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**DETERMINATION OF BORIC ACID IN ADMIXTURE
WITH CYANURIC ACID**

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**DETERMINATION OF BORIC ACID IN ADMIXTURE
WITH CYANURIC ACID**

by

Raymond N. Rogers

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ABSTRACT

Boric acid can be separated from cyanuric acid by methanol vapor distillation. Procedures for the separation and for a coulometric titration of the boric acid are described. Consistent recoveries of greater than 99.7% with a standard deviation of $\pm 0.21\%$ are obtained.

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I. INTRODUCTION

For more than ten years a simple, accurate, and precise method has been sought for the analysis of plastic-bonded atom-match mock explosives containing both boric acid and cyanuric acid. Although the mixture might appear simple to analyze, to date only one successful method has been found for determination of the boric acid fraction. The method reported has been used successfully by several different operators over a period of nine years.

II. UNSUCCESSFUL ANALYTICAL PROCEDURES

Several specific colorimetric methods for boric acid or borate ion were found in the literature;¹⁻⁴ however, all were extremely sensitive, leading to increased sampling error, and were quite inaccurate.

The flame photometric method, reported by Dean,⁵ appeared to be less sensitive, but proved to be only slightly more accurate than the microcolorimetric methods. The flame method requires removal of all associated cations, and still yields a minimum error roughly four times that of volumetric methods.

The acidimetric titration of boric acid in the presence of mannitol (or other polyhydroxy alcohols) as a complexing agent was the most

accurate method found in the literature.⁶⁻⁸ Mannitol forms an extremely stable complex ion with borate ion, causing boric acid to act as a fairly strong monobasic acid.

Several methods were tried for the titration of boric acid in the presence of cyanuric acid. Titration to the cyanuric end point, followed by addition of mannitol and titration of the boric acid, did not give the required accuracy either by potentiometric or conductimetric methods. A report was later found that helps explain these results.⁹

A titration based upon the addition of excess base and back titration of the borate ion could not be accomplished with any degree of accuracy. It should also be noted that cyanuric acid is too strong for a simultaneous titration of cyanuric acid and complexed boric acid.

Several systems were tried for the extraction of boric acid or cyanuric acid from the mixture; however, the solubilities of the two materials are remarkably similar in all systems investigated except water. Water could not be used as an extraction solvent owing to the occlusion of boric acid within the plastic-coated cyanuric acid particles. Not much effort was expended on extraction systems, as simple extraction is not normally capable of extreme accuracy.

It became evident that for acceptable results the boric acid and cyanuric acid must be separated quantitatively. On first inspection it would appear that, because cyanuric acid is an organic compound as are all other secondary components (binders) of the mixtures in question,

it could be removed by oxidation or pyrolysis. In practice, however, cyanuric acid is extremely resistant to oxidation, particularly in the presence of boric acid. It also was found that the vapor pressures of boric acid and its anhydride are too high for separation of the mixture by a simple pyrolysis.

Direct oxidation in a calorimeter bomb was so difficult as to be virtually impossible for quantitative work. When the sample was pelletized with a large amount of benzoic acid, combustion appeared to be complete; however, after careful recovery of the sample from the cup and walls of the bomb, results were still high. No oxygen bomb combustion was ever complete.

Schöniger oxygen flask combustions were tried. Even with additional fuel and combustion catalysts, quantitative results were never obtained.

Carius oxidations were attempted; however, oxidation was so incomplete in several trial runs that the method was soon dropped.

Several attempts were made to oxidize the sample in a sealed Parr bomb with 90% hydrogen peroxide. No appreciable reduction in the amount of cyanuric acid was observed at reasonable temperatures.

Considerable development work was done to apply a tube furnace combustion to the oxidation of cyanuric acid. Nitric acid is formed in a tube combustion; and, as nitric acid forms a maximum boiling solution with water, it cannot be boiled away from boric acid without considerable loss of volatile B_2O_3 . Elimination of nitric acid from tube washings by

ion exchange chromatography was unsuccessful. Addition of a copper spiral to the combustion tube was partially successful; however, at temperatures sufficiently high for complete nitric acid reduction, B_2O_3 fused into the tube. A nickel tube improved the method, but the lowest standard deviation obtained was $\pm 1.56\%$.

III. DEVELOPMENT OF THE METHOD

Methyl borate distillations had been used for the separation of boric acid from complex mixtures;¹⁰ however, it was feared that cyanuric acid would depolymerize into cyanic acid and codistill. Extensive tests proved that cyanuric acid did not depolymerize at the boiling point of methanol. It was also found that boric acid, in samples free of water, can be quantitatively distilled using only absolute methanol.

By using a simple semimicro steam distillation apparatus with absolute methanol, 25 mg of boric acid could be distilled with 99.4% recovery in the first 15 ml of distillate; however, distillation should be continued to at least 25 ml for quantitative recovery of the boric acid.

Owing to the volatility of methyl borate, the distillate was collected in a 50-ml volumetric flask immersed in an ice bath and containing a mannitol solution. It was found that the presence of a very small amount of acidic impurity in the methanol did not cause an appreciable error, and its presence was ignored.

For the accurate and precise titration of boric acid in amounts dictated by the nature of the mixture and size of the distillation apparatus, a coulometric titration with a potentiometric indication of the end point was chosen. The design of the coulometric cell is shown in Fig. 1. The total volume of the large compartment is approximately 15 ml. Handling and cleaning of the cell are simplified by mounting all electrodes in a common top.

