and filter. Rinse the bottom of the crucible with carbon tetrachloride to remove any remaining butyrolactone. Dry the crucible and stirring rod in a vacuum oven at 60-70°C for at least one hour. Cool to room temperature and weigh.

Calculations

$$\text{Procedure 1: \% Viton} = \frac{\text{mg residue}}{\text{mg sample}} 100$$

$$\text{Procedure 2: mg HMX, uncorrected} = (\text{mg residue}) - \frac{(\% \text{ Viton})}{100} (\text{mg sample})$$

$$\% \text{ HMX} = \frac{(\text{mg HMX, uncorrected})(1 + \text{correction factor})}{\text{mg sample}} 100$$

$$\% \text{ oxamide} = \text{by difference } (100 - \% \text{ Viton} - \% \text{ HMX})$$

$$\text{Procedure 3: \% oxamide} = \frac{(\text{mg residue})(1 + \text{correction factor})}{\text{mg sample}} 100$$

$$\% \text{ HMX} = \text{by difference } (100 - \% \text{ Viton} - \% \text{ oxamide})$$

Results and Discussion

Viton was determined by nitric acid Soxhlet extraction. Results for known mixtures, prepared by weighing the components into Soxhlet extraction thimbles are shown in Table V-1. The method is based on the oxidation and solution of HMX and oxamide by hot concentrated nitric acid which does not attack Viton.

Table V-1. Recovery of Viton by nitric acid Soxhlet extraction.

mg Viton taken	mg Viton recovered	% recovery
103.7	104.3	100.6
160.8	160.3	99.7
151.8	150.7	99.3
	Average	99.9
	Standard deviation	0.66

For the determination of HMX plus Viton an attempt was made to find a specific solvent for oxamide. Oxamide is quite insoluble in all common solvents at room temperature, but dissolves readily in hot water. The hot-water extraction method, however, is not entirely satisfactory. HMX usually contains some RDX which is appreciably soluble in hot water. A correction factor must, therefore, be established for the batch of HMX used before the analytical procedure can be applied. This can be done by using an amount of HMX equal to that expected in the explosive and carrying it through the analytical procedure. From Lot A134, using samples of approximately 700 mg, an average of 2.8% HMX was lost (see Table V-2).

An alternate procedure for the determination of oxamide was sought, requiring a solvent for HMX and Viton. The most suitable solvent found was γ -butyrolactone; however, small amounts of oxamide were lost. Again a correction factor must be determined (Table V-3).

Results for the analysis of a sample explosive are shown in Table V-4. Results for HMX and oxamide obtained by hot-water and butyrolactone extraction are compared. The averages of four replicates agree within 0.3%.

Table V-2. Recovery of HMX from HMX-oxamide mixtures by hot-water extraction.

mg HMX taken	mg HMX recovered	% recovery
711.5	691.9	97.3
712.9	695.1	97.5
773.9	751.5	97.1
714.4	696.1	97.3
723.2	701.5	97.0
717.3	693.8	96.7
	Average	97.2
	Standard deviation	0.28

Table V-3. Recovery of oxamide by γ -butyrolactone extraction.

mg oxamide taken	mg oxamide recovered	% recovery
113.7	108.8	95.7
122.5	118.2	96.5
97.5	93.6	96.0
90.6	86.2	95.1
	Average	95.8
	Standard deviation	0.63

Table V-4. Analysis of an explosive sample.

% Viton	Hot-water extraction		Butyrolactone extraction	
	% HMX*	% oxamide	% HMX	% oxamide*
15.37	81.1	3.5	80.8	3.8
15.39	81.1	3.5	80.7	3.9
15.38	80.9	3.7	80.5	4.1
	80.9	3.7	80.9	3.7
Average				
15.38	81.0	3.6	80.7	3.9

* Corrected.

On a routine basis the hot-water extraction is recommended since filtration is rapid and the crucibles can be used again after cleaning with acetone. In the butyrolactone extraction filtration is slow and the crucibles should be discarded after use.

Acknowledgment

The writer is indebted to Milton Finger for suggesting the hot water extraction method for the determination of oxamide.

Reference

¹Lee Monteith et al., Lawrence Radiation Laboratory (Livermore) Internal Document GCTN-49 (March 10, 1961).

VI. AN ANALYTICAL PROCEDURE FOR RDX IN RX-05*

Abstract

A procedure for determining the amount of RDX in RX-05 through carbon tetrachloride extraction of the binding material is described. By using an ultrasonic generator the use of hot CCl_4 is eliminated and the time of analysis reduced.

Introduction

This work describes an analytical procedure for RDX in plastic-bonded explosives of the approximate composition:

RDX	80 - 90%
Polystyrene	8 - 12%
Diethylphthalate (DOP)	2 - 3%

The procedure is a modification of one developed at LASL which required heating the sample to boiling with CCl_4 , followed by shaking with a wrist-action shaker for 30 minutes.

