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An automatic system for acidity determination based on sequential injection titration and the monosegmented flow approach

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ABSTRACT

An automatic sequential injection system, combining monosegmented flow analysis, sequential injection analysis and sequential injection titration is proposed for acidity determination. The system enables controllable sample dilution and generation of standards of required concentration in a monosegmented sequential injection manner, sequential injection titration of the prepared solutions, data collecting, and handling. It has been tested on spectrophotometric determination of acetic, citric and phosphoric acids with sodium hydroxide used as a titrant and phenolphthalein or thymolphthalein (in the case of phosphoric acid determination) as indicators. Accuracy better than |4.4|% (RE) and repeatability better than 2.9% (RSD) have been obtained. It has been applied to the determination of total acidity in vinegars and various soft drinks. The system provides low sample (less than 0.3 mL) consumption. On average, analysis of a sample takes several minutes.

1. Introduction

Titration is widely used for acidity determination in analytical practice. Automatic batch titrators are usually applied for this purpose. As their operation is often cumbersome, efforts have been made to rationalize the conventional titration procedure. A number of flow-based titration systems employed for acidity determination can be found in the literature, and some of them have been presented below.

Operation of some systems is analogous [1] or similar [2] to that of conventional batch titrators. In the systems, titration is performed using a single sample volume into which, e.g., a piston burette doses a titrant [1] or using many small sample volumes, which are titrated successively in order to obtain a titration curve [2]. Other systems, with solenoid valves incorporated, employ special optimization algorithms, like the Fibonacci method [3,4] or binary search concept [5,6] for the end point search. In these systems, the ratio of the introduced volumes of sample to titrant is successively varied to attain the end point of titration, which is usually gained when the established reference signal is obtained.

Regarding approaches based on continuous flow, a procedure exploiting variable flow-rate patterns to gradually increase the concentration of titrant in the system [7], has been presented. In the approach, determination of analyte concentration requires appropriate flow-rate measurements or additional calibration. Another strategy, carried out in a multicommutated flow system, is based on sequential insertion of increasing titrant and decreasing titrand volumes in a reactor in order to obtain a complete titration curve [8]. In this case, the method of assessing the end point is similar to that used in the conventional batch procedure.

Among flow injection (FI) approaches, a system based on exploiting signals corresponding to instantaneous concentration values of the sample or titrant obtained at given time intervals after injection [9] or a system that makes use of the merging-zone approach [10] are noteworthy. In the former case, the concentration gradient generated in the system has to be calibrated in order to convert the signals to instantaneous concentration values, whereas in the latter case, the titrant zone is merged in sequence with the sample zone diluted controllably during the analysis and the recorded peak area is used to construct a titration curve. Flow injection titration [11] has been applied to acidity determination in several systems [12–17]. In this approach, generally, a small volume of sample is injected into a stream of titrant and directed through a mixing chamber towards the detector. In conditions of high dispersion, the appropriately measured width of the registered signals can be treated as an analytical signal. It has been established, that a linear relationship between the peak width and logarithm of analyte concentration can be obtained in a relatively wide range. Calibration can be performed using the set of standards method [12–16] or the standard addition method [17]. FI titration has been successfully adapted to acidity determination using the sequential injection technique [18–21].

The above approaches have been applied to acidity determination in samples of vinegars [4,5,7,8,10,16,17,19,20], soft drinks

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[2,6,17,18], isotonic beverages [2,5], alcohol free beers [2], beers [7], industrial fruit juices [2,5], natural fruit juices [5–7,14,21,22], wines [3,7,9], colas [5,17], lemon soda [5], citric acids [7], oils [12,15] and rain drops [13].

In the monosegmented flow approach the sample zone is located between two gas bubbles, forming a monosegment [23]. This makes it possible to limit the influence of the liquid carrier on the analyte concentration in the sample located in the monosegment to such an extent that the dilution effect can be omitted during calculation of results. This concept has been applied in the rationalization of the calibration procedure using multicommutated [24] or sequential injection [25] systems. In both approaches, different, known quantities of a single standard solution are introduced into the monosegment, either after previous system calibration by controlling the time of introduction [24] or by direct control of the introduced volume [25].

