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Application of flow-injection potentiometric system for determination of total concentration of aliphatic carboxylic acids

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ABSTRACT

In this work, flow-injection system with potentiometric detection was tested for determination of total carboxylic acid concentration. Detection part of the examined system consists of ion-selective electrodes (ISEs) with polymer membranes of different compositions. First electrode is based on Zr(IV)-tetraphenylporphyrin as ionophore selective towards carboxylic acid anions, the membrane of second one contains only liphophilic anion exchanger – tridodecylmethylammonium chloride. Final response of the system is a result of combination of EMF signals from both electrodes. Combination of two detectors enables significant decrease of differences between potentiometric signals induced by mixtures of studied anions of various concentrations as compared to results obtained only with metalloporphyrin-based ISE. The use of anion-exchanger based detector allows for elimination of the influence of aliphatic carboxylic acids lipophilicity.

Proposed potentiometric flow-injection system was employed for determination of short-chain aliphatic carboxylic acids (so-called VFA – volatile fatty acids) in samples originating from an anaerobic digester. Results obtained for these relatively complicated samples are in good agreement with results obtained with the use of reference colorimetric method.

Linear response towards carboxylic acids was observed in the concentration range of 10^{-4} to 10^{-2} mol dm^{-3}, with the slopes in the range of −110 to −150 mV dec^{-1} (for acetate$^-$ and butyrate$^-$, respectively). System enables for determination of about 6 samples per hour. Life time of ISEs average about 2 months.

1. Introduction

Organic aliphatic acids are commonly present in wide range of samples that originate e.g. from food and pharmaceutical industry. They occur as products of partial hydrolysis of larger compounds – carbohydrates, lipids and proteins. Total concentration of aliphatic carboxylic acids (so-called volatile fatty acids, VFAs) is also the main parameter that should be controlled during the anaerobic digestion process [1,2].

The method commonly used for the determination of total acidity of the sample is alkali titration using an appropriate visual indicator. However, titration based methods are not sufficiently selective and sensitive to precisely detect small amounts of acid content [3]. The application of chromatographic methods to determine organic acids allows to avoid these problems. Because of its speed, selectivity and sensitivity, gas chromatography (GC) and high performance liquid chromatography (HPLC) are the most widely used techniques [4]. To determine the organic acids in real samples, different detection methods have been combined with above-mentioned separation procedures. The use of direct UV–vis and fluorescence detectors is impossible because of the lack of chromophore/fluorophore groups in analyte structure. Only indirect optical methods can be used for quantification of these compounds [5,6]. Because of high concentrations of aromatic compounds in real samples, these techniques require derivatization, and/or other sample clean up procedure. Moreover, the use of indirect photometric detection is usually connected with the presence of high background contribution in analytical signal [3].

Liquid chromatography with electrochemical detection (LC-ED) offers very attractive analytical scheme in terms of selectivity, sensitivity and wide dynamic range. The most popular electrochemical detection technique is amperometry. Determination of electroactive organic acids by anion-exchange chromatography with copper-modified glassy carbon electrode allowed for separation of acids in less than 20 min and detection limits between 2 and 5 pmol [7]. Main disadvantage of constant potential amper-

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ometric detection is the loss of activity of noble metal electrodes (Pt, Au) during anodic detection of organic substances [7]. The use of pulsed amperometric detection (PAD) overcomes this problem. Alternating cathodic and anodic polarizations enable reactivation and cleaning of electrode surface [8]. Casella and Gatta developed HPLC–PAD electroanalytical procedure for determination of aliphatic acids without the use of a derivatization procedure. LODs for studied acids are generally between 0.5 μM (for formic acid) and 7 μM (for tartaric acid) [3].

Application of capillary zone electrophoresis (CZE) for organic acid determination offers a number of promising features like short analysis time and separation selectivity which could be different from chromatographic methods [9].