Experimental

Equipment and Materials

Analytical balance.

Ultrasonic generator.

Sintered glass crucibles, medium porosity, 50 ml capacity.

Vacuum oven, maintained at room temperature.

Suction filtration equipment (Fisher Filtrator).

100 ml beakers.

Carbon tetrachloride, reagent grade.

Polystyrene, Dow Chemical.

Diethylphthalate.

RDX, Lot A033.

PBX samples.

*General Chemistry Technical Note. No. 97, dated December 28, 1962.

Procedure

Weigh approximately 2 g material into a tared 100 ml beaker. Add 30 ml carbon tetrachloride and place in ultrasonic generator for 10 minutes or until all lumps are broken up. Filter by suction through a tared 50 ml medium porosity sintered glass crucible and wash beaker and crucible with three successive 5 ml portions of carbon tetrachloride. Dry beaker and crucible in a vacuum oven at room temperature for one hour and weigh.

Calculations

1. Weight loss on carbon tetrachloride extraction = amount of DOP
+ polystyrene
2. Residue = amount of RDX

Results and Discussion

A first modification to the LASL method consisted of grinding up the material with a mechanical mortar and pestle, thus eliminating the use of a shaker. This modification, however, still required the use of hot CCl_4 which constitutes a health hazard.

Known samples prepared by weighing the components into sintered glass crucibles were extracted with 50 ml hot CCl_4 . The results are given in Table VI-1. The recoveries for RDX were high indicating incomplete extraction of polystyrene. This was probably due to the difficulty of dissolving unplasticized polystyrene pellets in CCl_4 . As a check on the efficiency of the method analyses were performed on an unknown material, as received and with added known amounts of RDX. The results are presented in Table VI-2. The advantage of grinding up the samples is seen from the results for the percent RDX recovered.

Finally, the procedure described under Experimental was adopted. It eliminates entirely the use of hot carbon tetrachloride and grinding up samples, and speeds up the analysis. Results obtained by this method are shown in Table VI-3.

Table VI-1. Recovery of RDX and plastic from synthetic sample.

Amount taken			mg recovered	% recovery
mg polystyrene	mg DOP	mg total		
164.5	48.0	212.5	203.2	95.62
167.5	43.8	211.3	198.7	94.04
158.7	44.5	203.2	190.8	93.90
161.9	44.8	206.7	194.0	93.86
166.6	45.2	211.8	200.9	94.85
			Average	94.45

<u>mg RDX taken</u>	<u>mg RDX recovered</u>	<u>% recovery</u>
1784.3	1793.6	100.52
1806.8	1819.4	100.70
1792.1	1804.5	100.69
1804.9	1817.6	100.70
1821.2	1832.1	100.60
Average		100.64

Table VI-2. RDX in sample Sn 4073, batch 1.

Amount taken			A. Pellets		Percent
mg sample	+ mg RDX	mg total	RDX recovered		
			mg recovered	mg calcd.*	
1956.9		1956.9	1737.0		88.78)Avg.
1762.8		1762.8	1569.0		89.01)88.885
1747.2	229.2	1976.4	1784.2	1782.2	99.89
1668.8	368.8	2037.6	1853.8	1852.1	99.91

* Calculation based on average 88.885% RDX in unknown.

RDX in sample Sn 4073, batch 1.

B. Ground sample

Amount taken			RDX recovered		Percent
mg sample	+ mg RDX	mg total	mg recovered	mg calcd.*	
1963.7		1963.7	1746.6		88.94)Avg.
1736.2		1736.2	1544.8		88.98)88.96
1648.6	310.5	1959.1	1777.3	1777.1	99.99
1775.2	223.8	1999.0	1803.5	1803.0	99.97

* Calculation based on 88.96% RDX found in unknown.

Table VI-3. % RDX in sample J. O. 4080, batch 1.

Ground-up sample hot CCl ₄	Ultrasonic generator pellets, cold CCl ₄
90.38	90.29
90.27	90.28

VII. THE ANALYSIS OF TUNGSTEN AND HMX IN RX-12*

Abstract

An analysis of a material consisting of tungsten, HMX, and Viton is presented. An acetone extraction removes HMX and Viton from tungsten. The acetone is evaporated and the HMX in the residue is determined photometrically. Viton is determined by difference.

Introduction

The nominal composition of RX-12 is

Tungsten	95.4%
HMX	2.8%
Viton	1.8%

This note presents a method for its analysis by a combination of extraction and photometric methods. The method of extraction depends on the particle size of tungsten used.

Experimental

Reagents and Equipment

Analytical balance.

Spectrophotometer, Beckman DK-2, or equivalent instrument, with
1 cm cells.

Sintered-glass crucibles, medium porosity, 50 ml capacity.

Vacuum oven, 60-70°C.

