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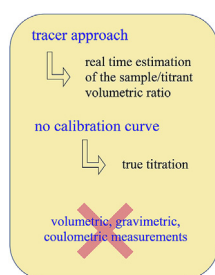
Tracer-monitored flow titrations

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HIGHLIGHTS

- Tracer-monitored titrations are efficiently implemented in flow analysis.
- Special components in the manifold are not required.
- True titrations are accomplished in a rugged, simple and portable flow analyzer.
- Measurements of volume, mass, charge or peak width are not required.
- Better figures of merit are attained with pulsed flows.

GRAPHICAL ABSTRACT

ABSTRACT

The feasibility of implementing tracer-monitored titrations in a flow system is demonstrated. A dye tracer is used to estimate the instant sample and titrant volumetric fractions without the need for volume, mass or peak width measurements. The approach was applied to spectrophotometric flow titrations involving variations of sample and titrant flow-rates (*i.e.* triangle programmed technique) or concentration gradients established along the sample zone (*i.e.* flow injection system). Both strategies required simultaneous monitoring of two absorbing species, namely the titration indicator and the dye tracer. Mixing conditions were improved by placing a chamber with mechanical stirring in the analytical path aiming at to minimize diffusional effects. Unlike most of flow-based titrations, the innovation is considered as a true titration, as it does not require a calibration curve thus complying with IUPAC definition. As an application, acidity evaluation in vinegars involving titration with sodium hydroxide was selected. Phenolphthalein and brilliant blue FCF were used as indicator and dye tracer, respectively. Effects of sample volume, titrand/titrant concentrations and flow rates were investigated aiming at improved accuracy and precision. Results were reliable and in agreement with those obtained by a reference titration procedure.

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1. Introduction

A tracer is "an identifiable substance introduced into a dynamical system to follow the course of a process, thus providing information on the pattern of events and/or on the redistribution of the parts or elements involved in the process" [1]. Tracer-monitoring has been exploited in different fields, and hydrological studies [2] and plant nutrition investigations [3] relying on dyestuffs and radioactive (or stable) nuclides are typical examples. A tracer should

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ideally present the same chemical properties and undergo the same chemical reactions as the species it mimics. It should be also easily detectable.

In analytical chemistry, tracer-monitoring is usual, especially for recovery assessment [4] and internal standardization [5]. Regarding titrations, an ingenious tracer-monitored strategy was proposed and applied to the spectrophotometric determination of total alkalinity in seawater [6]. A dye tracer in the titrant allowed real time estimation of both the sample-to-titrant volumetric ratio and the pH of the mixture after each titrant addition. Variations on sample/titrant volumetric ratio and the titration course are real-time followed. The entire titration curve was then obtained without physically metering volumes, masses, flow rates or electric charges.

The innovation was further applied to (i) acid-base titration, using brilliant blue as dye-tracer and potentiometric pH measurements; (ii) iodimetric titration of ascorbic acid, with chloride as tracer monitored by conductimetry and starch to assist end point detection; and (iii) complexometric titration of calcium with EDTA in the presence of calmagite, with simultaneous spectrophotometric measurements at two wavelengths [7]. Recently, a tracer-monitored titration was proposed for the determination of dissolved oxygen in seawater [8] relying on the classical Winkler method. Possibilities of using fluorescent or radioactive tracers were also highlighted [7].

As tracer-monitored titrations can be implemented whenever the tracer and titrant volumetric fractions are known, the aim of this work was to demonstrate the feasibility of the approach in flow analysis. To this end, the triangle programmed [9,10] or the flow injection [11,12] techniques were selected.

The triangle programmed titration exploits the flow rate variations of the sample and titrant convergent streams, and the combined stream is directed towards detection. Usually, the sample flow rate is maintained whereas the titrant one is linearly increased until reaching the titration end point. The flow rate yielding a titrant amount stoichiometrically equivalent to the analyte is taken into account for calculating the analytical result.

The classical flow injection titration exploits the concentration gradients along the sample zone. The sample is inserted into the titrant stream, undergoes controlled dispersion, and is thereafter monitored. The indicator color is monitored, and the time interval between two measurements related to identical sample-to-titrant volumetric fractions at the titration end-point is proportional to the logarithm of the analyte concentration [12]. As the strategy requires a calibration curve, it does not comply with IUPAC definition [13], and can be regarded as a pseudo titration.

