Talanta 79 (2009) 1006–1010

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Flow injection titration basing on the merging-zone technique

Marzena Wójtowicz, Joanna Kozak*, Karolina Danielewska, Paweł Kościelniak

Department of Analytical Chemistry, Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland

ARTICLE INFO

Article history:
Available online 9 March 2009

Keywords:
Titration
Flow injection analysis
Merging-zone technique

ABSTRACT

The proposed approach relies on titration of a sample that is gradually diluted in strictly controlled way in the flow injection system developed. On each step of sample dilution equal volumes of the sample and titrant solutions are simultaneously injected into two carrier streams and the zones are merged with each other. Then, they are mixed completely in the mixing chamber, merged with a stream of indicator and directed to a detector. It has been revealed that the method provides the results with accuracy better than ±3.3% (RE) and with mean repeatability lower than 1.0% (RSD). When the analyte concentration in a sample is too low to be determined directly, the procedure of titration with standard addition is exploited. The proposed approach has been successfully applied to the determination of total acidity in vinegars and magnesium and calcium in pharmaceutical products. The results obtained were comparable with those provided by the reference methods. The proposed procedure is characterized by low consumption of sample (usually less than 2 mL), titrant (about 3 mL) and indicator (about 0.6 mL). Average time of a single analysis is similar to time of traditional batch analysis.

1. Introduction

From many years, effort is made to rationalize titration with the use flow or related techniques. In this area, many interesting concepts arouse and some of them have become more popular among analysts, what is manifested in the number of papers concerning examples of their applications or development.

Among them, the titration based on continuous flow methodology can be found. This relatively large group of methods exploits the possibilities of programmable change of flow rates (in continuous or discrete way) and, as a result, formation of titrant and/or sample continuous concentration gradients during their flow to a detector [1–8]. According to them, titration can be performed, e.g. exploiting formation of a single [1,2] or double concentration gradient [3–6] or by the so-called feedback-based flow ratiometry [7,8]. An analyte can be determined without additional calibration process [4–8], after prior calibration [1,3] or for instance on the basis of instrumental parameters (appropriately measured sample and titrant flow rates) [1,2].

Regarding the possibilities of exploiting of injection techniques to improve titration, the most popular approach seems to be so-called gradient titration [9] (known also as "pseudotitration" [10,11]) performed in flow injection [12–14] or sequential injection [15–17] systems. The approach exploits a concentration gradient that is formed when a segment of sample is located in a stream of titrant (or between its two segments). In conditions that guarantee high dispersion, relatively wide peaks are obtained, of which appropriately measured width can be regarded as an analytical signal. An analyte concentration in a sample can be determined after calibration, performed usually with a set of standard solutions.

Titration can be also performed when known, increasing volumes of titrant are introduced in turn into a stream of sample, and a height of signal received is regarded as an analytical signal [18]. Titration exploiting a monosegment generation [19] can be realized in flow injection manner, when solutions prepared using the same volume of sample and increased volumes of titrant are subsequently injected in a form of monosegments to a detector [20]. In *the* above examples titration curve of a shape similar to traditional is obtained, but the methods need additional calibration with the use of standard solutions to determine the relationship between volume of the titrant and analyte concentration. Another approach constitutes a flow-batch hybrid system with solenoid valves incorporated, in which titration is performed in a reaction chamber, whereas sampling and signal processing are done as in usual flow systems [21]. The system do not need calibration because *known* volumes of titrant and sample added to the reaction chamber are successively varied according to an appropriate algorithm applied in order to find the end point of titration.

Finally, some methods should be mentioned, in which titration is performed in a single sample volume in accordance with the IUPAC definition of titration. According to these procedures monosegments are formed in sequential [22] or flow injection manner [23–25] and small portions of titrant are added to [22,23] or generated (coulometrically) in [24,25] a monosegment containing

* Corresponding author. Tel.: +48 126632232; fax: +48 126632232.
E-mail address: janiszew@chemia.uj.edu.pl (J. Kozak).

0039-9140/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2009.02.053

measured volume of sample. The procedures, generally, resemble traditional batch titration, but provide considerable decrease in sample consumption.