Vacuum filtration equipment (Fisher Filtrator).

Centrifuge.

Water bath, 70°C.

Funnel, Hirsch type, with coarse porosity fritted disc.

Centrifuge cones, 40 ml capacity, with outer 19/38 joints.

Condenser, inner 19/38 joints.

Volumetric glassware.

Stirrer and Teflon-coated stirring bars.

*General Chemistry Technical Note No. 141, dated January 23, 1964.

Sulfuric acid, concentrated, ACS specifications.

Acetone, ACS specifications.

Ferrous ammonium sulfate, prepared according to Semel, Laccetti and Roth¹:

Weigh 100 g ferrous ammonium sulfate hexahydrate into a 1 liter Pyrex volumetric flask and dissolve in about 500 ml distilled water. Add with caution 50 ml concentrated sulfuric acid. After the solution has reached room temperature, add 1 g iron filings and allow the evolved hydrogen to escape. Bring the volume to 1 liter with distilled water.

Preparation of Calibration Curve for HMX¹

Weigh several samples of HMX covering the range of 5 to 50 mg into 250 ml glass-stoppered Erlenmeyer flasks. Insert a Teflon-covered stirring bar, add 90 ml concentrated sulfuric acid, stopper, and stir until the HMX is in solution. Add 10.0 ml of the ferrous ammonium sulfate reagent, swirl the flask, and place it in a water bath at $25 \pm 5^\circ\text{C}$ for 45 minutes, swirling occasionally. Measure the absorbance of the solutions at 520 m μ against a reagent blank. Plot absorbance versus concentration of HMX.

This calibration curve must be prepared for each batch of HMX used in the material to be analyzed.

Extreme caution is called for in filling the cuvettes; automatic pipette fillers are recommended.

Procedure

1. For tungsten of particle size > 15 microns. Weigh about 1 g sample accurately into a 100 ml beaker containing a stirring rod. Add 20 ml acetone, cover with a watch glass, and bring to near boiling on a hot plate at low heat. Filter by suction while hot through a tared medium-porosity, 50-ml, sintered-glass crucible, collecting the filtrate in a 250 ml Erlenmeyer flask. Extract the material with three additional 10 ml portions of warm acetone, but do not place on hot plate (danger of bumping). Wash beaker and crucible with several portions of acetone, collecting all the washings in the 250 ml Erlenmeyer. Filtration is facilitated by transferring as little as possible of the tungsten onto the filter crucible. Dry beaker and crucible in a vacuum oven at 60-70°C for one hour. Cool to room temperature and weigh.

Evaporate the acetone solution in the Erlenmeyer to dryness under a stream of air. Insert a Teflon-covered stirring bar and proceed with the photometric determination of HMX as described above, with the following change: After 30 minutes in the water bath, filter the contents of the flask by suction through a coarse porosity Hirsch funnel into a 250 ml Erlenmeyer flask. Place the filtrate in the water bath for another 15 minutes, then proceed with the photometric determination.

To check on the complete removal of HMX and Viton from the tungsten, re-extract the residue with several 10 ml portions of warm acetone and again evaporate the acetone solution to dryness. If no visible white residue is obtained, the extraction is complete.

2. For tungsten of particle size < 15 microns. Weigh approximately 1 g sample accurately into a 40 ml centrifuge cone provided with a ground joint for accommodation of a condenser, add 20 ml of acetone, connect with a water-cooled condenser and immerse in a water bath at about 70°C. Let reflux for several minutes, remove from water bath, rinse down condenser with several ml of acetone, and centrifuge for 5 minutes at high speed. Decant the supernatant acetone into a 250 ml Erlenmeyer flask taking care not to transfer any tungsten. Repeat reflux, centrifugation, and decantation with four additional 10 ml portions of acetone. Dry the centrifuge cone in a vacuum oven at 60-70°C. Cool to room temperature and weigh.

Evaporate the acetone solution in the Erlenmeyer flask to dryness under a stream of air and proceed with the determination of HMX as above.

As in procedure 1, re-extract the residue with several portions of acetone to check on complete removal of HMX and Viton from the tungsten. If after evaporation of the acetone solution no white residue remains, the extraction was complete. If a white residue remains, repeat the photometric determination of HMX and correct the initial results. Also, re-weigh the tungsten residue.

Calculations

1. Residue after acetone extraction = amount of tungsten
2. Photometric determination = amount of HMX
3. Calculated by difference = amount of Viton

Results and Discussion

Viton and HMX are soluble in acetone; this is the basis of their separation from tungsten. The solubility of HMX in acetone at 30°C is 2.2 g/100 ml,² hence the amount of solvent used in the extraction procedures insures complete removal of HMX and Viton.

