Determination of Nicotine in Tobacco (nonaqueous titration)

Principles

The enhancement of acid or base strengths made possible by change of solvent can be used to extend the range of possible acid-base titrations (see Quantitative Chemical Analysis 6th ed., D.C. Harris, pp. 245-246). One of the most important applications of nonaqueous titrations is in the determination of weak acids and bases, (those for which water itself is a stronger cid or base). Selection of appropriate solvents will allow these titrations to be accomplished in nonaqueous media. The analysis of tobacco for alkaloid content is a good example.

A number of alkaloids and alkaloid derivatives have been identified in tobacco. The principal alkaloids are nicotine and nornicotine, nicotine forming 90%, nornicotine 8 or 9%, and other alkaloids 1 or 2% of the total alkaloid content. The structure of nicotine and its base dissociation constants are shown below:

\[
\begin{align*}
K_{b1} &= 7 \times 10^{-7} \\
K_{b2} &= 1.4 \times 10^{-11}
\end{align*}
\]

In glacial acetic acid solvent (HOAc), both nitrogens are sufficiently basic that they may be titrated with HClO₄, as shown in Equation 3-5:

\[
C_{10}H_{14}N_2 + 2H^+(HOAc) \rightleftharpoons C_{10}H_{16}N_2^{2+}
\] (3-5)

Although the titration really determines total alkaloid content, it is customary to report it as percent nicotine, the major factor.

Directions

The presence of H₂O in nonaqueous titration causes erratic results. All equipment should be free from H₂O. Rinse all glassware with acetone; air-dry pipets and burets (Note 1).

Prepare approximately 0.05 N HClO₄ by adding 1 mL of concentrated HClO₄ to 250 mL of glacial acetic acid. The solution is standardized with potassium hydrogen phthalate (KHP) by the following procedure:

Transfer about 1 g of KHP to a weighting bottle, and dry for 1 to 2 hr at 110°C. Weigh out 0.2-g samples (±0.1mg), and transfer to 125-mL Erlenmeyer flasks. Add 50 mL of glacial acetic acid, and heat carefully until the sample dissolves. Cool, add 4 drops of crystal violet indicator (Note 2), and titrate to the bright-blue endpoint (Notes 3, 4). Calculate the normality of the HClO₄ solution.

Obtain a tobacco sample (Note 5), and weigh out 3-g samples. Transfer to a 250-mL Erlenmeyer flask. Add 1 g of barium hydroxide and 15 mL of saturated barium hydroxide. Swirl the flask until the tobacco is thoroughly wetted, adding more barium hydroxide solution if necessary. Pipet 100 mL of a 90% toluene-10% chloroform mixture into the flask, stopper
tightly, and shake vigorously for 20 min. Pour off most of the organic solution through a fluted filter paper into a dry 125-mL Erlenmeyer flask. Add 2 g of anhydrous magnesium sulfate to the organic layer to dry it. Swirl the flask gently, stopper it, and let sit for at least 15 min. Pour the organic liquid through a fluted filter paper into a dry 250-mL Erlenmeyer flask.

Pipet a 25-mL sample of this organic solution into a dry 125-mL Erlenmeyer flask. Add a spin bar and 4 drops of crystal violet indicator solution. Titrate with 0.05 N perchloric acid in glacial acetic acid solution. Stir slowly while titrating. The volume required will be small, around 3 mL; so titrate cautiously. The endpoint color change is dark blue to forest green to yellow green to yellow. This occurs within 3 or 4 drops; so titrate very slowly, and stop at the first green.

When you carry out the calculations, do not forget that only 25 mL of the organic phase was titrated and that n = 2 for nicotine. Report the percentage of nicotine in the tobacco, and report the source of your tobacco sample.

Notes
1. Caution: The solutions used in these titrations are toxic. Glacial acetic acid is very corrosive; perchloric acid is a strong oxidant and can cause spontaneous combustion or explosion of organic material. Wear nitrile gloves when working with these solutions and perform all titrations in a fume hood.
2. Preparation of crystal violet indicator: Dissolve 0.2 g of crystal violet in 100 mL of glacial acetic acid.
3. Volumes in this experiment will be fairly small, and a 25-mL buret, if available, is useful.
4. Only a few drops make a difference in the color transition of violet blue to bright blue to green to yellow. Be careful to stop at the bright blue.
5. Pipe tobacco, available in cans, is a convenient source of tobacco for class use. Students may also use cigarette tobacco from an easily available brand. Analysis “as received” is acceptable for cigarette tobacco, but several days of air drying is recommended for pipe tobacco so that the analysis will not depend on the age of the can. Samples may be placed in desiccators for 3 to 7 days to accomplish air drying. Weight loss will be 5 to 10% for fresh samples.