Operation of most of the systems presented above was verified on the example of acid–base titrations [1,4,5,7–10,14–18,21,22]. The systems were subsequently applied to analysis of real samples. The acidity of vinegars [1,14], fruit juices [1,17], wine [1,21], beer [1], citric acid [1] and olive oil [12] was determined. Some of the approaches were implemented to the determination of ascorbic acid and Fe(II) in feed supplements [24] and to the determination of Fe(II) [20], phenothiazine derivatives [13] or amines and their hydrohalide salts [10] in pharmaceutical products. Examples of determination of hydrazine and ammonium in their mixtures [6], ionic surfactants [11], Fe(II) in commercial hydrogen peroxide [23], calcium and total hardness in water samples [22], chromium in high carbon ferrochromium [2] or bromine index and bromine number in petrochemicals [25] can be also found. Each of the presented approaches provides results with acceptable accuracy and precision. The precision of the reported results for all systems was lower than 6% (RSD). It can be noticed, that some of the systems can provide results with a very good precision (lower than 0.5%) [4,8,15,16] comparable with precision of conventional batch titrations. Regarding the time necessary for a sample analysis, it varies and hesitates between less than a half of minute [7] and about 12 min [2]. Sample consumption depends of the system used and, in the articles cited above, the least one was reported to be 100 μL [15,22].

In the approach proposed in this paper, titration is performed in a flow injection manner and exploits the merging-zone technique [26]. The concept of instrumental manifold is based on a versatile flow injection system designed to analytical calibration [27]. In the developed system, a procedure of controlled sample dilution has been introduced. According to it, a sample can be gradually diluted in the system and titrated at each dilution degree. Titration is performed when the same volumes of standardized titrant and sample are injected simultaneously into two streams of water and superimposed with each other during their flow a detector.

2. Experimental

2.1. Reagents and solutions

Analytical-reagent grade chemicals and doubly distilled water were used throughout.

Carbonate-free sodium hydroxide solution used as a titrant, of declared concentration 0.1 mol L^{-1} (Lach-Ner, Czech Republic), was standardized against potassium hydrogen phthalate (Lach-Ner, Czech Republic). EDTA solution used as a titrant was prepared by dissolving of the appropriately weighed amount of EDTA (Odczynniki Chemiczne, Polska) in buffer of pH 10.

The hydrochloric and acetic acid solutions used as synthetic samples were prepared from hydrochloric (35.6%, Chempur, Poland) and acetic (97.5%, Merck, Germany) concentrated acid solutions. Magnesium and calcium solutions used as standards and synthetic samples were prepared by appropriate dilution of Mg and Ca Titrisol solutions (Merck, Germany) with 1% (v/v) HCl.

Standards of water hardness WC-HARD-10X-1 (AccuStandard, USA) and IPE-MIN-001-AV (AccuStandard, USA), as well as certified reference material of natural river water ION-96.3 (Environment, Canada) were used for verification of the standard addition procedure.

Samples of vinegars commercially available in the Polish market were used. In pharmaceutical products: Magnum Forte (Zdrovit, Poland), Ozone Magnez (Sunlife, Poland) and Calcium Pliva (Pliva, Poland), Mg and Ca were determined. Tablets were dissolved in water and solutions were neutralized with 2 mol L^{-1} NaOH (POCh, Poland) before analysis.

The indicator solutions were prepared by dissolving of: (a) 0.4 g of bromothymol blue (POCh, Poland) in 25 mL of 96 % (m/m) ethanol (Polmos, Poland); (b) 0.2 g of phenolphthalein (POCh, Poland) in 70 mL of ethanol and (c) 0.5 g of eriochrome black T (POCh, Poland) in 75 mL of triethylamine (Chempur, Poland) and 25 mL of ethanol. Solutions (a) and (b) were filled up to 100 mL with water. Before measurements solutions (a) and (c) were diluted 100 times with ethanol:water mixture prepared in ratios 1:4 and 1:3 (v/v), respectively, whereas solution (b) was diluted 67 times with ethanol:water (1:3, v/v) mixture.

Solution of pH 10 were made by 10-fold dilution of the solutions prepared by dissolving of 67.5 g of NH_4Cl (POCh, Poland) in 570 mL of 25% NH_3 (POCh, Poland). 35.85 g of ethylenediaminetetraacetic acid magnesium disodium salt hydrate (Sigma–Aldrich, USA) was added if necessary. Solution was filled up to 1 L with water. Lanthanum chloride used as a spectral buffer was prepared by dissolving of 53.6 g of $LaCl_3$ (Merck, USA) in 1 L of water.

Chromium(III) nitrate (POCh, Poland) solution was used to establish experimentally (on the basis of spectrophotometric measurements) the capacities of some loops and tubes of the flow system.