Laccetti, Semel, and Roth^{1,3} modified the colorimetric ferrous sulfate method for the determination of organic nitrates to include aliphatic and cyclic nitramines. They were able to determine mixtures of HMX and RDX by this method, since plots of absorbance against concentration for these compounds give straight lines which have different slopes but intersect at the origin. The molar absorbances for the ferrous nitrosyl complexes of RDX and HMX are given in Table VII-1.

Table VII-1. Molar absorbances, ϵ , for ferrous nitrosyl complexes of RDX and HMX.

Compound	$\epsilon \times 10^{-2}$
RDX	5.29 ¹
HMX	3.65 ¹
HMX, Lot A-222	3.80 $\pm$ 0.06*

* Average of 6 runs, 95% confidence level.

Commercial HMX usually contains some RDX and possibly other nitramines as contaminants. In this work, however, the desired data is the amount of a particular batch of HMX in a formulation. Therefore, calibration curves must be prepared for every batch of HMX to be analyzed. Table VII-1 shows the molar absorbance of the ferrous nitrosyl complex of HMX, Lot A-222. Comparison with the data of Laccetti *et al.* indicates, as expected, the presence of impurities in this lot. The absorption spectrum for this batch is shown in Fig. VII-1 and its calibration curve in Fig. VII-2. Beer's Law applies up to 45 mg/100 ml.

Viton is insoluble in concentrated sulfuric acid. In the procedure for the photometric determination of HMX it tends to agglomerate. Filtration by suction through a coarse-porosity Hirsch funnel is suggested before the photometric determination.

Some typical results are shown in Table VII-2. The particle size of the tungsten in RX-12(6K-42-2) is 18.5 microns; no data on the particle size of J.O. 2606 were available. The speed of filtration of this material indicated that the particle size of the tungsten was probably greater than 18.5 microns. The nominal pore size of medium porosity filter crucibles is 10 to 15 microns. If tungsten of a particle size < 15 microns is used in a material, procedure 2 must be used.

Tungsten cannot easily be removed from the filter crucibles. When filtration becomes too slow (usually after two uses), the crucibles must be discarded.

Table VII-2. Analysis of RX-12 materials.

Sample	% tungsten	% HMX	% Viton	Method	
RX-12-AA (J. O. 2606)	95.46	2.69	1.85	Filtration	(1)
	95.48	2.78	1.74	"	
	<u>95.55</u>	<u>2.49</u>	<u>1.96</u>	"	
	Average 95.50	2.65	1.85		
	95.58	2.70	1.72	Centrifugation	(2)
	<u>95.37</u>	<u>2.98</u>	<u>1.65</u>	"	
	Average 95.48	2.84	1.69		
RX-12 (6K-42-2)	94.79	2.87	2.34	Filtration	(1)
	94.99	3.00	2.01	"	
	95.11	2.83	2.06		
	<u>95.07</u>	<u>2.74</u>	<u>2.19</u>		
Average	94.99	2.86	2.15		

References

- ¹S. Semel, M. A. Laccetti, and M. Roth, Anal. Chem. 31, 1050 (1959).
- ²J. T. Rogers, "Physical and Chemical Properties of RDX and HMX," Aug. 1962, Holston Defense Corp., Control No. 20-P-26, Series B.
- ³M. A. Laccetti, S. Semel, and M. Roth, Anal. Chem. 31, 1049 (1959).

Fig. VII-1. Absorption spectrum of ferrous nitrosyl complex of HMX, Lot A-222.

Fig. VII-2. Calibration curve for ferrous nitrosyl complex of HMX, Lot A-222 at 520 mμ.

VIII. THE ANALYSIS OF MOCK EXPLOSIVE 90010*

Abstract

An analysis of mock explosive 90010, consisting of barium nitrate, pentaerythritol, nitrocellulose, and tris- β -chloroethylphosphate (CEF) is presented. The CEF is extracted with methylene chloride or ethyl ether. Barium nitrate and pentaerythritol are extracted with water, and the barium nitrate is determined by EDTA titration. The residue, nitrocellulose, is qualitatively identified.

Introduction

Mock explosive 90010 is an inert material simulating the physical properties of PBX 9404. Its nominal composition is:

Barium nitrate	46 $\pm$ 1.0%
Pentaerythritol	48 $\pm$ 1.0%
Tris- β -chloroethylphosphate (CEF)	3.2 $\pm$ 0.3%
Nitrocellulose	2.8 $\pm$ 0.3%
Red dye	0.05%

This note presents a method for the analysis of 90010 by a combination of solvent extraction and titration methods. In addition, the nitrocellulose is characterized by a spot test.

Experimental

Reagents and Equipment

Analytical balance.

pH meter.

Machlett buret, 25 ml.

Magnetic stirrer and stirring bars.

Vacuum filtration equipment (Fisher Filtrator).

Sintered-glass crucibles, medium porosity, 50 ml capacity.

Vacuum oven, 60-70°C.

Glycerol or mineral oil bath.