In the present work, an automatic system for acidity determination in which preparation of a standard solution in a monosegmented sequential injection manner and sequential injection titration are coupled in a single procedure, is proposed. The results of system verification using synthetic samples and its application to determination of acidity of vinegars and soft drinks are presented.

2. Experimental

2.1. Reagents and solutions

Analytical-reagent grade chemicals and double distilled water were used throughout. Carbonate free sodium hydroxide solutions used as titrants were prepared manually by appropriate dilution of 0.1 mol L^{-1} NaOH stock solution (Lach-Ner, Czech Republic). The indicator stock solutions were prepared by dissolving 0.2 g of phenolphthalein (POCh, Poland) in 70 mL of ethanol or 0.3 g of thymolphthalein (POCh, Poland) in 90 mL of ethanol and making them up to 100 mL with water. 150 μL of phenolphthalein or thymolphthalein solutions were added to 100 mL of sodium hydroxide standard solution.

2.2. Samples

The phosphoric, acetic and citric acid solutions used as standards or samples were prepared from concentrated phosphoric (85%, Chempur, Poland) and acetic (96%, Merck, Germany) acid solutions or from citric acid monohydrate (Lach-Ner, Czech Republic), respectively. Vinegars and soft drinks samples used were commercially available on the Polish market. The samples of soft drinks were degassed for half an hour with the use of an ultrasonic bath (Polsonic, Poland).

2.3. Apparatus

The developed sequential injection system consisted of two valves: a 10-positional selection valve (Valco, USA) and a two-positional injection valve (Alitea Instruments, USA), and two pumps: peristaltic (Ismatec, Switzerland) and syringe (Alitea Instruments, USA); operation of the latter pump was modified in our laboratory. An electronic adapter designed by us (coupled to a computer) and appropriate software were applied to enable control of pumps and valves of the developed sequential injection system, on-time signal visualization, data acquisition and measurement of peak parameters. The syringe pump was used to control the volumes of solutions aspirated into the holding coil. Tygon tubes for carrier propulsion with the use of the peristaltic pump and PTFE tubing of internal diameters 0.8 (tubes and a mixing coil) or 1.6 mm (a holding coil and an auxiliary tube) were used. The length of the holding, mixing and auxiliary coils was 1000, 300 and 800 mm, respectively. A UV/Vis spectrometer model SPEKOL 11 (C. Zeiss, Germany) equipped with a 0.018 mL flow cell (Zhaofa, China) was used for detecting analytical signals at 553 (phenolphtalein) or 594 nm (thymolphthalein). The wavelength values correspond to the maximum absorption wavelength for the base states of the indicators.

2.4. Reference method

A conventional titration procedure with the use of a glass electrode and an automatic batch titrator (Mettler DL 25, Toledo, Spain) was applied as a reference method. In this case, sodium hydroxide solution of concentration 0.1000 mol L^{-1} used as a titrant was standardized against potassium hydrogen phthalate (Lach-Ner, Czech Republic).

2.5. Standard solutions generation

The sequential injection system developed for the research is presented in Fig. 1. Standard solutions necessary for analytical curve construction are prepared by successive aspirations to the holding coil of appropriate volumes of: air, diluent (water), standard, diluent (water) and air. This way, a monosegment of an established, known volume is created in the holding coil. Solutions in the monosegment are homogenized by mixing. This is performed by repeated, rapid moving of solutions in opposite directions. Then, the major part of the monosegment (segment of air and part of the standard solution) is directed to an auxiliary tube and, subsequently, the remaining part of the monosegment is removed from the holding coil and directed to the waste. Finally, the standard solution stored in the auxiliary loop can be titrated.

