



Technical Note

Estimation of ammonium perchlorate in HTPB based composite solid propellants using Kjeldahl method

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Abstract

Kjeldahl method has been applied to determine the percentage of ammonium perchlorate (AP) in hydroxyl terminated polybutadiene (HTPB) based composite solid propellants. It has been found that in pastes containing aluminium (Al) it is important to eliminate all the Al before starting the actual reaction (distillation). The results obtained are in the range of $\pm 0.05\%$ for pastes with and without Al whereas the range is $\pm 0.02\%$ for pure AP. End points are confirmed using pH meter.

1. Introduction

Ammonium perchlorate (AP) is a major component in HTPB based composite solid propellants. Various methods exist which can be used for the analysis of pure AP, i.e., fusion with sodium carbonate followed by argentometric determination of the chloride [1, 2], reduction with titanous chloride [3], reaction using formaldehyde [4] and liquid membrane electrode [5].

The fusion method can cause safety problems when applied to propellants. As sodium perchlorate appears as a major impurity in AP made by electrochemical process starting with commercial sodium chloride, an estimation of AP via the anion, either by fusion method or by reduction with titanous chloride, can lead to higher values unless proper corrections are made. Ion selective electrode method is subject to interferences by other ions [6].

Literature survey shows only one method applied for the estimation of AP in propellant compositions and that employs perchlorate ion-selective electrode [7]. Although it has been reported that the method is not effected by interfering ions such as ClO_3^- , Cl^- , NO_3^- , literature reveals that these ions can interfere in electrochemical

analysis [6]. Non-aqueous titrimetric method using tetrabutyl ammonium hydroxide as titrant and dimethyl sulphoxide, pyridine or dimethyl formamide as solvent has been applied for estimation of AP in pyrotechnic compositions but application of the method to propellant pastes is under investigation. This method is also subject to interfering species [8].

In this paper the Kjeldahl method for the estimation of AP in HTPB based composite propellants is reported. The method is simple, safe, accurate and not affected by the presence of sodium perchlorate.

2. Experimental

The chemicals used were 1,4-dioxane (BDH, England), 0.1 *N* sodium hydroxide (E. Merck), 1 *N* sulphuric acid (E. Merck), sodium hydroxide pellets (BDH, England), hydroxyl terminated polybutadiene (ARCO R45 HT), dioctyl phthalate (Aldrich, U.S.A), ammonium perchlorate (Kerr-McGee Chemical Corporation, U.S.A., 99.5%), aluminium powder (Aldrich, U.S.A., 99.95 + %), iron oxide (Aldrich, U.S.A), and mixed indicator (Buchi, Switzerland).

2.1. Apparatus

The titrations were carried out using Orion expandable ion analyser EA 920 pH meter. Small scale sigma blade mixer having a capacity of 1 kg was used to make propellant pastes.

2.2. Procedure

2.2.1. Analysis of AP for pastes without aluminium ($AP = 64\text{--}66\%$)

The paste is weighed (2.8 g) with an accuracy of ± 0.0002 g on a polytetrafluoroethylene (PTFE) slab. The slab with the sample is transferred to the Kjeldahl flask. 1,4-Dioxane (50 ml) is added followed by water (150 ml). The apparatus is set for distillation. The free end of the condenser is allowed to dip into a conical flask containing 1 *N* sulphuric acid (25 ml) and three drops of mixed indicator. After making sure that the apparatus is properly sealed, an aqueous solution of 40% sodium hydroxide (≈ 40 ml) is run into the Kjeldahl flask through an addition funnel. The addition is stopped when about 2 ml of sodium hydroxide is left in the funnel. The distillation is started and continued until green colour formation is no longer seen at the point where the distillate and 1 *N* sulphuric acid meet. To make sure the completion of the reaction, the distillation is normally carried out for 30–45 min. The condenser is disconnected and rinsed with a little water. The excess sulphuric acid is titrated against 0.1 *N* sodium hydroxide using a pH meter to an end point of 4.65 (± 0.02).

$$AP(\%) = \frac{11.75(N_2 V_2 - N_1 V_1)}{S}$$

where N_2 represents the normality of sulphuric acid, V_2 the volume of sulphuric acid taken, N_1 the normality of sodium hydroxide, V_1 the volume (ml) of sodium hydroxide consumed and S the weight of the sample.