Ethyl ether.

*General Chemistry Technical Note No. 133, dated October 29, 1963.

Methylene chloride.

Sulfanilic acid reagent: 1 g per 75 ml water and 25 ml glacial acetic acid.

1-naphthylamine reagent: 0.3 g per 70 ml water and 30 ml glacial acetic acid.

Ethylenediaminetetraacetic acid (EDTA), 0.05 M: Dissolve 18.61 g disodium ethylenediaminetetraacetate dihydrate in water and dilute to 1 liter in a volumetric flask.

Benzoin.

Sodium hydroxide, 6 M, freshly prepared.

METAB Indicator Tablets, Fisher Scientific Co.

Standardization of EDTA Solution¹

Weigh accurately 120 to 250 mg barium nitrate into a 250 ml beaker or use an aliquot of a standard barium nitrate solution. Dissolve and dilute to about 100 ml with distilled water. Adjust to pH 12 (using pH meter) with 6 M sodium hydroxide. Add one METAB tablet and dissolve. Titrate with EDTA until the color changes from blue to colorless. The titration is best performed without artificial light.

$$\text{Normality of EDTA} = \frac{\text{mg barium nitrate}}{(261.38)(\text{ml EDTA})}$$

Procedure

Weigh approximately 1 g of material accurately into a tared 100 ml beaker containing a glass stirring rod. Add 20 ml methylene chloride or ethyl ether, cover with a watch glass, and bring to boil on a hot plate at low heat. Remove from heat, macerate any lumps, and let cool to room temperature. Filter by suction through a tared 50 ml, medium-porosity, glass crucible. Wash beaker and crucible with four 5 ml portions of solvent. Dry in a vacuum oven at 60-70°C for one hour. Cool to room temperature and weigh.

Transfer most of the residue quantitatively into the previously used beaker, add 25 ml distilled water, and bring to boil on a hot plate. Filter through the previously used crucible collecting the filtrate quantitatively in a 100 ml volumetric flask. Wash beaker and crucible with several portions of hot water and collect the washings. Dry beaker and crucible in a vacuum oven at 60-70°C for one hour. Cool to room temperature and weigh.

Cool the filtrate in the volumetric flask to room temperature, dilute to 100 ml with water, and mix. Transfer an aliquot of 25 ml into a 250 ml beaker and do the EDTA titration as described for the standardization of EDTA.

Perform a qualitative test for nitrocellulose on the residue as follows²: Place a pinch of the sample (several mg) into a 3-inch test tube and add about 100 mg benzoin. Immerse the test tube in an oil bath preheated to 140°C. Cover the mouth of the test tube with filter paper moistened with Griess reagent, prepared by mixing equal volumes of the sulfanilic acid reagent and the 1-naphthylamine reagent. A positive test for nitrous acid is shown by the appearance of a red area on the filter paper.

Calculations

1. Weight loss after ether (or methylene chloride) extraction = amount of CEF.
2. Residue after water extraction = amount of nitrocellulose + red dye.
3. (ml EDTA)(normality EDTA)(1045.52)* = amount of barium nitrate.
4. By difference = amount of pentaerythritol.

Results and Discussion

CEF may be extracted with methylene dichloride or ethyl ether (the former is less hazardous). Pentaerythritol and barium nitrate are extracted with water. The barium nitrate is titrated with standard EDTA solution at a pH of 12. The 6 M NaOH used to adjust the pH to 12 must be free of CO₂ otherwise BaCO₃ precipitates. For standardization of the EDTA solution barium nitrate is recommended. No interference is caused by the pentaerythritol which is determined by difference.

The residue from the water extraction is nitrocellulose and a small amount of red dye. The presence of the nitrate group is verified by fusion with benzoin and detection of evolved nitrous acid by the Griess reaction.² A red color in an acetic acid solution of sulfanilic acid and 1-naphthylamine constitutes a positive test. The crucibles are cleaned for re-use with hot nitric acid which destroys the red dye. Since only approximately 0.5 mg of red dye is present in the nitrocellulose residue, no correction is necessary.

* 1045.52 = (261.38)(4), where 261.38 is the molecular weight of Ba(NO₃)₂.

Some typical results are shown in the following table.

Analysis of mock explosive 90010, sample A-192.

% CEF	% nitrocellulose	% Ba(NO ₃) ₂	% pentaerythritol (by difference)
3.30	2.72	46.23	47.75
3.29	2.68	46.44	47.58
3.33	2.73	46.37	47.57
3.25		46.10	
3.30		46.34	
3.34		46.22	
		46.26	
Average			
3.30	2.71	46.28	47.63

Acknowledgment

I am indebted to Charles H. Otto and Frederick B. Stephens for help with the EDTA titration of barium nitrate.

