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## IMPROVED SPECTROPHOTOMETRIC ANALYSIS OF BARIUM STYPHATE\*

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### ABSTRACT

A spectrophotometric procedure to determine the purity of barium styphnate monohydrate based upon the absorbance of the styphnate ion at 326 and 413.3 nm has been developed. The purity is determined by comparing the absorbance of the styphnate ion in barium styphnate and in styphnic acid. Our investigation has shown that the molar absorptivity and  $\lambda$  maxima of the styphnate ion are quite pH dependent; therefore, the pH is buffered to 6.8 - 7.0 with ammonium acetate. Under these conditions the molar absorptivity is  $1.6 \times 10^4$  L/mol-cm. Analyses following the procedure in the Navy specification WS13444A using water were found to give low molar absorptivities ( $1.3 \times 10^4$  L/mol-cm) for the styphnic acid calibration resulting in erroneous values for barium styphnate purity.

### INTRODUCTION

Barium styphnate monohydrate is being developed and characterized for use in explosive components as an igniter material. During this investigation, analyses were performed to determine the purity of barium styphnate and styphnic acid according to the procedures in the Navy specification (ref.1) for barium styphnate monohydrate, WS-13444A, and purity values of ~120% were obtained. Subsequent investigations showed significant shifts in the absorbance spectra for pH < 6 and that the ultraviolet/visible spectrophotometric analytical procedures do not require control of pH when the molar absorptivity of the styphnate ion is determined using styphnic acid as the standard. We found that the molar absorptivity of styphnic acid in slightly acid solutions is lower than in neutral or basic solutions; hence the purity of barium styphnate erroneously exceeds 100% when the purity is calculated.

We have developed an alternate ultraviolet-visible spectrophotometric procedure which uses a 10% ammonium acetate buffer solution (pH = 6.8) for both the styphnic acid calibration and the barium styphnate analysis. The solution

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controls the pH at 6.8 which insures that the styphnic acid (ref.2) is completely ionized ( $pK_1 = 1.74$ ,  $pK_2 = 4.86$ ).

### Experimental

Ultraviolet/visible spectrophotometric measurements were made on a Varian Cary 219 double beam spectrophotometer which had been calibrated with NBS potassium dichromate. Spectra were recorded with water or ammonium acetate solutions in the reference beam. pH measurements were made on a Corning model 130 pH meter which had been calibrated with standard buffer solutions. Styphnic acid was obtained from Eastman Kodak and Aldrich Chemical Company, and samples were recrystallized from ethyl alcohol. All other chemicals were reagent grade or higher purity. The volumetric glassware was Class A or equivalent. Note: Barium styphnate and styphnic acid are explosives and the appropriate safety precautions must be followed when handling the materials.

### Results/Discussions

The spectra in Figure 1 and the data in Table 1 show that the visible/ultraviolet absorption spectra of styphnic acid are strongly affected by the solution pH. Curve 1 (pH = 3.2) was obtained by dissolving styphnic acid in water to determine the molar absorptivity for the styphnate ion as described in WS13444A. Curves 2-4 were obtained at pH values from 4.25 to 9.5 by adjusting the pH with sodium hydroxide and curve 5 is at pH 6.8 in 10% ammonium acetate. The spectra for pH 6.1, 6.8 and 9.5 are essentially superimposable and indicate that styphnic acid is completely disassociated at these pH values. This is in agreement with the reported ionization constants (ref.2) of  $pK_1 = 1.74$  and  $pK_2 = 4.86$ . Other values reported (ref.3) are  $pK_1 = 0.32$  and  $pK_2 = 4.29$ .

When the calibration procedure in the Navy specification, WS13444A, to determine the molar absorptivity for the styphnate ion is followed (curve 1), the solution pH is about 3.2 and the anion in solution is primarily the bystyphnate ion which has an absorption maxima at 385 nm. The spectrum (curve 2) at pH = 4.25 shows a shift in  $\lambda_{max}$  from 390 to 405 nm as the composition of the absorbing ions in solution change. Curve 3 (pH = 6.1), curve 4 (pH = 9.5) and curve 5 (pH = 6.8 in 10% ammonium acetate) are essentially identical and are due to absorption by the styphnate ion which has an absorption maxima at 413 nm. The 10% ammonium acetate solution (curve 5) offers several advantages in the determination of the molar absorptivity of styphnic acid and analyzing barium styphnate. It is a strong buffer solution with a pH where the styphnic acid is completely disassociated and it is also a better solvent for barium styphnate than water. Studies were also conducted in 10% ammonium acetate to determine if the presence of barium ions

(3.1 mol/mol) have an effect on the absorption characteristics and no effect was observed.

A series of styphnic acid samples were dissolved in 10% ammonium acetate to determine the molar absorptivity with a 10% ammonium acetate solution in the reference beam and with automatic baseline correction from 500 to 300 nm. The average molar absorptivity for 7 samples was determined to be  $1.63 \pm 0.03 \times 10^4$  L/m.cm. This is slightly higher than  $1.58 \times 10^4$  L/m.cm reported for styphnic acid and  $1.576 \pm 0.008 \times 10^4$  L/m.cm reported (ref.3) for barium styphnate dissolved in water.

Using the molar absorptivity of  $1.63 \pm 0.03 \times 10^4$  L/m.cm, a series of 6 different barium styphnate samples were analyzed for purity. The ultraviolet/visible absorption curves were recorded from 500 to 300 nm and no extraneous absorption peaks were noted. The calculated purities ranged from 98.7 to 103%.

