< FIA Award for Science >

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**Development of Flow-Based Procedures for Titrimetric and Two-Component Analysis**

Flow techniques provide great potential for improvement and automation of analytical methods. Development of flow techniques started also a novel approach to a registered signal. It drew attention to the possibility of using for analytical purposes not only the value of the signal registered at its plateau, peak height or the peak area, but also each point of the analytical signal registered in repeatable conditions [1]. It created an opportunity to not only "imitate" methods designed for batch analysis with the use of flow systems, but also to develop novel analytical methods. These characteristics were taken into consideration in the development of novel procedures for titrimetric and two-component analysis.

Regarding titrimetric analysis, the contribution included developing several novel titration procedures conducted with the use of flow injection analysis (FIA) [2-6] or sequential injection analysis (SIA) [7] systems. Most of the advances were proposed for the flow injection (FI) titration [3-7]. FI titration is generally based on the formation of a concentration gradient of an analyte in a sample zone introduced into a stream of titrant. In conditions of properly large dispersion, a characteristic peak of a cut-off profile is registered. It was proved that the peak width (measured in an appropriate way) can be a measure of the analyte concentration. In this kind of titration it is necessary to perform calibration to determine the analyte concentration. Calibration was proposed to be performed in interpolative way on the basis of a series of calibration solutions prepared from a single standard solution with the use of FIA [3] and SIA [7] systems. Moreover, to reduce the number of calibration solutions, the systems were developed in which calibration was performed by varying the dilution factor of two [4] or a single stock standard solution [3]. This way four parallel calibration graphs [4] or a multi-line single-point calibration graph [3] were constructed. Other contribution to this topic addressed the development of a method in which a signal for a sample was always included in the calibration range [5]. The approach relied on successive dilution of a solution containing a sample with standard addition and on titration of the solutions obtained until receiving a signal lower than the signal measured for the sample alone. An attempt was also made to demonstrate that the flow injection gradient titration should not be considered as the classical titration but rather as the indirect calibration method [6]. Several other flow-based approaches concerning automation [8-13], improvement [14-16] or development of novel calibration procedures [8,10,13,17-21] were also developed. The advances in this area were described in two review papers [24,25].

The fundamental contribution in this topic addressed the group of flow methods developed for two-component analysis. Simultaneous determination was proposed to be performed on the basis of different parameters of a signal registered with the use of various flow systems [26-29]. Moreover, an original concept of applying two calibration methods to simultaneous determination of different analytes with the use of the same calibration graph [30] was introduced.

Flow injection titration performed in the mode of the reversed flow was proposed to be employed to two-component analysis in which various parameters of the registered peak were applied to simultaneous determination of different analytes [26-28]. Generally, the principle of the method implemented with the use of a FIA system with spectrophotometric detection is as follows. Two reagents are added to a sample and each of them reacts with one of the analytes to form a complex. The sample is introduced into the flow system in a continuous way and a steady signal coming from both complexes (signal BC) is registered. Then, a third reagent is injected into the stream of the sample. The reagent reacts selectively with one of the analytes to form a more stable complex that does not absorb radiation at the wavelength applied. The value of the signal BC, the width and/or the area of the registered peak can be used as a measure of the concentration of the analyte (forming the less stable complex) in the sample whereas the signal for the second analyte is measured at the plateau (or at a point corresponding to an extremum) of the registered peak. Using the developed FIA [26-28] or SIA [29] systems, different analytes were determined simultaneously on the basis of the peak width [26], the peak area [27-29], the signal BC [28,29] and the values of signal registered at peak maximum [26] or minimum [27-29]. Calibration was performed with the use of two-component standard solutions of concentrations established in accordance with $2^2$ factorial design [26,28,29] or traditionally [29], when the mutual influence of analytes on their signals were not detected.

Regarding the two-component analysis based on the simultaneous use of different calibration methods, the developed method was applied to speciation analysis [30]. In the proposed method, one of the forms of an analyte was determined in extrapolative way whereas the second form was determined, after appropriate chemical treatment, in interpolative way with the use of the same calibration graph. The method was implemented using the SIA and Lab-in-Syringe systems. It has a potential to be applied to multicomponent analysis.

The developed methods were validated and their applicability was proved by applying them inter alia to acid-base and complexometric titrations, to the determination of total acidity in vinegars [2,3,5,7] and soft drinks [5,7], to the determination of chorite ions in water [6], magnesium and calcium in pharmaceutical products [2], to simultaneous determination of Fe(II) and Fe(III) [26,27,29,30], Cr(III) and Cr(VI) [30] and phosphate and silicate ions [28] in various kinds of water and wastewater.

**References**

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