Recently, it has been shown that metalloporphyrin-based polymeric-membrane ion selective electrodes (ISEs) can be successfully employed for acetate anion determination. Metalloporphyrins have become interesting ionophore species [10], which enable to obtain anion sensors with selectivity patterns significantly different from the sequence based on ions' free energy of hydratation (so-called Hofmeister selectivity pattern). It has been shown that unique potentiometric selectivities observed for membranes doped with various metalloporphyrin results from selective interaction of analyte anion with the metal center of the porphyrin structure.

Yuchi and co-workers have shown that Zr(IV)-porphyrins can induce high selectivity towards acetate anions. However, no comprehensive research was conducted on this topic [11]. First, fully described potentiometric, polymeric-membrane ISE-based acetate sensor has been described in our group [12]. Among tested ionophores, Zr(IV)-tetra(tert-butylphenyl)porphyrin was found to be the best in terms of response time (20 s) and detection limit (2×10^{-4} M acetate$^-$). This compound induces the following selectivity sequence: $Cl^- < NO_3^- < SCN^- < ClO_4^- <$ acetate$^-$ $< F^-$, when incorporated into polymeric membranes.

In this work, novel flow-injection analysis system for the determination of total concentration of water-soluble aliphatic organic acids is described. Detection part of the system consists of two polymeric membrane ISEs with different membrane compositions. First electrode is based on Zr(IV)-tetraphenylporphyrin (ZrTPP) as ionophore selective towards carboxylic acid anions, the second one contains liphophilic anion exchanger – tridodecylmethylammonium chloride (TDMAC). Final response of the system is a result of combination of EMF signals from both electrodes. Theoretical basis of system final response calculations is discussed. Application of developed detection system for analysis of VFAs samples from methane fermentation reactor is also presented.

2. Theory

The aim of this work is to develop a potentiometric detector for the determination of total concentration of aliphatic organic acids. To achieve that, the selectivity of this detector towards all tested anions should be the same. This is, however, hard to accomplish using single polymeric-membrane ISE, as the selectivity of such electrode depends on both: ion–carrier interactions (described by complex formation constants) and liphophilicity of analyte and interfering ions (described by ion partition coefficients). It can be reasonably assumed that the interaction between metalloporphyrin molecule and carboxylic group of various aliphatic organic acids is very similar. However, the lipophilicity of different carboxylic acid anions vary significantly and depends strongly on the length of the aliphatic chain. Accordingly, more lipophilic anions (i.e. with longer aliphatic chain) generate stronger potentiometric response, as compared to anions of short-chain acids. It is therefore evident that to achieve similar potentiometric response towards various carboxylic acid anions, the lipophilicity component should be suppressed. The application of additional, ion-exchanger based electrode seems to be feasible for that purpose, as the selectivity of such electrodes depends only on the liphophilicity of tested ions. Thus, by subtracting the potentiometric signal recorded for ion-exchanger based electrode from the ionophore-based electrode signal, the information on the total concentration of carboxylic acid anions could be obtained.

Selectivity of ISEs is usually shown using selectivity coefficients. In 1976 IUPAC commission recommended two procedures enabling determination selectivity coefficients: separate solution method (SSM) and fixed solutions method (FIM) [13]. Both methods can be used for consideration of the selectivity of our two-electrode system, as SSM and FIM are derived from Nikolski–Eisenman equation. SSM is used in this paper just for convenience.

Selectivity coefficient according to separate solutions method is defined as [14]:

$$\log\ K_{I,J}^{pot} = \frac{(E_J - E_I)z_I F}{RT \ln 10} + \left(1 - \frac{z_I}{z_J}\right) \log\ a_I \tag{1}$$