References

- ¹F. J. Welcher, The Analytical Uses of Ethylenediamine Tetraacetic Acid (D. Van Nostrand Co., Princeton, N. J., 1961), pp. 143-4.
- ²F. Feigl, Chemist-Analyst 52, 47 (1963).

IX. THE ANALYSIS OF A MOCK MATERIAL FOR LX-04-1*

Abstract

An analysis of a mock material for LX-04-1 consisting of cyanuric acid, barium nitrate, and Viton is presented. Barium nitrate and cyanuric acid are extracted with water, leaving a residue of Viton. Barium nitrate is converted to the sulfate and determined as such; cyanuric acid is determined by difference.

Introduction

This note presents a method for the analysis of a mock material for LX-04-1 having a nominal composition of:

Viton	15%
Cyanuric acid	72%
Barium nitrate	13%

Experimental

Reagents and Equipment

Analytical balance.

Vacuum filtration equipment (Fisher Filtrator).

Vacuum oven, 60-70°C.

Drying oven, 110°C.

Sintered-glass crucibles, medium porosity, 50 ml capacity.

Sulfuric acid, 1:10.

Procedure

Weigh approximately 1 g of material accurately into a 100 ml beaker. Add 50 ml hot distilled water, cover with a watch glass, and bring to gentle boiling on a hot plate. Remove the beaker periodically from the hot plate and macerate the material with a glass stirring rod flattened out at one end into a disc of approximately 5 mm diameter. Add distilled water to keep the volume at about 50 ml. The extraction is complete when no more white particles are imbedded in the Viton. This requires at least 2 hours.

*General Chemistry Technical Note No. 137, dated December 2, 1963.

Filter the hot solution by suction through a tared 50 ml medium-porosity sintered-glass crucible, collecting the filtrate quantitatively in a 250 ml beaker. Rinse beaker and crucible with enough hot water so that only the Viton residue remains. (Cyanuric acid may precipitate in the beaker or funnel on cooling.) After filtration rinse the bottom of the crucible and the funnel with hot water, collecting all the washings in the 250 ml beaker. Dry the crucible in a vacuum oven at 60-70°C for one hour, cool to room temperature, and weigh.

Heat the filtrate to near boiling on a hot plate, add 10 ml 1:10 sulfuric acid, and keep near boiling for at least 15 minutes. Filter through a tared medium-porosity glass crucible and wash beaker and crucible thoroughly with hot water. Dry the crucible in an oven at 110°C for one hour, cool to room temperature, and weigh.

Calculations

1. Residue after water extraction	= amount of Viton
2. (Barium sulfate)(1.11974)	= amount of barium nitrate
3. By difference	= amount of cyanuric acid

Results and Discussion

The extraction of cyanuric acid and barium nitrate by water from the matrix of Viton requires repeated maceration and boiling. The extraction is complete when inspection reveals no more white material imbedded in the red-dyed Viton. For a 1 g sample a minimum extraction time of 2 hours is required with macerations at 15-minute intervals. The filtration must be done while the solution is hot since cyanuric acid is only sparingly soluble in cold water (0.25 g per 100 ml water at 17°C).

Barium nitrate could not be determined in the presence of cyanuric acid by EDTA titration at pH 10 as in 90010 (see Section VIII). During adjustment of the pH by means of sodium hydroxide a white precipitate appeared at a pH of about 7-8.

Cyanuric acid could not be determined by titration with standard base in the presence of barium nitrate. Again a white precipitate (probably barium cyanurate) formed at a pH of about 7-8 which interfered with the titration.

Preliminary experiments indicated that barium ion could be quantitatively removed from mixtures with cyanuric acid as the sulfate and determined gravimetrically. This procedure was adopted. Cyanuric acid is determined by difference.

Some typical results are shown in Table IX-1.

Table IX-1. Results of analyses of mock materials for LX-04-1.

Sample	% Viton	% Ba(NO ₃) ₂	% cyanuric acid
RM-04-BA	15.27	13.07	71.75
	15.30	12.92	71.68
	15.14	13.06	71.77
	15.12		
	15.14		
	15.18		
	15.26		
	15.31		
Average	15.22	13.02	71.73
RM-04-BB	15.09	12.41	72.38
	15.00	12.73	72.03
	15.13	12.46	72.27
	15.21		
	15.24		
	15.27		
Average	15.16	12.53	72.23
RM-04-BC	15.66	13.27	71.07
	15.46	13.10	71.44
	15.62	12.78	71.60
	15.53	12.89	71.58
	15.87	13.26	70.87
	15.70	12.84	71.46
Average	15.64	13.02	71.46

X. THE DETERMINATION OF CYANURIC ACID, MELAMINE, AND VITON IN MIXTURES (LM-04-0)*

Abstract

A method is described for the analysis of LM-04-0. Melamine and cyanuric acid are determined as the melamine cyanurate. Viton is determined by nitric acid extraction. The presence of melamine cyanurate in pressed pellets may be ascertained from x-ray powder patterns.