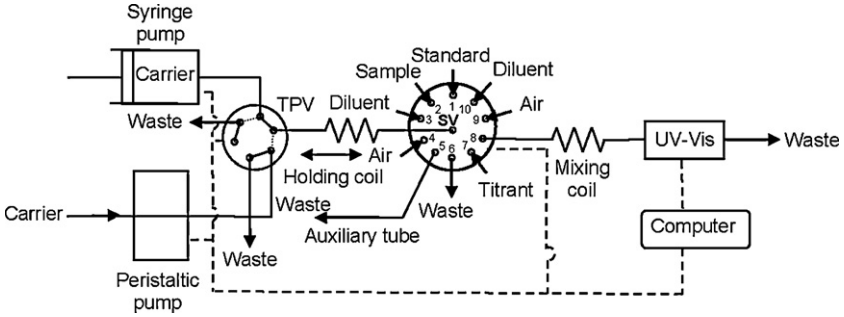

Fig. 1. Sequential injection system developed for acidity determination; TPV – two-positional valve, SV – selection valve.

2.6. Titration

The approach includes titration of the series of subsequently generated standard solutions and titration of a sample. The sample can be aspirated to the holding coil directly (without dilution) or can be diluted before the titration analogically to the standard solution.

The titration procedure encompasses aspiration of volumes of: titrant, sample or standard and titrant into the holding coil in the appropriate sequence. Then, the position of the two positional valve is changed and the carrier (water) which is propelled by a peristaltic pump, washes the solutions stored in the holding coil and directs them to the detector. As the dispersion in the system is high, relatively wide peaks are registered and the width of a peak is exploited as an analytical signal [26].

3. Results and discussion

3.1. Study of the titration system

A study of the titration system was performed using acetic acid as a sample, phenolphthalein as an indicator and sodium hydroxide (0.001 mol L^{-1}) as a titrant. At the beginning, standards prepared manually, with concentrations in the range from 0.0171 to 0.1882 mol L^{-1} were titrated. Concentrations of four synthetic samples of acetic acid were chosen in the range from 0.0343 to 0.1710 mol L^{-1}. The choice of the range was imposed by the average contents of acetic acid in commercially available vinegars (5–10%). A volume of 50 μL of standard or sample was selected to be introduced into the holding coil during titration. Solutions were introduced into a holding coil with a constant flow rate of 1.25 mL min^{-1}. The flow rate of carrier was 1.3 mL min^{-1}. Volumes of titrant equaling 1500 and 750 μL were introduced into the holding coil before and after the sample, respectively. The introduction of such volumes enabled peaks of various widths to be obtained, which could be measured in a repeatable way. A precision of width measurements of registered signals lower than 1.5% (RSD) was obtained. In these conditions, each standard solution of acetic acid was titrated three times and the mean of peak widths was taken into account during analytical curve preparation. The procedure was performed on three different days and linear calibration curves showing the dependence between peak width and the logarithm of sample concentration were obtained (R = 0.9992, 0.9962, 0.9997). Using the above analytical curves, the concentration of acetic acid samples was determined with both, accuracy (RE – relative error (%), RE = $((C_{det.} - C_{exp.})/C_{exp.}) \times 100$, $C_{exp.}$ – concentration of an analyte (calculated) in a synthetic sample (concentration expected), $C_{det.}$ – concentration of the analyte determined in the sample) and precision (RSD) lower than 2.3%.