In the case of all studied short chain carboxylic acid anions (acetate$^-$, propionate$^-$, butyrate$^-$), $z_I = z_J = -1$, so Eq. (1) can be simplified to:

$$\log\ K_{I,J}^{pot} = \frac{(E_J - E_I)F}{RT\ \ln\ 10} \tag{2}$$

for E_J and E_I defined as:

$$E_J = E_{J_C} - E_{EX} \tag{3}$$

$$E_I = E_{I_C} - E_{I_{EX}} \tag{4}$$

where E_{J_C} and $E_{J_{EX}}$ are potentials for electrode with membrane containing ionophore (C-index) and for electrode with membrane with ion exchanger (EX-index) obtained using separate solution method for primary ion I and interfering ion J, respectively. The membrane potential for membrane with incorporated ionophore can be described as:

$$E_{J_C} = \frac{RT}{F} \ln\ a_{J_C} \tag{5}$$

The respective membrane potential for membrane containing ion exchanger $E_{J_{EX}}$ can be written in complete analogy. For membranes without incorporated ionophore, the ion activity is given by the charge balance equation (according to [15]):

$$a_{J_{EX}} = \frac{\gamma_J R_{T_{EX}}}{Z_J} \tag{6}$$

where γ_J is the activity coefficient for the ion J (or I, respectively) and R_T is the concentration of lipophilic anionic site additives (TDMAC). Ion activity for membrane containing ionophore, according to [15], can be defined as:

$$a_{J_C} = \frac{\gamma_{IL_n} R_{T_C}}{Z_J \beta_{IL_n}(L_T - nR_{T_C}/ZJ)} \tag{7}$$

Eqs. (3) and (4) can be rewritten using the combination of Eqs. (5)–(7):

$$E_J = \frac{RT}{F} \ln \left[\frac{R_{T_C}}{\beta_{JL}(L_T - R_{T_C})R_{T_{EX}}} \right] \tag{8}$$

$$E_I = \frac{RT}{F} \ln \left[\frac{R_{T_C}}{\beta_{IL}(L_T - R_{T_C})R_{T_{EX}}} \right] \tag{9}$$

where β_{JL} and β_{IL} are the complex formation constants for the primary (I) and interfering (J) ion–ionophore complex with the stoichiometric factor n, which for all studying complexes equals 1. The

Table 1
Compositions of the membranes of electrodes used as detectors in flow-injection system dedicated to volatile fatty acids (VFAs) determination.

	Ionophore-based membrane	Ion-exchange-based membrane
Ionophore/ion exchanger	Zr(IV)[TPP]Cl_2 1 wt%	TDMAC 1 wt%
Polymer	PVC 33 wt%	PVC 33 wt%
Plasticizer	oNPOE, 66 wt%	oNPOE, 66 wt%
Ionic additives	KTFPB 5 mol %[a]	–

[a] According to ionophore.

symbol L_T is the total concentration of ionophore in the membrane. Eq. (10) arises by inserting Eqs. (8) and (9) to Eq. (2).

$$\log K_{I,J}^{pot} = \frac{\ln R_{T_C}/\beta_{IJ}(L_T - R_{T_C}) \cdot \beta_{IJ}(L_T - R_{T_C})/R_{T_C}}{\ln 10} \quad (10)$$

Eqs. (8) and (9) differ only with complex formation constants. In studied case, all measured anions (acetate$^-$, propionate$^-$, butyrate$^-$), interacting with ionophore through carboxylic group. If we assume that $\beta_{JL} = \beta_{JL}$, because the length of aliphatic acid chain does not have an influence on the complex formation constant, Eq. (10) can be rewritten as:

$$\log K_{I,J}^{pot} = 0 \quad (11)$$

$$K_{I,J}^{pot} = 1 \quad (12)$$

Thus, the selectivity of the two-detectors system equals 1 and the total concentration of aliphatic carboxylic acid anions can be determined.

3. Experimental

3.1. Reagents

All aqueous solutions were prepared with salts, bases or acids of the highest purity available from Fluka. Solutions of aliphatic carboxylic acids anions were prepared by dissolving sodium salts of examined anions (acetate$^-$, propionate$^-$, butyrate$^-$) in buffer solutions. The 0.1 M glycine (Gly), adjusted to pH 3.0 using H_3PO_4, was used as a buffer solution for all measurements.

