A LIQUID CHROMATOGRAPHIC - SPECTROPHOTOMETRIC
ASSAY FOR TATB IN TATB

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QUALITY DIVISION

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Process Development
Endeavor No. 106

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SUMMARY

A liquid chromatographic technique is used for determining the purity of weapons-grade TATB. A blended sample of TATB is dissolved in dimethylsulfoxide (DMSO), and an aliquot of the solution is injected onto a 2-meter Corasil II column. The carrier is DMSO at a 2 ml/min flow rate. The amount of TATB is directly proportional to the peak height, as measured by a spectrophotometer at 350 nm. Any impurity which absorbs at 350 nm and is eluted with the TATB would interfere with the assay.

INTRODUCTION

Due to the wide range of uses of TATB, a large amount of effort has been expended in chemical characterization of the TATB and the intermediary products of its manufacture. A critical assay for any HE qualification is the purity of the explosive itself - in this case, the percent TATB in the TATB. Until this time, no direct assay for the TATB itself or its major organic impurities existed. A major difficulty was the relative insolubility of the TATB in known solvents(1). Also, the TATB synthesis processes could produce a variety of impurities from batch-to-batch.

It was known, however, that TATB has a limited solubility in DMSO (~ 10 mg/100 ml). Therefore, a liquid chromatographic technique for TATB assay was developed based on this solubility.

EXPERIMENTAL

Equipment

All liquid chromatographic assays and separations were performed using a Perkin-Elmer Model 601 chromatograph. A 2-meter Corasil II column was used, and the carrier was DMSO at 2 ml/min. Sample detection was made by a Coleman Model 55 digital spectrophotometer at 350 nm.

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Standard Preparation

A representative sample of TATB was washed twice with copious quantities of H₂O and DMSO, in order to remove both inorganic and organic impurities. Later tests showed no chlorine impurities in the washed product, and the TATB was assumed to be pure. Another source of "pure" TATB was material recrystallized from biphenyl(2). Chromatographic scans of the two standards were identical.

Sample Preparation

Because of the extremely small sample size, great care must be exercised in sampling procedures. The TATB powder is blended and then sampled with a "thief." A 10 mg sample (± 0.01 mg) is weighed into a 125 ml erlenmeyer, and 100 ml DMSO are pipetted into the flask.

The mixture is warmed gently on a steam bath until the TATB goes into solution and then is cooled to room temperature prior to analysis.

DISCUSSION

Preparation of Standards Curve

Two stock solutions (10 mg/100 ml and 20 mg/100 ml) of TATB in DMSO were prepared, from which dilutions were taken. Two of the concentrations purposely overlap, in order to check the accuracy of the weighing procedure. A sample calibration curve is given in Fig. 1. The absorbance of TATB at 350 nm is linear over the concentration range studied. The nearly identical peak heights for the duplicate stock solutions shows acceptable accuracy and care in weighing procedures.

Fig. 1. Calibration for TATB.

Separation of Impurities

It is well known that the TATB synthesis processes cause a variety of impurities to appear in the final batch. Thin layer chromatography by Yasuda and Fritz at LASL(3,4) has shown the presence of about 17 impurities. It was therefore deemed desirable, if possible, to separate the TATB peak from the impurity peaks. In order to concentrate the impurities with respect to TATB, sample 088 (containing a large percent of DMSO solubles) was extracted with DMSO and the extract injected into the LC. Using a 100% DMSO carrier, all peaks are eluted at the solvent front. However, at a 35 to 65 DMSO-CCl₄ ratio, complete separation of the organic impurities appears to be accomplished (Fig. 2). However, due to low solubility of

TATB in the carrier, the TATB peak disappears. Any solvent combination powerful enough to elute the TATB will also bring the impurities at the solvent front. If, however, the major impurities in TATB have low molar extinction coefficients with respect to TATB, the analysis can still be performed. Based on previous experience(5), it is to be assumed that the major inorganic impurity in TATB is NH₄Cl and the main organic impurity is triamino-dinitromonochlorobenzene. Determination of the molar coefficients of extinction for these materials is given in Table I. As can be seen, the major impurities have very little absorbance in the region of interest. Any impurity which has a relatively large absorption at 350 nm will obviously interfere with the analysis.

Fig. 2. Chromatographic Separation of Organic Impurities in TATB (Concentration)

Table I. Extinction Coefficients
of TATB Related Materials

Sample	Extinction Coefficient (350 nm)
TATB	2.58×10^4
NH_4Cl	0

7.25

Analysis of Samples

Six representative samples of TATB were then selected for analysis. Table II shows the auxiliary analyses for these samples. As can be seen, the sample group encompasses a wide range of impurities, as measured by other analysis techniques. These samples were injected into the chromatograph and resultant peak heights compared with a standards curve (Table III). In order to estimate accuracy, all inorganic Cl₁₀ was calculated as NH_4Cl and organic Cl₁₀ (total-inorganic) was calculated as the monochloro species. When the TATB results are added to those of the impurities, closure is well within $\pm 1\%$, with the exception of sample 088. This sample had the largest amount of DMSO solubles, and it is possible that another impurity exists in this sample which has not been detected as yet. The precision of these six assays is calculated by an analysis of variance. Three operators performed the assays. The individual values are given in Table IV, and statistical values in Table V. The relative standard deviation of measuring TATB is thus shown to be about 0.6%.

Accuracy was also checked by spiking standard TATB with known quantities

of the major impurities. A 90-10 TATB- NH_4Cl mixture was prepared and assayed by this technique. No bias was observed. Next, a 90 - 10 mixture of TATB and the monochloro species was prepared and assayed. The results for TATB showed a positive bias of 1% over the weighed amount.

CONCLUSION

A liquid chromatographic-spectrophotometric technique has been employed for the assay of TATB for TATB. Because of small sample size, extreme caution must be used during sampling procedures. Analysis results are accurate to within $\pm 1\%$, but should be coupled with impurity chloride and chlorine analysis to assure that no impurity interference is present.

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Table II. TATB Chem Lab Analyses

Sample	Total Cl (%)	Inorganic Cl (%)	DMSO Solubles (%)
12-02-76-0812-080	0.63	0.45	1.43
12-02-76-0813-081	0.44	0.45	0.02
12-02-76-0815-088	0.62	0.45	1.61
12-03-76-0727-092	0.59	0.45	0.39
12-02-76-0815-094	0.44	0.45	0.12
12-02-76-0804-099	0.47	0.45	0.14

Table III. Assay of TATB

Sample	TATB (%)	NH Cl (%)	Percent Organic Impurities	Closure
12-02-76-0812-080	98.75	0.68	1.26	100.69
12-02-76-0813-081	99.17	0.68	0	99.85
12-02-76-0815-088	93.33	0.68	1.19	95.99
12-02-76-0727-092	98.58	0.68	0.98	100.24
12-02-76-0815-094	98.75	0.68	0	99.43
12-02-76-0804-099	98.73	0.68	0	99.41

Table IV. Individual Assays of TATB

Samples	Operator 1	Operator 2	Operator 3
080	98.33	98.75	98.75, 98.80
081	-	99.17	93.67, 99.56
088	93.33	93.33	92.93, 93.46
092	97.58	98.14	99.58, 99.75
094	97.83	98.63	98.75, 98.89
099	-	98.72	98.73, 98.75

Table V. Analysis of Variance

Source of Variation	Sums of Squares	Degrees of Freedom	Mean Squares
Rows	98.98941	5	19.79788
Error	4.80905	16	0.30056
Total	103.79847	21	

$$Se = 0.30056 = 0.55\%$$