2.2. Instrumentation

The automated flow injection system designed for the proposed approach is presented in Fig. 1. It consists of two LZ 2010 (Zhaofa, China) and two Minipuls 3 (Gilson, France) multichannel peristaltic pumps, two-positional valve (Zhaofa, China), two flowmeters (Alborg, USA), glass mixing chamber of capacity 1.5 mL, and the sample reservoir (SR). Magnetic stirrers MM 2A (Laboratorni Přistroje, Czech Republic) and MR 1000 (Heidolph Instruments, Germany) were also used. Tygon tubes and PTFE tub-

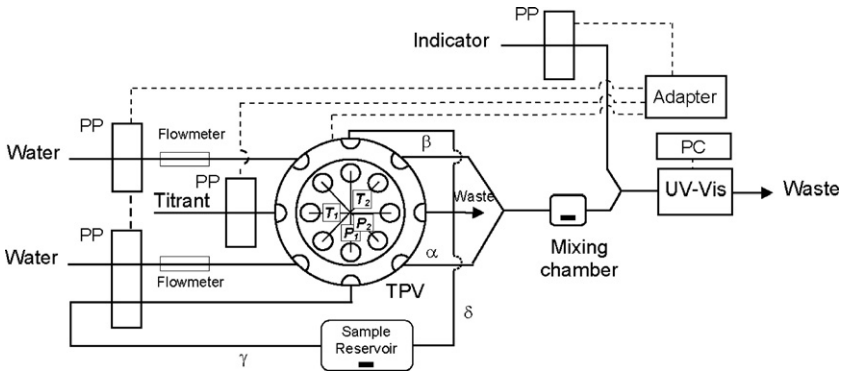

Fig. 1. Flow injection system. T_1, T_2, P_1, P_2 – injection loops, α, β, γ, δ – tubes, PP – peristaltic pump, TPV – two-positional valve.

ing (0.8 mm i.d.) were installed to the flow system. The system was operated under control of an electronic adapter made in our laboratory. Lambda 25 UV/VIS (PerkinElmer, USA) spectrometer equipped with a flow cell of width 10 mm (Hellma GMbH & Co., Germany) was used for detecting analytical signals at 620, 553 and 650 nm when bromothymol blue, phenolphthalein and eriochrome black T, respectively, were used as indicators. *The selected wavelength corresponds to the maximum absorption wavelength for the base and free states of the acid–base indicators and metal indicator, respectively.* Software UV WinLab (Perkin Elmer, USA) was applied for data collecting and handling.

2.3. Reference methods

Potentiometric titration and flame atomic absorption spectrometry were applied as reference methods. Mettler DL 25 (Metler-Toledo, Spain) automatic titrator equipped with glass electrode was used for the determination of total acidity with standardized sodium hydroxide solution (0.100 mol L^{-1}) as a titrant. Perkin Elmer 3100 (Perkin Elmer, USA) spectrometer with acetylene-air flame was used for the determination of Ca and Mg [28]. Magnesium and calcium hollow cathode lamps were operated at 8 and 10 mA, respectively. The wavelengths were set to 285.2 and 422.7 nm, respectively, with a spectral slit width of 0.7 nm.

2.4. Proposed procedure of titration

A sample solution of appropriate volume V_S (usually about 2 mL) was dosed to a SR. In initial valve position (shown in Fig. 1) the sample and titrant solutions filled loops P_1 and T_1, respectively, and diluent (water) was propelled through loops P_2 and T_2, merged with a stream of indicator and directed to a detector. When the valve position was changed clockwise, diluent was injected from loop P_2 to the sample reservoir causing dilution of the sample. At the same time, titrant and sample were simultaneously injected from loops T_1 and P_1 respectively, to the diluent streams. As loops P_1, P_2, T_1, and T_2 were of equal volumes, tubes α and β were of the same length (see Fig. 1) and two streams of diluent flowed with the same flow rates, the titrant and sample zones had a chance to be totally overlapped and then mixed and react with each other. The reaction product zone was then merged with indicator and directed to the detector. When the valve position was changed anticlockwise, titrant and diluted sample were injected again from loops T_2 and P_2, respectively, and the sample was titrated in the way described above. At the same time the sample was diluted again by diluent injected from loop P_1.

