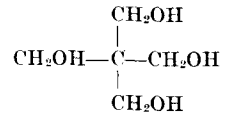
Cerate Procedure for Pentaerythritol

LOUIS SILVERMAN, 827 South Gramercy Place, Los Angeles, California.

THE pentaerythritol [$C(CH_2OH)_4$] oxidation reaction with perchlorato-ceric acid has not been reported. G. F. Smith (4) has shown that a solution of perchlorato-ceric acid, $H_2Ce(ClO_4)_6$, in 4-normal perchloric acid easily oxidizes (alcoholic) hydroxyl groups. As examples, ethylene glycol and glycerol are stoichiometrically oxidized to formic acid; one mole of ethylene glycol yields two moles of formic acid and one mole of glycerol yields three of formic acid.

These two are examples of straight carbon chains with an hydroxyl group attached to each carbon atom. Pentaerythritol, on the other hand, contains a central carbon atom which is attached to four other carbon atoms:



Each of the outer carbon atoms is expected to be oxidized to carboxyl-carbon, but experimental proof is required to determine whether the central atom is converted to acetic acid, formic acid or carbon dioxide. The possible equations are:

$$C(CH_2OH)_4 + 10\ H_2Ce(ClO_4)_6 + 4H_2O \longrightarrow 3H\ COOH + CH_3COOH + 30\ HClO_4 + 10\ Ce(ClO_4)_3 \quad (1)$$

$$C(CH_2OH)_4 + 14\ H_2Ce(ClO_4)_6 + 6H_2O \longrightarrow 5H\ COOH + 42\ HClO_4 + 14\ Ce(ClO_4)_3 \quad (2)$$

$$C(CH_2OH)_4 + 16\ H_2Ce(ClO_4)_6 + 6H_2O \longrightarrow 4H\ COOH + CO_2 + 48\ HClO_4 + 16\ Ce(ClO_4)_3 \quad (3)$$

By equation (1), the equivalent weight for pentaerythritol would be $\frac{1}{10}$ mol; by equation (2), $\frac{1}{14}$ mol; and by equation (3), $\frac{1}{16}$ mol.

In order to select the proper equation a sample of pentaerythritol, 96.1% assay by the acetic anhydride-pyridine procedure (1), (2), and (5), was run by the perchlorato-cerate method. Equation (3) requiring 16 oxidation equivalents per mole of pentaerythritol was found to give a result of 96.1%, while equations (1) and (2) would give results well above 100%. The results for 3 samples are listed in Table I.

TABLE I

Pentaerythritol (P.E.)

Sample No.	P. E. (Proposed method) %	P. E. (Acetic anhydride) %	Melting Point °C.	Ash %	Moisture %
1	96.0	96.1			
2	96.1 (c)		198 (a) 220 (b)	0.05	0.12
3	98.0	98.0	..... 260 (b)		

(a) Incipient.
(b) Final.
(c) Calculated, as 48%, (OH).

The equivalent weight for pentaerythritol is 8.508, and a 0.10-gram sample requires 23.5 ml. of a 0.5-normal perchlorato-ceric acid solution. In the actual titration an excess of 10 to 20% of cerate is convenient (4).

The procedure for the determination is similar to that for ethylene glycol or for glycerol in soap (3), and alcohols other than pentaerythritol must not be present (4).

Reagents

Ultimate Standard. Dry sodium oxalate, Bureau of Standards. Weigh 13.412 grams and dissolve in one liter of a 1:9 solution of 72% perchloric acid. This standard is 0.2N. and the solution will maintain its strength for six months. A working standard of c.p. sodium oxalate may be used for economy.

Ammonium perchlorato-cerate. This solution may be purchased from G. F. Smith Chemical Co., Columbus, Ohio, as 0.5N reagent in 6N perchloric acid. It may also be prepared in the laboratory (4). Some analysts may prefer a 0.2N reagent, in which case 2 volumes of reagent are mixed with 3 volumes of 1:1 (approx. 6N) perchloric acid.

Nitro-ferroin, ferrous sulfate complex with nitro-o-phenanthroline. The prepared indicator may be purchased.

Perchloric acid. Seventy-two per cent, reagent grade.

Procedure for the Determination of Pentaerythritol

(Absence of other alcohols)

Weigh a 1.0000-gram sample, and transfer the solid to a 500-ml. volumetric flask. Half-fill the flask with water, shake to dissolve the solid, then dilute to the mark with water and mix well.

Pipette a 50-ml. aliquot (0.100 g.) into a 400-ml. beaker and add 25 ml. of 72% perchloric acid. Stir. Also prepare a beaker containing 75 ml. of water and 25 ml. of perchloric acid, to be used for standardizing the perchlorato-cerate solution. These solutions are approximately 4N in perchloric acid. Carefully pipette 25 ml. of 0.5N perchlorato-cerate into the pentaerythritol solution; also pipette 10 ml. into the solution to be used for the standardization. Heat the solution to 50°C. and maintain at this temperature for 12 to 13 minutes, stirring occasionally. Each beaker should be provided with a thermometer. At the end of the reaction period, remove the beaker from the heat, add 100 ml. of water, and let stand for 5 or more minutes to a convenient time for titration.

To titrate the excess cerate, add two drops of nitro-ferroin indicator and titrate slowly with standard 0.2N oxalate solution. The blue indicator becomes colorless about 0.1 ml. short of completion, then pink at the end point.

Calculation:

$$\% \text{ Pentaerythritol} = 100 \times \frac{[(\text{ml. cerate} \times N) - (\text{ml. oxalate} \times N)] \times 0.008508}{\text{Aliquot weight of sample, g.}}$$

Acknowledgment

The author wishes to thank Susan Goyne for check results.

REFERENCES

1. Freed, M., and Wynne, A. M., I. E. Chem., Anal. Ed., *8*, 278 (1936).
2. Petersen, J. W., Hedberg, K. W., and Christensen, B. E., I. E. Chem., Anal. Ed., *15*, 225 (1943).
3. Silverman, Louis, J. A. O. C. S., *24*, 410 (1947).
4. Smith, G. F., "Cerate Oxidimetry," G. Frederick Smith Chemical Co., Columbus, Ohio (1942). A gratis publication.
5. Verley, A., and Bolsing, F., Ber. *34*, 3354 (1901).