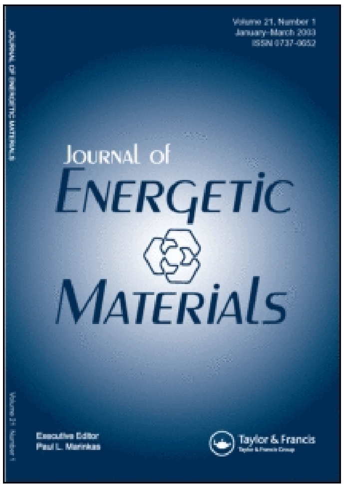

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Improved spectrophotometric analysis of barium styphnate

Norman E. Brown[a]; Jane A. Blasi[a]
[a] Sandia National Laboratories, Albuquerque, NM

To cite this Article Brown, Norman E. and Blasi, Jane A.(1985) 'Improved spectrophotometric analysis of barium styphnate', Journal of Energetic Materials, 3: 4, 311 — 318
To link to this Article: DOI: 10.1080/07370658508012344
URL: http://dx.doi.org/10.1080/07370658508012344

IMPROVED SPECTROPHOTOMETRIC ANALYSIS OF BARIUM STYPHNATE

Norman E. Brown and Jane A. Blasi
Sandia National Laboratories
Albuquerque, NM 87185

ABSTRACT

A spectrophotometric procedure to determine the purity of barium styphnate monohydrate based upon the absorbance of the styphnate ion at 326 and 413 nm has been developed. The purity is determined by comparing the absorbance of the styphnate ion in barium styphnate and styphnic acid at pH 6.8. Our investigation has shown that the molar absorptivities and maxima of the aqueous solution of styphnic acid are quite pH dependent; therefore, the pH is buffered to 6.8-7.0 with ammonium acetate. Under these conditions the molar absorptivity is $(1.63\pm0.03)\times10^4$ l/mole cm. Analyses following the procedure in the Navy specification WS13444A using water were found to give low molar absorptivities (1.3×10^4 l/mole cm) for the styphnic acid calibration resulting in erroneous values for barium styphnate purity.

Journal of Energetic Materials vol. 3, 311-318 (1985)

Published in 1985 by Dowden, Brodman & Devine, Inc.

INTRODUCTION

Barium styphnate monohydrate is being developed for use in explosive components as an igniter material. A parallel effort exists between the explosive component engineers to develop the component and materials personnel to chemically and physically characterize the barium styphnate. During this investigation, analyses were performed to determine the purity of barium styphnate and styphnic acid according to the procedures in the Navy specification[1] for barium styphnate monohydrate, WS13444A, 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 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 buffer solution controls the pH of the sample at 6.8 which ensures that the styphnic acid[2] is essentially completely ionized ($pK_1 = 1.74$, $pK_2 = 4.86$) to form the styphnate ion.

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. The 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 Fig. 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 essentially dissociated to form styphnate ion at these pH values. This is in agreement with the reported ionization constants[2] of pK_1 = 1.74 and pK_2 = 4.86. Other values reported[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 bistyphnate ion which has absorption maxima at 390 and 336 nm. The spectrum (curve 2) at pH = 4.25 shows a shift in λ_{max} from 390 to 405 nm and 336 to 328 nm as the composition of the absorbing ions in solution changes. 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 absorption maxima at 413 and 325 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 buffer solution with a pH where the styphnic acid is essentially completely dissociated to form styphnate ion, 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 mole Ba^{2+}/mole styphnate ion) has 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 $(1.63\pm0.03)\times10^4$ l/mole cm. This is slightly higher than 1.58×10^4 l/mole cm reported for styphnic acid and $(1.576\pm0.008)\times10^4$ l/mole cm reported[3] for barium styphnate dissolved in water.

Using the molar absorptivity of $(1.63\pm0.03)\times10^4$ l/mole 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±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 was noted after 3 hours at 60°C.

TABLE 1. UV/Visible Spectra of Styphnic Acid in Solutions (cell length = 1.00 mm, concentration = 0.1217g/l)

		Peak 1		Peak 2	
	pH	λ_{max}	A	λ_{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

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 ensures that quantitative measurements are made on the styphnate ion at a controlled pH of 6.8. The analyses of 6 samples of barium styphnate and 7 samples of styphnic acid indicate that the explosives are 100±2% pure. These results 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 led to the acceptance of impure explosives.

ACKNOWLEDGMENT

This work was performed at Sandia National Laboratories supported by the U. S. Department of Energy under Contract Number DE-AC04-76DP00789.

REFERENCES

1. Material Specification for Styphnate Monohydrate, WS13441A, dated Sep. 8, 1970, U. S. Naval Ordnance Laboratory, White Oak, Silver Springs, MD 20910.

2. P. J. Pierce and R. J. J. Simkins, Can. J. Chem 46, 241 (1968).

3. D. J. Glover, "Analysis of Lead Azide and Lead Styphnate in Mixtures of Both," NSWC/WOL/TR 76-118.

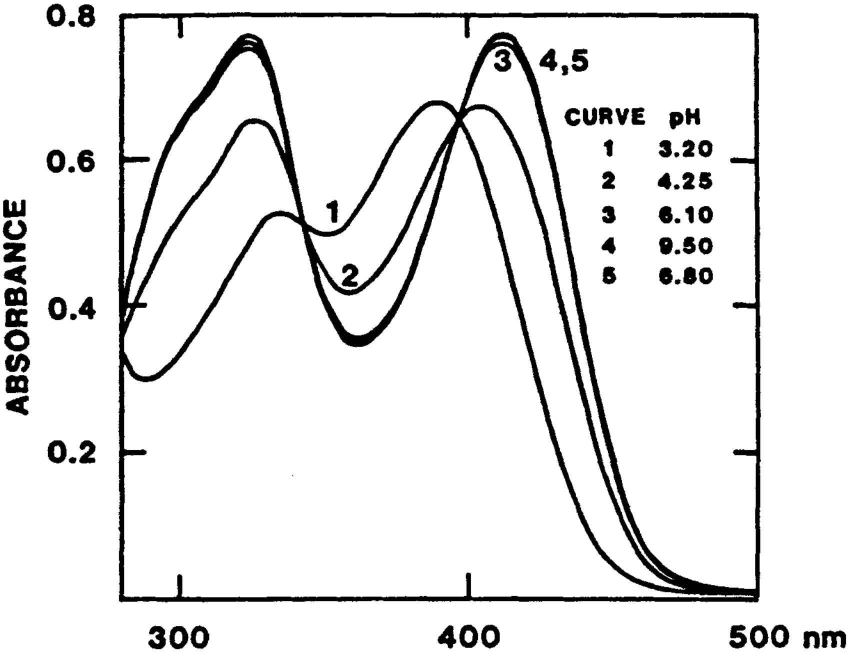

FIGURE 1.

Figure 1. Absorbance of styphnic acid (0.1217 g/l) in solution. 1.00 mm cell length.