By this means, when the valve is turned off clockwise and anticlockwise, the sample solution is gradually diluted and successively titrated. Single dilution step took about 1 min. Degree of the sample dilution, k_n, at each of subsequent n step of dilution was calculated from the following equation:

$$k_n = \frac{V_D}{V_D - V_L} k_{n-1}; \quad k_0 = 1 \tag{1}$$

where V_L is the volume of injection loop and V_D is a total volume of dilution system (i.e. including volumes of sample: in sample reservoir, in tubes γ and δ and loop L). In the experiments described below volumes V_D and V_L were equal to 2046.7 and 74.8 μL (as mean volume of these established experimentally for the loops), respectively.

The signals were measured in the form of peaks. Depending on chemical and instrumental conditions peaks could increase or decrease during titration course. The titration curve was constructed as the relationship between peak area (integrated absorbance) and logarithm of the sample dilution degree (see Fig. 2). It has been experimentally revealed that dilution degree,

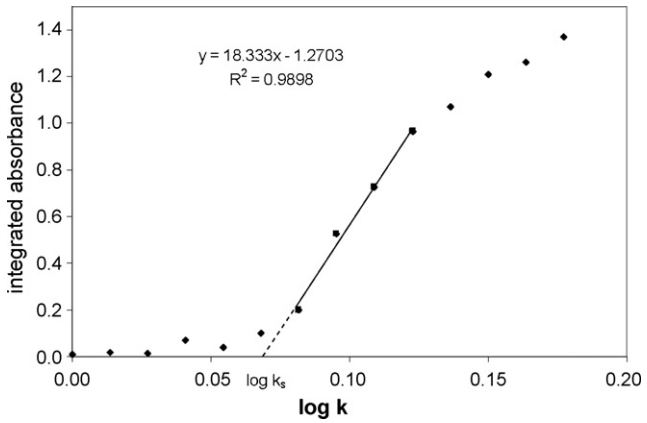

Fig. 2. Titration curve obtained in case of titration of HCl (0.220 mol L^{-1}) with the use of NaOH (0.100 mol L^{-1}); x – log k, y – integrated absorbance.

k_s, corresponding to the end point of titration can be found with good accuracy as shown in Fig. 2, i.e. by fitting the line to titration points and extrapolating this line to zero signal. In case of colour samples (e.g. samples of balsamic vinegar), the end point of titration was determined as an intersection point of two linear parts of titration curve. The analyte concentration, C_a, was calculated on the basis of k_s value, titrant concentration, C_T, and stoichiometry of reaction between the sample and titrant. For reaction of type $aA + bB \rightarrow cC + dD$ (where A is sample and B is titrant) the following equation is valid:

$$C_a = \frac{a}{b} C_T k_s \tag{2}$$

3. Results and discussion

3.1. Preliminary studies

In order to be sure that the sample and titrant zones are mixed totally and reaction is completed, the appropriate mixing device has been experimentally selected. Namely, hydrochloric acid (0.110 mol L^{-1}) was titrated with sodium hydroxide solution (0.100 mol L^{-1}) using bromothymol blue as indicator with: (a) no mixing device, (b) glass mixing device in a shape of tube (40 mm i.d., 70 mm length), and (c) mixing chamber of capacity 2 mL. The flow rates of the carrier and indicator streams were 1.8 and 3.0 mL min^{-1}, respectively. When no mixing device was used the results of determination were much different from the expected ($|RE| \cong 36\%$). Mixing device in a shape of tube did not improved the results satisfactorily ($|RE| \cong 19\%$), whereas the mixing chamber of capacity 2 mL allowed the results to be accurate ($|RE| \cong 0.3\%$). It was also checked that the chamber capacity can be reduced to 1.5 mL with no significant loss in accuracy of the determination.

In order to study the repeatability of peak area measurements, NaOH solution (0.100 mol L^{-1}) was used for titration of three solutions: water and hydrochloric acid of concentrations 0.090 and 0.135 mol L^{-1}. Each titration was repeated 12 times.

Since titrant and sample were injected alternately from loops T_1, P_1 and T_2, P_2, volumes of which differed slightly (randomly) from each other, fluctuations of peak area values were observed. When very low signals were measured (integrated absorbance <0.15, as for 0.135 mol L^{-1} HCl titrated) they fluctuated much more (RSD = 105%) than signals of integrated absorbance equal to about 1.00 (for 0.090 mol L^{-1} HCl titrated; RSD = 4%) and 2.00 (for water titrated; RSD = 0.7%). It shows that titration conditions (both chemical and instrumental) have to be preliminarily established to ensure the measurements of appropriately great signals.