The ratio of the molar absorptivity at 413 and 326 nm was also investigated in 10% ammonium acetate. The ratio for all samples analyzed was  $1.00 \pm 0.02$ , and the shapes of the absorption bands were comparable. A small shoulder is evident at about 300 nm in all samples analyzed.

Additional work may be necessary to determine the molar absorptivity of the styphnate ion in styphnic acid more accurately since the accuracy of the purity determination is directly related to the accuracy of the molar absorptivity. The purification of styphnic acid is best accomplished by recrystallization from organic solvents and vacuum drying to remove residual solvent. The drying step is important and must be carefully controlled to avoid decomposing the styphnic acid since discoloration at 60°C was noted after 3 hours.

TABLE 1 UV/Visible Spectra of Styphnic Acid in Solutions

Cell length = 1.00 mm, Concentration = 0.1217 g/L

	pH	Peak 1		Peak 2	
		$\lambda_{\max}$	A	$\lambda_{\max}$	A
Styphnic Acid in Water	3.20	390	0.678	336	0.523
	4.25	405	0.671	328	0.654
	6.1	413	0.773	325	0.759
	9.5	413	0.766	325	0.759
Styphnic Acid in 10% Ammonium Acetate vs. Water	6.8	413	0.758	325	0.751

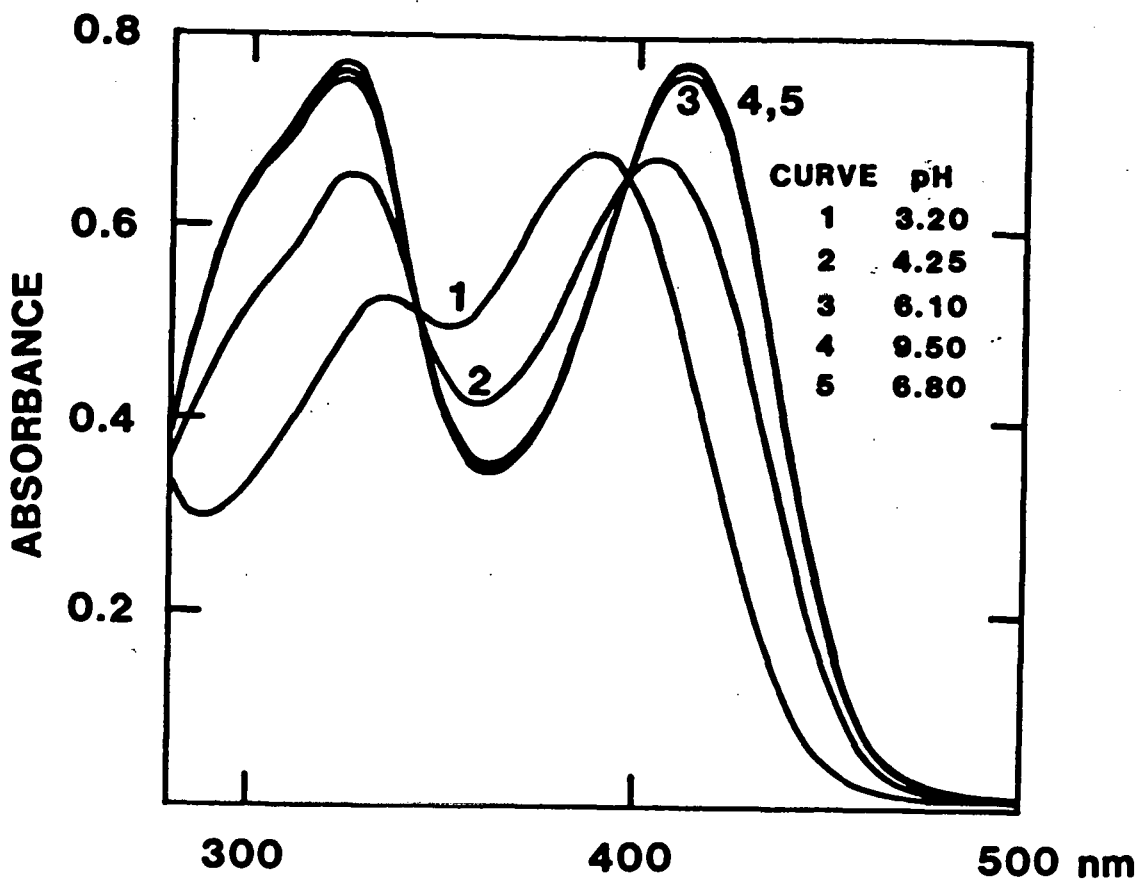


Figure 1. Absorbance of Styphnic Acid (0.1217g/L) in Solution. 1.00mm Cell Length

#### CONCLUSION

The accurate ultraviolet/visible spectrophotometric analysis of barium styphnate and the parent compound, styphnic acid, requires control of solution pH. A procedure based upon the use of a 10% ammonium acetate buffer solution has been developed which eliminates absorption band shifts due to changes in the absorbing species. The analyses of 6 samples of barium styphnate and 7 samples of styphnic acid indicate that the explosives are  $100 \pm 2\%$  pure. These analyses indicate that the barium styphnate and styphnic acid which are commercially available are of high purity and the analytical bias introduced by lack of pH control probably has not lead to the acceptance of impure explosives.

## REFERENCES

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