3.2. Study of the standard generation system

In the presented procedure, it was proposed that a series of standard solutions of various concentrations should be generated in a monosegment formed in the holding coil using a single standard solution. To this end, acetic acid solution of concentration 0.2143 mol L^{-1} was used as a stock standard solution. NaOH solution (0.001 mol L^{-1}) and phenolphthalein were used as titrant and indicator, respectively. The total volume of monosegment was selected to be 500 μL. This volume was small enough to make it possible to completely homogenize the solution created. At the same time, this volume was sufficiently large to generate a number of standard solutions of required concentration. A schematic diagram of the standard generation procedure is presented in Fig. 2A–D. In order to create a monosegment into the holding coil: carrier (water, 200 μL), air (200 μL), diluent (water), standard, diluent (water) and air (150 μL) were introduced (Fig. 2A). Standard solutions of required concentrations, were generated by aspiration of the stock standard solution and diluent in various volume ratios (e.g., diluent-200 μL, standard-50 μL and diluent-250 μL) to obtain a total volume of 500 μL. Then, the generated standard solution was homogenized. For this purpose, 250 μL of

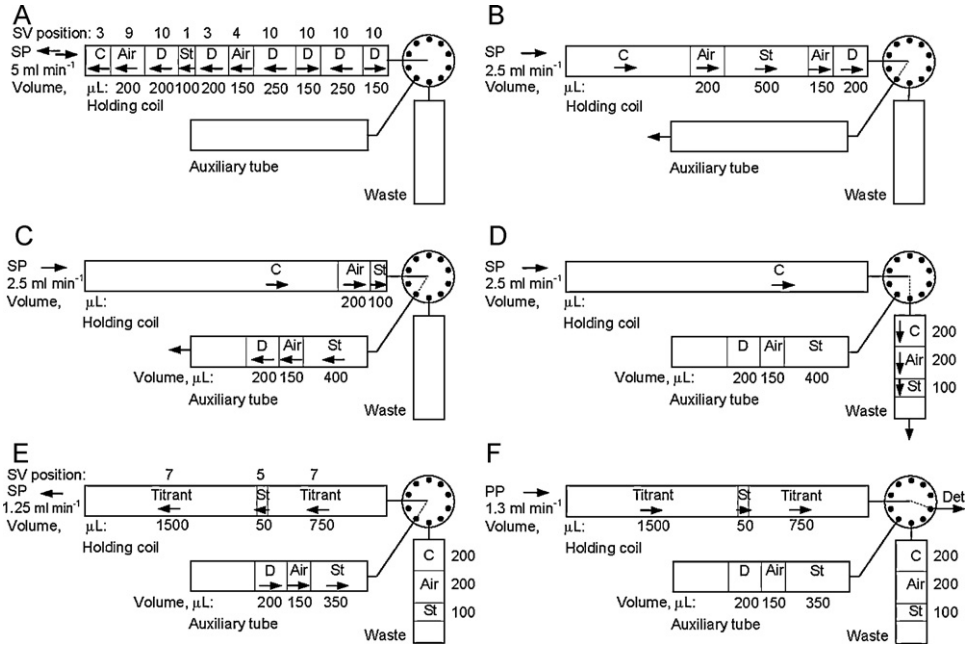

Fig. 2. Schematic diagram presenting procedures of standard generation (A–D) and titration (E and F); A – generation of a monosegment in the holding coil and homogenization of the generated standard solution, B – standard solution generated in the monosegment, C – transport of the generated standard solution from the holding coil to the auxiliary tube, D – transport of the solutions that remained in the holding coil to the waste, E – aspiration of titrant and the solution to be titrated to the holding coil, F – flow reversal and transport of the solutions to the detector; St – standard, D – diluent (water), C – carrier (water), SV position – selection valve position (according to Fig. 1), SP – syringe pump, PP – peristaltic pump.