Table 1
Results of titration of synthetic samples according to the proposed procedure.

Analyte	Concentration, mol L^{-1}			
	Expected	Found	RSD, %	RE, %
HCl	0.1100	0.1096	0.23	−0.35
	0.1100	0.1099[a]	0.14	−0.07
	0.2200	0.2187	0.26	−0.63
	0.4401	0.4544	0.31	3.26
	0.8801	0.9019	0.52	2.47
CH_3COOH	1.028	1.061	0.71	3.21
	1.714	1.763	0.39	2.86
Mg	0.01276	0.01284	0.43	0.63
Ca	0.01871	0.01888	0.73	0.91

[a] Mean value of results obtained for the sample analyzed in three different days.

3.2. Titration of test samples

The method was verified on the examples of acid–base and complexometric titrations including the determination of hydrochloric and acetic acids as well as magnesium and calcium in synthetic samples.

For acid–base titrations NaOH solution (0.100 mol L^{-1}) was used as a titrant, *and* bromothymol blue, and phenolphthalein were used as indicators in case of titration of hydrochloric and acetic acids, respectively. For complexometric titrations the EDTA solution of concentration 0.010 mol L^{-1} was used as titrant solution and eriochrome black T solution as an indicator [29]. In order to ensure the appropriate pH value for the reaction, titrant was prepared in buffer of pH 10. Moreover, in order to make the determination of Ca possible in such conditions, ethylenediaminetetraacetic acid magnesium disodium salt was added to the buffer. Water was used as a carrier during both acid–base and complexometric titrations.

In all cases titration was repeated thrice and mean value was regarded as an analytical result. *The results are presented in* Table 1.

All results were obtained with very good precision. The accuracy of the results is satisfactory and for all results lower than 3.3%. Time of a single analysis was comparable with time required for classical titration. The procedure proposed was characterized by low consumption of sample (about 2 mL or less), titrant (usually below 3 mL) and indicator (about 0.6 mL).

If the sample is too concentrated in relation to the titrant concentration, titration can take too much time. However, it is easy to solve this problem by diluting sample appropriately before titration. More serious difficulty appears when the analyte concentration in a sample is too low to be determined with the titrant used. The common approach is to use the titrant of less concentration (diluted). However, by doing so the signals measured can be so low that the end point of titration would be established with great error or it would be even not possible to be established at all. Therefore, another approach has been suggested in such cases: to add analyte in well-known amount to the sample and to determine the total analyte concentration in the sample by means of titration.

Table 3
Results of the determination of total acidity in samples of vinegars.

Sample	Vinegar	Total acidity, mol L^{-1}		
		Reference method	Proposed method	RSD, %
1	Vegetable	1.050	1.062	0.29
2	Wine	1.005	1.023	0.52
3	Wine	1.179	1.205	0.45
4	Wine	0.996	1.011	1.02
5	Balsamic	1.001	1.050	0.46
6	Balsamic	1.011	1.069	0.43
7	Balsamic	1.022	1.077	0.90
8	Spirit	1.670	1.708	0.42

In order to verify the proposed approach, three samples of HCl in concentration range from 0.022 to 0.088 mol L^{-1} were analyzed and water hardness was determined in three samples of water reference materials. In the former case, NaOH solution of concentration about 0.100 mol L^{-1} was a titrant and bromothymol blue an indicator. A solution of HCl of concentration 0.330 mol L^{-1} was used as the standard addition. In the *latter* case, EDTA titrant solution of concentration 0.010 mol L^{-1} and indicator eriochrome black T were applied. Solution containing Mg in concentration 0.0329 mol L^{-1} was exploited as the standard addition. Standards were added to samples in various amounts to reach increment factors IF (i.e. the ratio of the analyte concentration added, ΔC_a, to initially present in a sample) in the range from 1 to about 12. As during such a treatment the sample and standard solutions were diluted with each other with degrees k_a and k_Δ, respectively, analyte concentration in the sample was calculated according the following formula:

$$C_a = \left(\frac{a}{b} C_T k_s - \frac{\Delta C_a}{k_\Delta}\right) k_a \quad (3)$$

The results obtained are collected in Table 2.

It is seen that analytical results obtained by titration with using of standard addition can be obtained with satisfactory accuracy and precision in conditions typified by IF lower than 3. It is interesting that similar assumption is valid in the case of conventional calibration by the standard addition method [30].