Introduction

A procedure was required for the determination of the components of LM-04-0: cyanuric acid, melamine, and Viton. This work describes a gravimetric method for the determination of melamine and cyanuric acid by formation of melamine cyanurate. Viton is then determined by nitric acid extraction.¹

The approximate composition of the mixtures for analysis is

Cyanuric acid	60%
Melamine	23%
Viton	17%

Prior to this work only the analysis of Viton was required. Although Viton can be determined by a micromethod using the Schöniger combustion technique,² by using a larger sample, errors due to segregation of the material may be minimized. For this reason, Viton was determined by nitric acid extraction.

Experimental

Materials and Equipment

Nitric acid, reagent grade, sp. gr. 1.42.

Beakers, 150 ml, with stirring rods.

Sintered-glass crucibles, 35 ml capacity, medium porosity.

Analytical balance.

Steam bath or hot plate.

Vacuum oven, maintained at 60-70°C.

*General Chemistry Technical Note No. 67, dated March 6, 1962.

Vacuum oven, maintained at room temperature.

Suction filtration equipment.

Platinum-tipped tongs.

Procedure

Weigh 0.5 to 1 g of material into a tared 150 ml beaker containing a stirring rod. Add 50 ml distilled water, cover with a watch glass, and bring to boiling on a hot plate. Break up any lumps with the stirring rod, stir occasionally, and wash the sides of the beaker down occasionally with water. Digest for about 15 minutes, taking care not to lose any material.

Filter by suction through a tared 35 ml medium-porosity, sintered-glass crucible. Wash beaker, stirring rod, and filter crucible with several portions of distilled water. Discard the filtrate.* Dry the beaker plus stirring rod, and the filter crucible in a vacuum oven at 60-70°C for at least one hour. Cool to room temperature and weigh.

Place the crucible inside the beaker. Introduce about 15 ml concentrated nitric acid into the beaker, and a like amount into the crucible, rinsing down the sides of both. Put the beaker on a hot plate and boil until only the Viton is left in the crucible. Stir the contents of the crucible occasionally to facilitate solution.

Remove the crucible from the beaker by means of platinum-tipped tongs, and place in the suction apparatus. Filter, pouring the contents of the beaker into the crucible. Rinse beaker and crucible with several portions of concentrated nitric acid, then thoroughly with distilled water to remove all the acid. Dry beaker, stirring rod, and filter crucible in a vacuum oven at 60-70°C for at least one hour. Cool to room temperature and weigh.

All operations with concentrated nitric acid are to be carried out in a hood, with proper precautions.

Calculations

1. Residue after water extraction	= amount of Viton + melamine cyanurate
2. Residue after nitric acid extraction	= amount of Viton
3. By difference	= amount of melamine cyanurate
4. (Melamine cyanurate)(0.49422)	= amount of melamine
5. Sample - (Viton + melamine)	= amount of cyanuric acid

*If desired, the aqueous filtrate may be collected and titrated with standard base to the phenolphthalein endpoint.

If a titration is carried out on the water extract, the amount of free cyanuric acid is

$$\text{mg cyanuric acid} = (\text{normality base})(\text{ml titration})(129.08).$$

Results and Discussion

Melamine and cyanuric acid are moderately soluble in hot water. They form, however, a very insoluble salt, melamine cyanurate, in which the components are present in a 1:1 ratio.³ This compound precipitates as a very fine powder when aqueous solutions of the components are mixed. An elemental analysis of melamine cyanurate, $\text{C}_6\text{O}_3\text{H}_9\text{N}_9$, is given in Table X-1. Its melting point is near 390°C . X-ray diffraction patterns and infrared spectra of the complex and its components are shown in Figs. X-1, X-2, X-3, and X-4.

Table X-1. Elemental analysis of melamine cyanurate.

Element	Theoretical	Found
% carbon	28.24	27.69
% nitrogen	49.40	49.32
% hydrogen	3.55	3.45

The materials investigated have a large excess of cyanuric acid hence all the melamine is converted to the cyanurate by digestion in water. The excess cyanuric acid is removed by filtration. From the weights of the dry salt the amount of melamine in the original mixture is

$$\text{mg melamine} = (\text{mg melamine cyanurate})(0.49422).$$

The factor 0.49422 is derived as follows: In melamine cyanurate the ratio

$$\frac{\text{cyanuric acid}}{\text{melamine}} = \frac{129.08}{126.13} = 1.023389$$

Let x = mg melamine, then

$$\text{mg melamine cyanurate} = x + 1.023389x = 2.023389x$$

and

$$\text{mg melamine} = \frac{\text{mg melamine cyanurate}}{2.023389} = (\text{mg melamine cyanurate})(0.49422).$$

If desired, the excess cyanuric acid can be collected and titrated with standard sodium hydroxide to the phenolphthalein endpoint. As seen from Table X-4, this step is not necessary; satisfactory results are obtained when determining the cyanuric acid by difference.