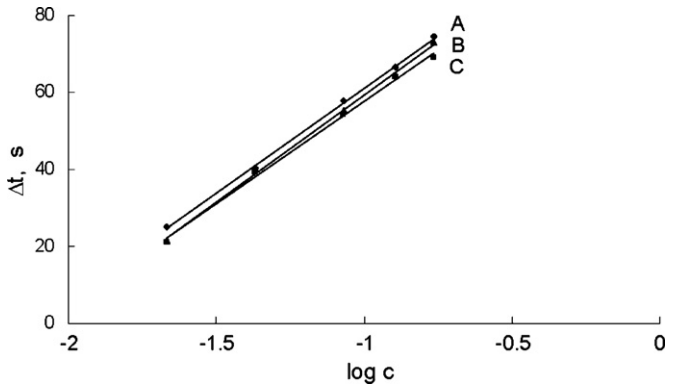

Fig. 3. Analytical curves obtained during titration of acetic acid in three different days; $y-\Delta t$ – width of a peak, c – concentration, $x-\log$ c; (A) $y=54.375x+115.51$, $R^2=0.9992$; (B) $y=53.237x+110.89$, $R^2=0.9974$; (C) $y=55.655x+114.99$, $R^2=0.9978$.

water (diluent in Fig. 2A) was aspirated into the holding coil, then the flow was reversed and 150 μL of water was removed. This procedure was repeated twice. The aspiration and mixing were performed with a flow rate of 5 mL min^{-1}. As the volumes of standard and diluent introduced into the holding coil were known, the concentration of generated standard solution (Fig. 2B) was calculated directly. After homogenization, water remaining in the holding coil (200 μL), air and generated standard solution (400 μL) were introduced into auxiliary tube (Fig. 2C). Then, the rest of the standard solution, air and some water were directed to waste (Fig. 2D). Subsequently, 50 μL of generated standard solution was taken from the auxiliary tube and titrated in the way described in the previous Section (Fig. 2E and F). The precision of signals obtained in such a mode was lower than 3% (RSD). Each standard solution was titrated two times and the mean was taken into account during construction of an analytical curve. Analytical curves registered in these conditions on three different days are presented in Fig. 3. As linear analytical curves were obtained, it was assumed that the system can be exploited for the purpose of controlled dilution not only of a standard but also of a sample solution, if necessary.

3.3. Procedure verification

The developed procedure was tested on determination of acetic, phosphoric and citric acids. Phenolphthalein (for acetic and citric acid titration) and thymolphthalein (for phosphoric acid titration) were applied as indicators. NaOH solutions of concentration

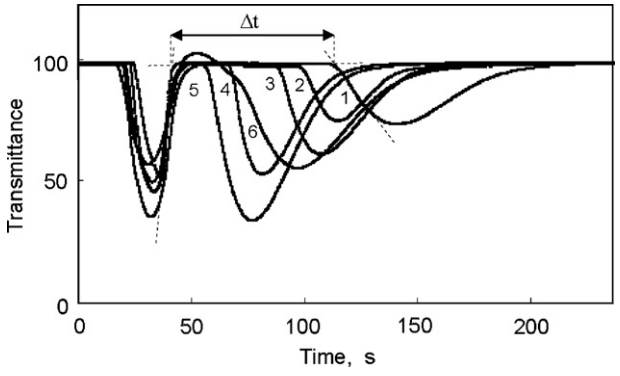

Fig. 4. Signals obtained during titration of standard solutions of phosphoric acid (1–5) of various concentration (0.0189, 0.0151, 0.0113, 0.00756, 0.00378 mol L^{-1}, respectively) and a sample of cola drink (6) and the way of peak width (Δt) measurement.

Table 1
Results of application of the proposed verification approach to titration of various acids.

Analyte	Concentration, mol L^{-1}		RSD, %	RE, %
	Expected	Determined		
Acetic acid	0.0429	0.0439	2.85	2.30
	0.107	0.105	1.07	−1.67
	0.171	0.170	1.19	−1.02
Phosphoric(V) acid	0.00966	0.0101	1.37	4.00
	0.0118	0.0113	0.66	−4.35
	0.0151	0.0148	0.32	−1.75
Citric acid	0.00784	0.00788	1.22	0.48
	0.0105	0.0101	0.60	−4.10