3.3. Titration of real samples

The developed procedure has been exploited for the determination of total acidity in commercially available vinegars and of magnesium and calcium in pharmaceutical samples. Titration of each sample was repeated three times and mean result was considered as the final analytical result.

In case of the determination of total acidity, NaOH solution of concentration 0.100 mol L^{-1} was a titrant. Phenolphthalein was used as an indicator for titration of vinegars. Vinegar samples were diluted before determination. *An example of signals registered during a sample of wine vinegar titration is shown in* Fig. 3. The results are presented in Table 3 in comparison with those obtained by the potentiometric titration.

For the determination of Mg and Ca in pharmaceutical products, EDTA solution of concentration 0.010 mol L^{-1} and eriochrome black

Table 2
Results of titration performed according to the proposed procedure with standard addition.

Sample	Analyte	IF	Concentration, mol L^{-1}			
			Expected	Determined	RSD, %	RE, %
1	HCl	1.21	0.0880	0.0890	0.54	1.11
2		3.87	0.0275	0.0299	0.41	8.88
3		11.64	0.0220	0.0255	2.38	15.87
WC-HARD-10X-1	Water hardness	1.06	0.00999	0.00998	1.07	−0.13
ION-96.3		7.70	0.00336	0.00374	3.67	11.3
IPE-MIN-001-AV		12.23	0.00209	0.00251	2.46	20.4

Table 4
Results of the determination of Mg and Ca in pharmaceutical products.

Sample	Analyte	Concentration, mol L^{-1}		Concentration, mg/tablet		
		Reference method	Proposed method	Declared	Determined	RSD, %
Magnum Forte	Mg	0.01224	0.01203	300	292.5	0.23
	Mg	0.01284	0.01254	300	304.8	0.13
Ozone Magnez	Mg	0.01618	0.01558	200	189.3	0.31
Calcium Pliva	Ca	0.01792	0.01845	177	177.7	0.50
	Ca	0.01893	0.01920	177	184.9	0.15
	Ca	0.01850	0.01868	177	179.9	0.51

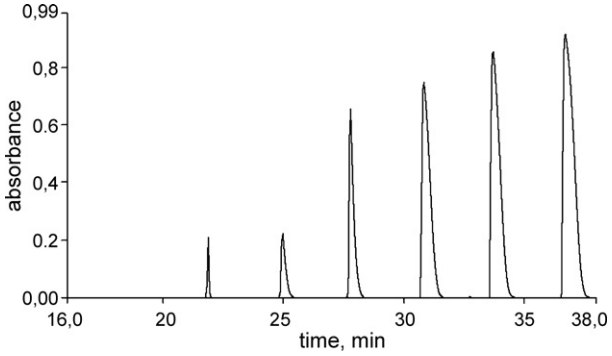

Fig. 3. Signals registered during titration of a wine vinegar.

T solution were used as titrant and indicator, respectively. Samples were diluted, if necessary. The results obtained by the method proposed and by FAAS as the reference method are shown in Table 4.

As seen, the results were obtained with good precision, mostly not exceeding 0.6% (RSD), comparable with the precision commonly provided by the reference methods used (it can be assumed to be <0.5% for potentiometric titration and <1.0% for FAAS). In all cases they were also in good agreement with the results obtained by the reference methods as well as with the results declared by the producers of pharmaceutics.

4. Conclusions

The concept of titration basing on the merging zones approach has been presented and verified. It is example how the flow injection titration procedure can imitate the conventional titration procedure, i.e. when well-known volumes of titrant are introduced into the sample and the analyte concentration is calculated on the basis of the titration curve constructed. However, in contrast to other similar flow injection approaches, the analytical result is calculated directly from measurement data obtained and no additional calibration with the use of standard solutions is needed to determine the relationship between the titrant volume and the analyte concentration. In addition, due to the merging-zone technique applied, *a small volume of a sample (about 2 mL) is titrated by a similar volume of a titrant and the total consumption of both solutions is very low.* The flow injection system used allows the sample dilution process to be strictly controlled and the titration procedure to be performed automatically. In general, it is simple, cheap and easily operated.

From the analytical point of view, the advantage of the developed procedure is that it provides results with good accuracy and precision comparable with precision of conventional titration procedures. The method can be recommended to analysis of real samples, especially to the determination of acidity in samples of vinegars or calcium and magnesium in pharmaceutical products. It can be especially useful for analysis of relatively concentrated samples, which should be, if necessary, appropriately diluted before titration. However, as revealed, if a sample is originally too diluted, the standard addition procedure can be applied provided that the ratio of the analyte concentration added to this initially present in the sample is lower than 3.