Tables X-2, X-3, and X-4 show results obtained with known samples, prepared by mixing the dry ingredients. In samples of LM-04-0, melamine and cyanuric acid are blended with a solution of Viton in methylethyl ketone, methylisobutyl ketone, n-butyl acetate, or a similar solvent. The solvent is then removed by application of heat and vacuum. Due to this processing the analysis of LM-04-0 is more difficult than that of the known mixtures; some melamine and/or cyanuric acid may be encapsulated by the Viton. Also, the material is not of uniform particle size, and may therefore show segregation.

The results for some LM-04-0 samples are given in Table X-5.

As Table X-6 shows, when the analysis of Viton only is required, the nitric acid extraction method is preferable. If, however, the analysis of melamine and cyanuric acid is also required, the procedure given here is recommended. Alternatively, a check on the Viton analysis may be performed on a separate sample. The presence of melamine cyanurate in pressed pellets may be ascertained from x-ray powder patterns, or from the infrared spectrum of the solid in KBr. Absorption peaks found in the cyanurate, but not in melamine or cyanuric acid, occur at the following wavelengths: 3.74, 3.95, 9.23, 10.85, and 13.03 microns.

References

¹L. Monteith, G. Crossman, G. Lopez, Lawrence Radiation Laboratory (Livermore) Internal Document GCTN-49 (March 10, 1961).

²W. Selig and D. M. Colman, UCRL-6639 (April 30, 1961), p. 29.

³E. M. Smolin and L. Rapoport, s-Triazines and Derivatives (Interscience Publishers, N. Y., 1959), p. 326.

Table X-2. Recovery of Viton from LM-04-0.

Sample No.	mg taken	mg recovered	% recovery
1	91.5	91.3	99.8
2	102.8	102.5	99.7
3	98.3	97.9	99.6
4	109.8	109.6	99.8
5	87.7	88.1	100.5
6	127.5	127.7	100.2
7	125.2	124.6	99.5
8	196.2	196.0	99.9
9	259.5	259.5	100.0
10	245.3	245.5	100.1
Average % recovery		99.91	
95% confidence limits $\pm$		0.21	

Table X-3. Recovery of melamine from LM-04-0.

Sample No.	mg taken	mg recovered	% recovery
1	86.7	86.6	99.9
2	92.0	92.2	100.2
3	93.3	93.5	100.2
4	101.4	101.8	100.4
5	106.8	107.1	100.3
6	96.3	96.3	100.0
7	125.2	125.7	100.4
8	163.1	163.2	100.1
9	198.0	199.0	100.5
10	208.1	209.9	100.4
Average % recovery		100.24	
95% confidence limits $\pm$		0.14	

Table X-4. Recovery of cyanuric acid from LM-04-0, by difference.

Sample No.	mg taken	mg recovered	% recovery
1	207.6	207.9	100.1
2	215.7	215.8	100.1
3	215.4	215.6	100.1
4	208.8	208.6	99.9
5	220.0	219.3	99.7
6	199.6	199.4	99.9
7	255.3	255.4	100.0
8	313.1	313.2	100.0
9	460.4	459.4	99.8
10	610.1	609.1	99.8
Average % recovery		99.94	
95% confidence limits $\pm$		0.10	

Table X-5. Analysis of some LM-04-0 samples.

Sample	Viton HNO ₃ extraction	New method	% melamine	% cyanuric acid
HE 101, No. 1	14.98 15.06	15.42 15.56 15.54 15.39	24.22 24.27 24.30 24.50	60.35 60.17 60.16 60.11
Average	15.02	15.48	24.32	60.20
Avg. Deviation	0.06	0.07	0.09	0.08
HE 101, No. 2	17.20 17.18	17.11 17.11	23.54 23.43	59.35 59.46
Average	17.19	17.11	23.49	59.41
Avg. Deviation	0.01	0	0.06	0.06
HE 115	16.53 16.48 16.54 16.49	16.45 16.36 16.61 16.40	23.81 23.91 23.56 23.74	59.74 59.72 59.83 59.87
Average	16.51	16.46	23.76	59.79
Avg. Deviation	0.03	0.08	0.11	0.06

Table X-6. Recovery of Viton from known mixtures by nitric acid extraction.

mg taken	mg recovered	% recovery
227.5	226.4	99.5
196.4	195.4	99.5

MELAMINE CYANURATE

CYANURIC ACID

GLB-646-3108

MELAMINE

Fig. X-1. X-ray powder patterns of melamine, cyanuric acid, and melamine cyanurate.

Fig. X-2. Infrared spectrum of cyanuric acid.

Fig. X-3 Infrared spectrum of melamine

Fig X-4. Infrared spectrum of melamine cyanurate.