Ionpohore: dichloro(5,10,15,20-tetraphenylporphyrinato) zirconium(IV) (Zr(IV)[TPP]Cl_2) was received from Porphyrin Systems, Norderstedt, Germany.

For membrane preparation, poly(vinyl chloride) (PVC), *o*-nitrophenyloctylether (*o*-NPOE), potassium tetrakis[3,5-bis(triflouromethyl)phenyl]borate (KTFPB), tridodecylmethylammonium chloride (TDMAC) and tetrahydrofuran (THF) were used as received from Fluka. The concentration of VFAs was determined using Macherey-Nagel Nanocolor LKT 3000 test tubes (method no. 0-50).

3.2. ISE membranes formulation

Polymer membranes employed for ISE measurements consisted of 1 wt% of Zr(IV)[TPP]Cl_2 or TDMAC, PVC/*o*-NPOE (1:2) polymeric matrix and, for ionophore-based membrane, 10 mol% of lipophilic additives (see Table 1). All components were dissolved in 2 ml of THF and the mixture was cast into 24-mm-i.d. glass ring placed on a glass slide. The solvent was allowed to evaporate overnight, leaving an approximately 0.15 mm-thick membrane. Five-mm diameter discs were cut out from this parent membrane and mounted in Philips electrode bodies (IS-561) (Glasblaserei, W. Moller AG, Zurich, Switzerland). Before use, electrodes were conditioned overnight in sodium chloride 0.01 M solution (with the addition of sodium butyrate -10^{-5} M for ionophore-based membrane).

3.3. EMF measurements in stationary system

Electrochemical potentials were measured with the following galvanic cell: Ag/AgCl(s), KCl (1 M)/bridge electrolyte/sample solution/ion-selective membrane/inner filling solution/AgCl(s)/Ag. The bridge electrolyte of the double-junction reference electrode was 1 M KCl. A 10^{-2} M NaCl served as the inner filling solution. EMF values were measured at ambient temperature (~22 °C) with Lawson multichannel mV-meter coupled to a computer for data acquisition.

3.4. EMF measurements in flow-injection system

Syringe pump (New Era Pump System Inc., model: NE-1000, Hamilton Co., UK), equipped with 100 mL syringe, was used to induce a flow through the system. An injection valve (Upchurch Scientific, Inc., USA) with 300 μL sample loop was employed to introduce samples into the system. Ion-selective electrodes, working as detectors, were mounted in a wall-jet mode using custom made adapter. Whole flow-through system was assembled using Teflon tubing of 0.8 mm internal diameter.

Concentrated solutions of carboxylic acids mixtures, artificial as well as real samples, because of its high total lipophilicity, interact strongly with membrane of ISEs, what causes signals tailing and asymmetry. Thus, the signal analysis in this work was based on signal area, rather than signal height.

3.5. Anaerobic digestion process

The experimental set-up used in this study is shown in Fig. 1. It consisted of a stirred tank bioreactor Biostat Bplus (Sartorius, Germany) of 2L working volume, equipped with temperature regulation, pH monitoring systems and water displacement system for biogas collecting. The batch fermentation in mesophilic conditions (35 ± 0.2 °C) was carried out without pH regulation. Bioreactor worked in sequential mode witch different cycle times. Bioreactor content was agitated by paddle stirrer (50 rpm). Aqueous solution of low-fat milk powder served as a substrate for fermentation (20 g L^{-1}). Bioreactor was seeded by fully developed anaerobic sludge. The supernatant from liquid samples, that were taken irregularly during the stable methanogenic fermentation process, was used for the volatile fatty acids concentration measurements for the sensor investigations.

3.6. Sample preparation

Supernatant from biomass separation (centrifugation: 5 min, 8000 rpm) was used for all VFAs concentration measurements. VFA concentration was determined using developed flow injection potentiometric system, described above. As a reference method, Macherey-Nagel Nanoclor LKT 3000 test tubes (method no. 0-50), was used. Samples were diluted with water (for colorimetric analysis) or glycine buffer solution (for potentiometric measurements). All spectrophotometric measurements were carried out on Perkin Elmer Lambda 25 UV-Vis spectrophotometer.