0.001 (for acetic acid titration) and 0.0005 mol L^{-1} (for phosphoric and citric acid titration) were used as the titrant. Stock standard solutions of acids of concentrations: 0.2143 (acetic acid), 0.0189 (phosphoric acid) and 0.0131 mol L^{-1} (citric acid) were applied. Using these solutions, five (acetic acid) or four (remaining acids) standard solutions in concentration ranges: 0.0214–0.2143 (acetic acid), 0.00380–0.0189 (phosphoric acid), 0.00261–0.0131 (citric acid) mol L^{-1} were generated. For each of the generated solutions, two signals were registered. Examples of peaks registered for phosphoric acid and the way of peak width measurement are shown in Fig. 4. Each sample was titrated three times and the results are presented in Table 1. It is seen, that the procedure can provide results with good precision (RSD < 2.9%) and accuracy (RE < 4.4%). A total amount, of less than 300 μL of sample is necessary to perform the whole procedure of titration (including three repetitions of the titration procedure). In the above conditions, about 7 mL of titrant is employed for a sample titration. The time necessary for dilution of a sample in the system and signal registration is about 7 min.

3.4. Analysis of real samples

The developed procedure was applied to acidity determination in samples of vinegars, cola drinks and drinks prepared on the basis of citric acid. Stock standard solutions of acetic (for vinegars titration), phosphoric (for cola drinks titration) and citric acids (for remaining drinks titration) of the same concentrations as in the previous Section were used. Drinks were degassed before analysis. Samples were diluted in the system before titration (vinegars ten times, other drinks in the ratio 3:2 (drink:water)). In the case of titration of a spirit vinegar sample, the first part of the titrant introduced into the holding coil had to be increased to 1800 μL in order

Table 2
Results of total acidity determination in vinegars and soft drinks.

Drink	Standard	Total acidity, mol L^{-1}		RSD, %
		Reference method[a]	Proposed method	
Balsam vinegar	Acetic acid	1.00	1.02	1.55
Spirit vinegar		1.67	1.67	1.71
Vegetable vinegar		1.05	1.06	2.05
Wine vinegar		1.01	1.03	2.71
Cola 1	Phosphoric(V) acid	0.00775	0.00744	0.88
Cola 2		0.00887	0.00871	2.16
Cola 3		0.00900	0.00867	0.96
Cola 4		0.00719	0.00732	1.43
Drink 1	Citric acid	0.0152	0.0153	1.76
Drink 2		0.0136	0.0139	0.50
Drink 3		0.0140	0.0143	3.02
Drink4		0.0126	0.0128	1.70
Drink 5		0.0144	0.0146	2.61

[a] Potentiometric batch titration.

to make it possible to measure signals width using the assumed mode. Each sample was titrated three times and the results are shown in Table 2 together with the results of traditional batch titration with potentiometric detection.

The results obtained with the proposed and reference methods do not differ by more than 4.2%. The precision (RSD) of the results obtained using the developed procedure is always lower than 3.1%, whereas the precision of the results achieved using traditional batch titration-lower than 0.5%. However, it should be noted, that the former precision is influenced by the precision of aspiration of the applied pump.

4. Conclusions

An automated sequential injection system, in which procedures of standard generation and titration can be performed simultaneously, has been developed and verified. The system enables one to generate a set of standard solutions by dilution of a single stock standard solution in a monosegment using the sequential injection approach and to subsequently titrate both, the standard solution generated and the sample. The system also enables controllable dilution of the sample, if necessary. Titration is performed by FI titration, carried out using sequential injection approach.

The system has been used for acidity determination in real samples. Results of good precision were obtained and they showed consistency with those given by the reference method. The proposed titration procedure is characterized by very low sample consumption (less than 300 μL). The consumption of titrant per sample titration was about 7 mL. The time necessary to obtain a sample signal is similar to that of other gradient titration methods. Sample dilution or standard generation in the system takes 3–4 min. The system is versatile and simple in terms of operation. The developed approach makes gradient titration easily adaptable to routine or process analysis. The above advantages make the developed approach competitive with other titration methods and easily adaptable to various kinds of titration.

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