Criteria for selection of the dye tracer, potentialities of the innovation, design of the flow manifolds and influence of the main involved parameters were discussed. As application, the spectrophotometric determination of total acidity in vinegars was selected.

2. Theoretical aspects

In flow analysis, every fluid element in the sample zone results from the combination of the involved solutions, e.g. sample, reagents and diluents [14]. The sample volumetric fraction (X_S) in the fluid element yielding the analytical signal provides information on the degree of sample dispersion, whereas the transient X_S-values along a fluidic zone are also relevant, especially in flow-based procedures exploiting concentration gradients for implementing the standard additions method [15], differential kinetic analysis [16] or titrations [11].

In flow systems with spectrophotometric detection, X_S can be evaluated by taking advantage of the dye approach [17], which usually requires additional experiments. With multichannel spectrophotometers, this approach is worthwhile for implementation of tracer-monitored flow titrations. To this end, a dye tracer is added

for monitoring the variations in sample/titrant volumetric fractions during the titration course. In this way, information on the volumetric proportions of the analyte/titrant solutions at every stage of the titration is gathered. The titrant and the tracer should undergo the same dispersion, i.e. tracer and analyte (or titrant) should present similar diffusion coefficients, otherwise differences in diffusional effects should be minimized.

Eq. (1), derived from Ref. [7] and adapted to flow conditions, describes the titration mass balance.

$$C_A - Q\, C_T = C_{0A}\, X_S - Q\, C_{0T}\, X_T \qquad (1)$$

where: A = analyte; T = titrant; C_A and C_T = concentrations in the fluid element after mixing; C_{0A} and C_{0T} = original concentrations; X_S and X_T = sample and titrant volumetric fractions; Q = stoichiometric factor.

As Eq. (1) holds for any point of the titration course, the entire titration curve can be obtained by successive applications. In general, the titrant solution is added until the end point is reached, as indicated by e.g. a sudden color variation of the indicator. Negative concentration values after end point are avoided by interchanging the positive and negative operators in Eq. (1). At the end point, Eq. (1) equals zero:

$$C_{0A}\, X_S - Q\, C_{0T}\, X_T = 0$$

or:

$$C_{0A} = Q\, C_{0T}\, X_T\, (X_S)^{-1} \qquad (2)$$

As $X_T + X_S = 1$, Eq. (2) is modified to:

$$C_{0A} = Q\, C_{0T}\, X_T\, (1 - X_T)^{-1} \qquad (3)$$

Eq. (3) can be simplified to Eq. (4) by assuming that:

- X_S and $X_T = C_A\, (C_{0A})^{-1}$ and $C_T\, (C_{0T})^{-1}$ [C and C_0 = instant and original concentrations];
- X_T is ideally the same for the tracer and the titrant;
- The detector response is linear in the measurement interval.

So:

$$C_{0A} = Q\, C_{0T}\, [M_{0T}\, (M_T)^{-1} - 1]^{-1} \qquad (4)$$

where: M_{0T} and M_T = measurements related to tracer in the undispersed titrant solution and in the fluid element associated to end point, respectively.

Analysis Eq. (4) reveals that the analyte determination does not depend on the original tracer concentration and this is an important feature of the proposed strategy. Furthermore, no measurements of volume or mass are required, and limitations associated with volume expansions in conventional titrations are overcome.

3. Experimental

3.1. Solutions

All solutions were prepared with deionized water (resistivity > 18.2 MΩ cm) and analytical grade chemicals. Brilliant blue FCF ($C_{37}H_{34}N_2Na_2O_9S_3$; CAS number 3844-45-9) and phenolphthalein, herein assigned as BB and phen, were purchased from Sigma–Aldrich Co (St. Louis MO).

The titrant was a 0.01 mol L^{-1} NaOH solution standardized against potassium hydrogen phthalate. Immediately before use, a few drops of a 0.5% (m/v) phen in 50% (v/v) ethanol solution and a minute mass of BB powder (ca. 6 mg L^{-1} in the titrant solution) were added.

Vinegar samples were purchased at the local market and 20-fold diluted in water.