

Method. Place in the inner tube sufficient quantity of the liquid or previously melted substance to be examined, to cover the thermometer bulb and determine the approximate freezing point by cooling rapidly. Place the inner tube in a bath about 5 °C above the approximate freezing point until all but the last traces of crystals are melted. Fill the beaker with water or a saturated solution of sodium chloride, at a temperature about 5 °C lower than the expected freezing point, insert the inner tube into the outer tube, ensuring that some seed crystals are present, and stir thoroughly until solidification takes place. Note the highest temperature observed during solidification.



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2.2.19. AMPEROMETRIC TITRATION

In an amperometric titration, the end-point is determined by following the variation of the current measured between 2 electrodes (either one indicator electrode and one reference electrode or 2 indicator electrodes) immersed in the solution to be examined and maintained at a constant potential difference as a function of the quantity of titrant added.

The potential of the measuring electrode is sufficient to ensure a diffusion current for the electroactive substance.

Apparatus. The apparatus comprises an adjustable voltage source and a sensitive microammeter; the detection system generally consists of an indicator electrode (for example, a platinum electrode, a rotating-disc electrode or a carbon electrode) and a reference electrode (for example, a silver-silver chloride electrode).

A three-electrode apparatus is sometimes used, consisting of an indicator electrode, a reference electrode and a polarised auxiliary electrode.

Method. Set the potential of the indicator electrode as prescribed and plot a graph of the initial current and the values obtained during the titration as functions of the quantity of titrant added. Add the titrant in not fewer than 3 successive quantities equal to a total of about 80 per cent of the theoretical volume corresponding to the presumed equivalence point. The 3 values must fall on a straight line. Continue adding the titrant beyond the presumed equivalence point in not fewer than 3 successive quantities. The values obtained must fall on a straight line. The point of intersection of the 2 lines represents the end-point of the titration.

For amperometric titrations with 2 indicator electrodes, the whole titration curve is recorded and used to determine the end-point.



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2.2.20. POTENTIOMETRIC TITRATION

In a potentiometric titration (volumetric titration with potentiometric end-point determination) the end-point is determined by recording the variation of the potential difference between 2 electrodes (either 1 indicator electrode

and 1 reference electrode, or a combined electrode) immersed in the solution to be examined as a function of the volume of titrant added.

Apparatus. The apparatus used comprises a millivoltmeter. Commercial autotitrator instruments may be used and are operated in accordance with the manufacturer's instructions, using electrodes recommended for the type of titration described.

The indicator electrode to be used depends on the substance to be determined and may be a glass or metal electrode (e.g. platinum, gold or silver).

For acid-base titrations, a glass-silver-silver chloride electrode combination is generally used.

Method. Prepare the sample solution as described. Add the titrant in suitable aliquots paying particular attention to the rate of addition and the volume increments near the end-point. Continue the titration beyond this point to allow a clear detection of the end-point.

The end-point of the titration is reached when the maximum change in potential occurs in a plot of potential versus volume of titrant, and is expressed as the corresponding volume of titrant. Recording the first or second derivative curve can facilitate the determination of the end-point. In potentiometric titrations of weak acids or bases using non-aqueous solvents, if necessary, either carry out a blank determination or pre-neutralise the solvent mixture. Where it is impracticable to use potentiometric detection for this purpose, the solvent mixture can be pre-neutralised by titration using a suitable indicator. Some examples are given below:

Titrant	Indicator
Perchloric acid	Crystal violet solution R
Tetrabutylammonium hydroxide	3 g/L solution of thymol blue R in methanol R
Ethanollic sodium hydroxide	Thymolphthalein solution R



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2.2.21. FLUORIMETRY

Fluorimetry is a procedure which uses the measurement of the intensity of the fluorescent light emitted by the substance to be examined in relation to that emitted by a given standard.

Method. Dissolve the substance to be examined in the solvent or mixture of solvents prescribed in the monograph, transfer the solution to the cell or the tube of the fluorimeter and illuminate it with an excitant light beam of the wavelength prescribed in the monograph and as near as possible monochromatic.

Measure the intensity of the emitted light at an angle of 90° to the excitant beam, after passing it through a filter which transmits predominantly light of the wavelength of the fluorescence. Other types of apparatus may be used provided that the results obtained are identical.