2.2.2. Analysis of AP for pastes containing aluminium (AP = 64–66%, Al = 18%)

The procedure in the presence of Al is slightly different. In this case after addition of 1,4-dioxane (50 ml) and water (50 ml) all the joints are fitted tightly and 40% sodium hydroxide (≈ 40 ml) is run into the flask through an addition funnel until about 2 ml of sodium hydroxide is left in the funnel. Reaction starts between Al and sodium hydroxide with the evolution of hydrogen. The free end of the condenser must be dipped in 1 N sulphuric acid (25 ml) before the addition of sodium hydroxide (40%). Distillation should only be started when all the Al has reacted and no more hydrogen is evolved. This takes about 30–60 min. Evolution of hydrogen is complete when no more effervescence is seen in the reaction mixture. Water (≈ 150 ml) is added through the additional funnel until about 2 ml of water is left in the funnel. Distillation is then started.

3. Results and discussion

Propellant pastes were made in the laboratory in a 1 kg capacity sigma blade mixer. All the ingredients, i.e., AP 64–66%, Al 18%, iron oxide about 0.2%, dioctyl phthalate (DOP) about 6% and HTPB about 12% were added into the mixer and mixing was carried out for two hours at 40 °C. For pastes without Al, AP was taken 64–66%, iron oxide about 0.2% and any ratios of HTPB and DOP were taken above 12%. Good mixing is important to achieve accurate results. At the end of the mixing, about 50 g of the paste is removed into a beaker and allowed to cool down to room temperature. Before taking a portion of the paste for weighing, it is important that the paste should be mixed with the help of a spatula inside the beaker for about one minute. Our experiments show that without mixing at this stage the results are in the range of $\pm 0.4\%$ or even higher. This can be attributed to the settling down of the paste on keeping. At least four samples should be taken for analysis and it is recommended to mix the paste before taking every sample.

The analysis procedure is similar to the conventional Kjeldahl method [9] for pastes without Al, but in the presence of Al it becomes important to eliminate all the Al before starting the distillation. This is because the evolution of hydrogen as a result of reaction between Al and sodium hydroxide is so strong that it takes ammonia gas along with it and the results obtained are lower than the actual results. Sodium hydroxide is therefore allowed to react with Al at room temperature for about 30–60 min until the effervescence is not seen. It is only then that the distillation is started.

A pH meter was used to ascertain the end point during titrations. Experiments revealed that visual end points using mixed indicator did not lead to accurate results and also visual end points varied from individual to individual, which is not the case when pH meter is used.

It is recommended to use solutions of known strengths, i.e., 1 *N* sulphuric acid and 0.1 *N* sodium hydroxide, supplied commercially because a slight error in the normality of the solutions can lead to a prominent error in the final results.

Burettes used during the titration and for measuring 25 ml of 1 *N* sulphuric acid must be such that on being filled with distilled water and the water withdrawn, only an unbroken film of water remains. If water sticks to the burette walls then that burette cannot be used and should be washed before starting the experiment. Out of the various methods known for cleaning [9], the alcoholic solution of potassium hydroxide is found to be the best [10]. If the burette is filled with this solution and kept overnight then it can be used after washing with water.

The results obtained for pastes with and without Al are in the range of $\pm 0.05\%$.

The method can be applied to pure AP as described in Section 2.2.1 except that 1,4-dioxane is not used and 1.8 g sample is weighed. 1,4-Dioxane is used only to help disperse the paste during the reaction. The results are obtained in the range of $\pm 0.02\%$.

4. Conclusions

The Kjeldahl method can be applied for the estimation of AP in propellant pastes with and without Al with great accuracy and repeatability of the results. The results obtained are in the range of $\pm 0.05\%$ for pastes and $\pm 0.02\%$ for pure AP.

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