A Keithley Instruments Model 210 electrometer, operating from the glass and calomel electrodes, is used for end point detection in our apparatus. The electrometer has a recorder output, making it possible to record the progress of the titration as a function of time. The position of the end point on the chart can be located by the method of concentric arcs.¹¹

A direct coulometric titration of boric acid was found to give a precision at the 95% confidence level of $\pm 0.17\%$ on a 1.3- to 1.5-mg sample. This corresponds to an expected relative error of $\pm 0.06\%$ on mix analyses, assuming the mixtures to be 25% to 28% H_3BO_3 . However, the accuracy of the coulometric titration was found to vary markedly with the working electrode current density. By checking current efficiency with and without mannitol, and with different supporting electrolytes, the variation was found to be due, surprisingly, to the reduction of mannitol.¹² No effect of current density on current efficiency can be observed below a current density of 1.0 ma/cm^2 .

Fig. 1. Coulometric titration cell

Automatic coulometric titrations were done with an Assembly Products, Inc., "Versatrol" meter/controller, consisting of a double-adjustable-contact voltmeter operating two double-pole, double-throw relays. The voltmeter function of the controller was hooked into the recorder output of the Keithley electrometer and was used to turn the generating current off at the end point. The controller also could be used to turn the current off shortly before the end point to allow an accurate manual completion of the titration. Under fully automatic operating conditions at fairly high currents (30 ma) on approximately 1×10^{-4} equivalent samples, a 95% confidence level of $\pm 0.56\%$ was obtained. Better results were obtained at lower currents.

Routine boric acid assays are now run semi-automatically with a standard deviation of $\pm 0.1\%$. It should be noted, however, that this does not represent the accuracy and precision of the entire procedure including sampling and distillation.

IV. EXPERIMENTAL PROCEDURE

Reagents:

AR absolute methanol

Saturated sodium nitrate solution

Mannitol-sodium nitrate solution (Dissolve 68 g mannitol in 300 ml water and add 15 ml saturated sodium nitrate.)

Standard boric acid solution (Dissolve approximately 500 mg AR boric acid, accurately weighed, in one liter of boiled, distilled water.)

Apparatus:

Titration cell, as shown in Fig. 1
Distillation apparatus, as shown in Fig. 2
Suitable constant-current power supply
pH meter or electrometer for end point detection

Procedure:

1. Sampling

The sample as received should be ground and quartered. The final sample is ground as finely as possible, and a sample of sufficient size to contain 20 to 40 mg of boric acid is weighed out. The ground sample should not be sieved, as this often leads to segregation of components. The relatively large sample size is specified to minimize sampling error, which can be the major source of error in the analysis of this type of mixture.

2. Distillation

The outer tube of the apparatus shown in Fig. 2 is filled with 25 to 26 ml of absolute methanol, and a few 10-grit carborundum grains are dropped in. The sample is transferred into the inner tube, rinsed in by the smallest possible volume of methanol. The sample must be reasonably dry. The apparatus is assembled, using silicone stopcock grease on all joints.

A 7.5-ml portion of the mannitol solution is placed in a 50-ml volumetric flask, and the flask is immersed in an ice bath. A delivery

Fig. 2. Distillation apparatus

tube the length of the flask neck is inserted into the flask, and is then connected to the condenser of the apparatus.

The apparatus is heated by use of a "Glascol" heating mantle of the proper size to slip over the outer shell up to the side-arm. Distillation is continued until the outer tube of the apparatus is dry. The volume of suspension in the inner tube should remain nearly constant; an infrared heating lamp can be used, if necessary, to warm the upper joint and reduce the volume of methanol in the inner tube. The volume of distillate should be approximately 25 ml.

When distillation is complete, the distillate is warmed to redissolve any mannitol that has precipitated. Upon cooling to 20°C, the distillate is made up to volume with water and is mixed by inverting at least six times.

3. Titration

A 1-ml sample of saturated sodium nitrate is placed in the small compartment of the coulometric cell, and water is added to approximately the correct height to match the expected volume in the large compartment. The liquid level in the large compartment should be slightly above that in the small compartment during the titration. Time is allowed for complete wetting of the fritted disc. An aliquot of distillate, containing the desired amount of boric acid, is pipetted into the large cell. Immediately after the sample, 7.5 ml of mannitol-sodium nitrate solution is added to the cell, and the cell is assembled. The sample is

titrated by usual coulometric technique (generating electrode negative). The current density must not exceed 1.0 ma/cm^2 during the process.

The current output of the constant-current power supply used in the titration should be checked during a titration. If the current varies significantly with load, the current/time curve should be integrated by Simpson's Rule to give an accurate value for the total number of coulombs used.

The method of end point location and the necessity for integrating the current/time curve will depend upon the desired accuracy and precision.

The weight of boric acid in milligrams in the sample can be calculated from the following equation:

$$\text{mg} = \left[\left(\frac{It}{96.497} \right) 61.82 - B \right] D$$

where:

I = current (amps)

t = time (sec)

B = blank (see below)

D = dilution factor of aliquot

The blank, expressed as milligrams of boric acid, can be determined by running known boric acid solutions, and should remain constant for each batch of mannitol-sodium nitrate solution. Many times the blank will be found to be negligible.

V. RESULTS

Consistent recoveries of greater than 99.7% have been obtained from the distillation of AR boric acid samples. Note that no "primary standard" boric acid sample exists. A true value for the accuracy of the method as applied to mixtures would be impossible to give, as standard mixtures have not been possible to prepare with complete assurance. A reasonable value for precision can be calculated from the analytical data by the method of Youden.¹³ The standard deviation of the method, calculated from data obtained over a period of eight years with four different operators and three different types of distillation apparatus, has been found to be $\pm 0.21\%$.

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