Although the approach has many advantages, the instrumental system developed seems still to be not flexible enough. The result of it is relatively long time of a sample analysis (comparing with time of other reported methods), similar to time of conventional titration performed manually. The modification of the system might concern incorporation in the system of solenoids valves in order to obtain possibility of optional sample and titrant volumes changing during the titration process. This would enable one to accelerate titration process by selecting of sample dilution degree during titration. The research work in this direction is going to be conducted in our laboratory.

References

[1] J. Marcos, A. Ríos, M. Valcárcel, Anal. Chim. Acta 261 (1992) 489.
[2] H. Katsumata, N. Teshima, M. Kurihara, T. Kawashima, Talanta 48 (1999) 135.
[3] O.T. Guenat, B.H. van der Schoot, W.E. Morf, N.F. de Rooij, Anal. Chem. 72 (2000) 1585.
[4] C.N. Yarnitzky, N. Klein, O. Cohen, Talanta 40 (1993) 1937.
[5] I. López-Garcia, P. Vinas, N. Campillo, M. Hernández Córdoba, Anal. Chim. Acta 308 (1995) 67.
[6] Z.K. He, B. Fuhrmann, U. Spohn, Anal. Chim. Acta 409 (2000) 83.
[7] P.K. Dasgupta, H. Tanaka, K.D. Jo, Anal. Chim. Acta 435 (2001) 289.
[8] H. Tanaka, T. Baba, Talanta 67 (2005) 848.
[9] J. Růžička, E.H. Hansen, H. Mosbaek, Anal. Chim. Acta 92 (1977) 235.
[10] C.A. Georgiou, M.A. Koupparis, Analyst 113 (1988) 755.
[11] C.J. Dowle, B.G. Cooksey, J.M. Ottaway, W.C. Campbell, Analyst 113 (1988) 117.
[12] E. Mariotti, M. Mascini, Food Chem. 73 (2001) 235.
[13] I. Němcová, K. Nesměrák, P. Rychlovský, J. Koutníková, Talanta 65 (2005) 632.
[14] M. Wójtowicz, J. Kozak, P. Kościelniak, Anal. Chim. Acta 600 (2007) 78.
[15] J.F. van Staden, H. du Plessis, Anal. Commun. 34 (1997) 147.
[16] J.F. van Staden, M.G. Mashamba, R.I. Stefan, Talanta 58 (2002) 1089.
[17] J. Jakmunee, T. Rujiralai, K. Grudpan, Anal. Sci. 22 (2006) 157.
[18] J. Bartroli, L. Alerm, Anal. Chim. Acta 269 (1992) 29.
[19] C. Pasquini, W.A. Oliviera, Anal. Chem. 57 (1985) 2575.
[20] M. Assali, I.M. Raimundo Jr., I. Facchin, J. Autom. Method Manag. Chem. 23 (2001) 83.
[21] R.S. Honorato, M.C.U. Araújo, R.A.C. Lima, E.A.G. Zagatto, R.A.S. Lapa, J.L.F. Costa Lima, Anal. Chim. Acta 369 (1999) 91.
[22] L. Alerm, J. Bartroli, Anal. Chem. 68 (1996) 1394.
[23] E.V. de Aguino, J.J.R. Rohwedder, C. Pasquini, Anal. Chim. Acta 438 (2001) 67.
[24] E.V. de Aguino, J.J.R. Rohwedder, C. Pasquini, Anal. Bioanal. Chem. 386 (2006) 1921.
[25] C. Pasquini, E.V. de Aguino, M. das Virgens Reboucas, F.B. Gonzaga, Anal. Chim. Acta 600 (2007) 84.
[26] E.A.G. Zagatto, F.J. Krug, F.H. Bergamin, S.S. Jorgensen, B.F. Reis, Anal. Chim. Acta 104 (1979) 279.
[27] P. Kościelniak, M. Wieczorek, J. Kozak, M. Herman, Anal. Chim. Acta 600 (2007) 6.
[28] International Standard PN-EN ISO 7980, 2002.
[29] International Standard PN-ISO 6059, 1999.
[30] P. Kościelniak, Chemometr. Intell. Lab. Syst. 47 (1999) 275.