Highlights

Titrimetry

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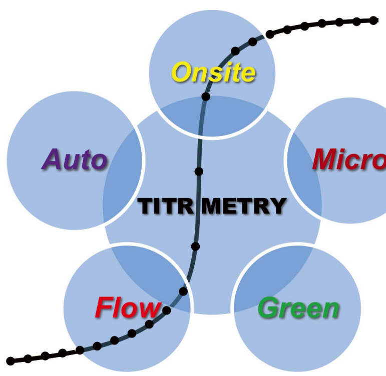
Titrimetry is among absolute methods, that rely upon accurately known fundamental constants for calculating the amount of an analyte. The origin of this technique goes back to Geffroy in 1729; he determined the concentration of vinegar by noting the amount of solid potassium carbonate that could be added before effervescence stopped.[1] Titrimetry was developed in the eighteenth century, but is still widely used today due to its high precision and versatility. For example, Masadome *et al.* reported a photometric colloidal titration method of polyhexamethylene biguanide hydrochloride, which is used for disinfectants in personal-care products, using crystal violet as a color indicator.[2] Zhi *et al.* applied the Karl Fischer coulometric titration method to determine the water content of nitrogen-containing hydrogen sulfide.[3] Anderson *et al.* utilized a potentiometric titration curve to calculate the concentration of polyquaternium polymers which are used for medical studies, wastewater treatment, and environmental contaminant remediation.[4] Routine tests of the chemical oxygen demand (COD) is mostly achieved by batch-wise titration, but in recent years several alternative methods have been reported. Chen *et al.* proposed a gas-phase molecular absorption spectrometry-based COD analyzer.[5] The proposed method improved the analysis speed, efficiency, accuracy, and stability compared to the traditional batch-wise titration. Hue *et al.* reported a 3-step chemiluminescence method for COD determination, *i.e.*, i) treatment of a sample with permanganate under heating, ii) treatment of excess permanganate with pyrogallol, and iii) measurement of excess pyrogallol by chemiluminescence reaction with permanganate.[6] This method was continuous, sensitive, and low cost compared to the conventional titration method. To achieve green analytical chemistry, many techniques have been integrated into titrimetry. Kanna *et al.* proposed reusable solid-phase sorbed indicators for reducing reagents used in titrimetry.[7] The indicator-sorbed-solids, using anion exchange resins and kaolin clay as supports, demonstrated promising results for determining acidity in weak acid samples. Paengnakorn *et al.* constructed a sequential injection analysis-lab-at-valve system for automated micro-scale titration.[8] This system readily reduced the volume of sample/reagents on only a micro-liter scale, significantly lower than that used in conventional batch titration. Ochiai *et al.* studied a feedback-based and subsequent fixed triangular wave-controlled flow ratiometry.[9] They introduced air-segmentation to suppress axial dispersion in flow titration, and found that the applicable range was extended especially to lower titrand concentrations. Kawakubo *et al.* designed a microtitration system based on the counting of titrant droplets for precise on-site analysis.[10] On-site measurements of tap water collected in an office kitchen were performed, and the analytical results agreed with those of conventional titration with an error of 3%.

Titrimetry, developed about 300 years ago, has never lost its importance despite the emergence of various new analytical methods. This classical analytical method will continue to evolve and develop with changing the needs of the times.



Evolution of titrimetry.

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Keywords Titrimetry, automated analysis, on-site analysis, flow analysis, green chemistry

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