

EQUIVALENT WEIGHTS OF HEAVY ORGANIC AMINES BY NON-AQUEOUS POTENTIOMETRIC TITRATION

UOP Method 704-70

SCOPE

This is a general procedure for determining the equivalent weights of heavy organic amines.

OUTLINE OF METHOD

The basicity of the amine is determined by titrating the sample, dissolved in mixed toluene-glacial acetic acid, with standard perchloric acid in glacial acetic acid. The endpoint of the titration is detected potentiometrically.

APPARATUS

Beakers, titration, 250-ml, tall form

Burets, 10- and 25-ml (for use in manual titration)

Electrode, calomel, sleeve type

Electrode, glass

Stirrer, magnetic

Stirring bar, magnetic

Titration, mechanical, or pH meter. An apparatus capable of recording graphically the volume of titrant vs. apparent pH is convenient, but not essential. Non-recording titrators or a pH meter may be used. Suitable types include Metrohm Models E-336 and E-436 titrators, Precision Scientific Company "Dual Titrometer", Shell-Precision "Recordomatic Titrometer" and the Beckman "Zeromatic" pH meter.

REAGENTS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society where such specifications exist, unless otherwise stated.

Acetic acid, glacial

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

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Perchloric acid, standard 0.1 *N* in glacial acetic acid. Standardize against potassium acid phthalate, sodium carbonate or “*THAM*” [tris(hydroxymethyl)aminomethane].

Toluene

PROCEDURE

Heavy organic amine samples consist of pasty, semi-solid materials with or without separated liquid present. Obtain a representative sample by completely melting the sample in an oven or by means of a hot water bath if the sample is thermally unstable or if it contains volatile constituents. After the sample is melted, shake or stir to ensure a homogeneous sample. Weigh 0.2-0.3 g of the well-mixed sample to the nearest 0.1 mg into a titration beaker and dissolve it in approximately 30-50 ml of toluene as required to effect solution. When the sample is in solution add, with mixing, glacial acetic acid equivalent to the volume of toluene used plus 25 ml additional. Titrate the sample potentiometrically with the 0.1 *N* perchloric acid. The endpoint of the titration is found by locating the inflection point on the chart of the titration, if an automatic titrator is used; or, from the inflection point found by plotting the data obtained manually. The inflection point will occur at an apparent pH of 2 to 4 so that a 0-7 pH or full pH range instrument setting is suitable.

CALCULATION

$$\text{Equivalent weight} = \frac{1000 W}{NV}$$

where:

W = weight of sample, g

V = volume of perchloric acid solution used to reach endpoint, ml

N = normality of perchloric acid solution

NOTES AND PRECAUTIONS

1. Avoid over-heating in melting the sample. Melt completely and mix very thoroughly before sampling.
2. Many samples are soluble in acetic acid alone and in such instances, the use of toluene is not necessary. In those instances where it is used, it is important that the solvent system contains sufficient acetic acid to assure adequate conductivity of the solvent.
3. Some unusual samples may require preliminary solution in a solvent other than toluene. A judicious choice of another solvent, if indicated, is permissible. This option serves to reinforce the general application of the method.

PRECISION

Duplicate determinations on amine samples should not differ by more than 1.7 in the 130 to 275 equivalent weight range. The estimated standard deviation (esd) calculated from the mean range and based on 34 pairs is 0.6.

TIME FOR ANALYSIS

The elapsed time for duplicate determinations run simultaneously is 1.0 hour. The labor requirement for each determination is 0.5 man-hour.