Towards Green Titration: Downscaling the Sequential Injection Analysis Lab-at-valve Titration System with the Stepwise Addition of a Titrant

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A downscaling in true titration based on a simple sequential injection analysis-lab-at-valve (SIA-LAV) has been proposed. A titrant solution was stepwise aspirated into a titration LA V chamber and a titration curve was obtained by monitoring the change in the solution color spectroscopically. This fully-automated SIA-LAV system required less volume of the sample/reagents, only a micro-liter scale, compared to the conventional method. The system was investigated with complexometric titration and acid-base titration. Application of the developed technique to some real samples has been demonstrated.

Keywords Titration, sequential injection analysis-lab-at-valve, green analytical chemistry

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Introduction

Titration is a widely-used analytical technique that has been employed in various applications. According to the International Union of Pure and Applied Chemistry (IUPAC), titration is the process of determining the quantity of a substance of interest (titrand) by adding measured increments of another substance, with which it reacts (almost always as a standardized solution, known as a titrant) with provision for some means of recognizing the endpoint, at which essentially all of the substance of interest have reacted.1 To achieve green analytical chemistry, many techniques have been integrated into titrimetry focusing on automation, miniaturization of the procedures and instrumentation.2,3

A titration system using various flow-based analysis techniques has been developed, such as flow injection analysis (FIA)4 and sequential injection analysis (SIA),5 including sequential injection analysis-lab-at-valve (SIA-LAV).5,7 However, those systems determined the analyte concentration via pseudo titration using a calibration curve, not true titration. However, some true titration methods employing a flow-based technique were reported previously.4-10

In this study, a sequential injection analysis-lab-at-valve (SIA-LAV) system for automated micro-scale true titration was proposed. In recent years, the SIA-LAV systems have been developed and successfully used for downscaling chemical analysis in various applications, such as kinetics study, microextraction and potentiometry.7,11-13 Here, the proposed method is based on stepwise dispensing of the micro-volume of the titrant into a titrand-containing chamber of the LA V unit. A fiber-optic UV-Vis spectroscopy served as a detector, which enabled monitoring solution absorbance at a specific wavelength. A titration curve can easily be followed, and the end point can be estimated. The analyte concentration can then be evaluated. This can be done with simple instrumentation. The performance of the proposed system was investigated with complexometric titration for hardness determination, and the application to real samples was demonstrated. In addition, the system was applied to acid-base titration for the standardization of sodium hydroxide.

Experimental

SIA-LAV for a micro-volume step titration system was set up as illustrated in Fig. 1. The SIA system consisted of a 1.0 or 2.5 mL syringe pump (Cavro, USA), a 10-port selection valve with a microelectric actuator (Valco Instruments, USA) and 1/8” OD PTFE tubing (Upchurch, USA) for a holding coil (HC). The titration chamber was modified from a 1000-μL pipette tip situated on the selection valve. An optical fiber-based UV-Vis spectrophotometer was employed as a detector (USB2000 UV-Vis and LS-1 LL tungsten halogen lamp, Ocean Optics, USA). All SI titration procedures were controlled by the program FIAlab® for window 5.0 (FIAlab Instruments, USA).

Notes

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The SIA-LAV step titration system was demonstrated using complexometric titration as a model. The total calcium and magnesium content, so-called total hardness, could be determined by complexometric titration with ethylenediaminetetraacetic acid (EDTA, Scharlau, Spain) using a complexometric indicator, Eriochrome black T (Fluka, Switzerland). For optimization, standard calcium and magnesium solutions were used (CaCO₃, 99.9%, J. T. Baker and MgSO₄, Panreac, Spain). The stepwise titration was performed by first dispensing of the sample solution, an indicator and a buffer solution into the titration chamber via a selection valve, following by stepwise dispensing of a certain volume of the solution (see chemical and reagents section in Supporting Information). At the titration chamber, the solution absorbance at a certain wavelength was constantly monitored. The total hardness content was reported as being mg/L CaCO₃.

Results and Discussion

A spectrophotometric titration curve of the SIA-LAV system was studied in comparison with that of batch titration. Any change in the solution color was followed spectroscopically throughout the titration. The corrected absorbance was obtained by multiplying the observed absorbance with the dilution factor, as expressed below;

\[ A_{\text{corr}} = A_{\text{obs}} \left( \frac{V_0 + v}{V_0} \right) \]

where \( A_{\text{corr}} \) and \( A_{\text{obs}} \) are the corrected absorbance and the observed absorbance, respectively. \( V_0 \) and \( v \) are the starting volume and the added titrant volume, respectively.

In Figs. 2a and 2b, the signal profiles from the spectrophotometric titration of the total hardness assay were obtained from the batch method and the SIA-LAV method, respectively. By following the absorbance of the free indicator (610 nm), the end point could be determined at an inflection point of a titration curve, which was close to be an equivalence point where EDTA competitively formed a complex with all metal ions, and the free indicator was released. This suggested that the titration curve of the SIA-LAV titration system was comparable to that of the conventional batch titration.

The procedure of the SIA-LAV system for hardness determination, including the cleaning step, was investigated as shown in Table S1 (Supporting Information). Several system parameters and conditions were studied, including the injection sequence, the sample and indicator volumes, the titrant volume per cycle, and the flow rate.

The volumes of the titrant and reagents used were optimized. An injection sequence of the titrand and indicator significantly affected the degree of solution mixing in the chamber. For a hardness assay, the complexation reaction occurred at pH 10, and a buffer solution was required in the titration chamber. Two small segments of buffer pH 10 were added before the injection sequence of the titrand and indicator to help them mix thoroughly.

The volume of the titrant dispensing per cycle in the SIA-LAV system corresponds to the drop size of the titrant in batch titration, i.e. the smaller is titrant drop, the closer is the end point to the equivalence point. On the other hand, the flow rate of titrant dispensing is a key force to assist mixing the solution in the titration chamber. With an optimized flow rate, the dispensed titrant should be homogenously mixed with the titrand in the chamber. For the titration of 1.00 and 10.00 mM Ca²⁺ solutions, an EDTA volume of 5 μL per cycle with a flow rate of 50 μL s⁻¹ was found to be suitable (see Fig. S1, Supporting Information).

The working range of the SIA-LAV titration system depended on the volume and concentrations of the titrant used in the
Table 1 Determination of the total hardness in various Ca\(^{2+}\) and Mg\(^{2+}\) solution mixtures (n = 3)

| Molar ratio Ca\(^{2+}\):Mg\(^{2+}\) | Total hardness, mg/L CaCO\(_3\) |
|-----------------------------------|---------------------------------|
|                                   | Calculation | SIA titration |
| 0:10                              | 102         | 104 ± 2       |
| 2:8                               | 102         | 103 ± 1       |
| 4:6                               | 101         | 104 ± 2       |
| 6:4                               | 101         | 101 ± 1       |
| 8:2                               | 100         | 101 ± 1       |
| 10:0                              | 100         | 100 ± 2       |

The downscaling SIA-LA V system for green true titration methods is proposed. With the aim of miniaturization in chemical consumption, the SIA-LA V step titration method was developed. The SIA-LA V system was able to reduce the volume of chemicals used to a microliter scale, significantly lower than that used in conventional batch titration. The obtained titration curve corresponded to that of the spectrophotometric batch titration. The automation of the system also helped to shorten the analysis time.

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