4. Results and discussion

First fully described, polymeric-membrane ISE selective towards acetate anion, has been described in our group [12]. It was shown that zirconium porphyrin-based electrodes induce strong potentiometric response towards acetate ion, when incorporated into polymeric membranes. During further studies, it was found that these electrodes show potentiometric response also towards other aliphatic carboxylic acid anions, like formate$^-$, propionate$^-$, and butyrate$^-$. Calibration curves obtained for

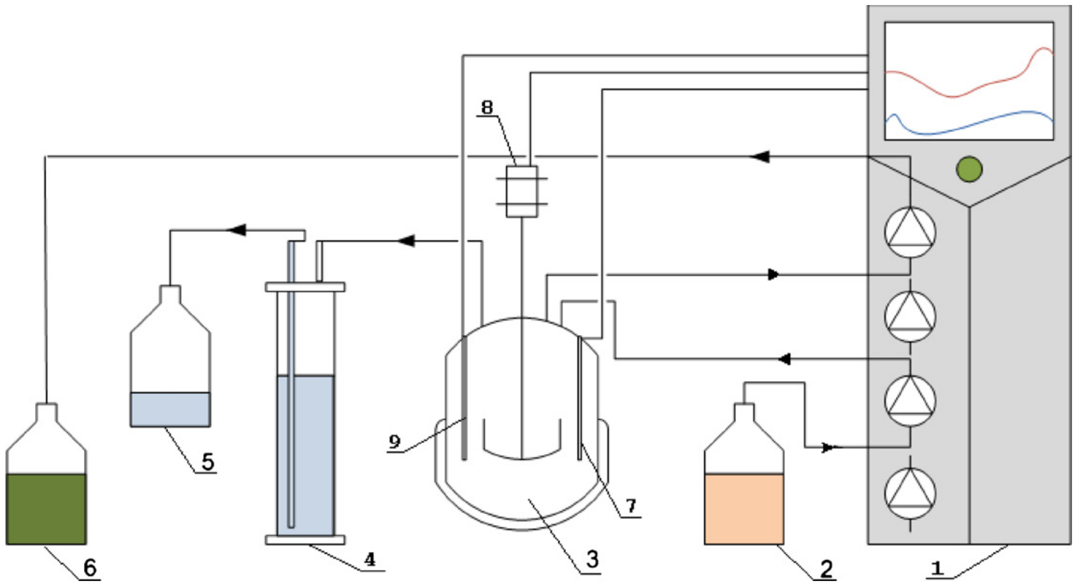

Fig. 1. Anaerobic digestion set-up: 1 – biostat B plus control unit, 2 – substrate container; 3 – 2L bioreactor vessel; 4,5 – water displace system for biogas collecting, 6 – effluent container; 7 – temperature sensor; 8 – impeller, 9 – pH sensor.

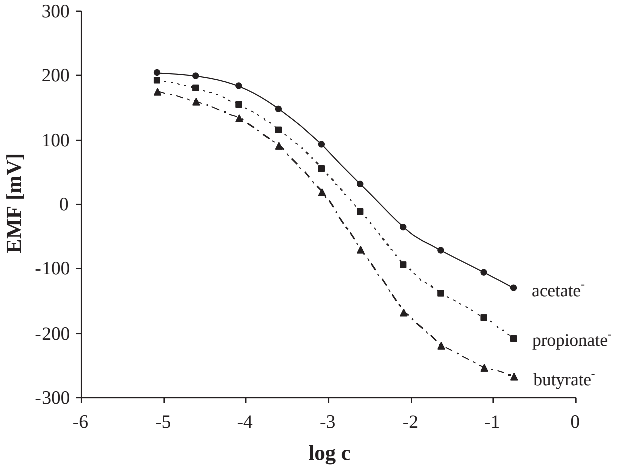

Fig. 2. Calibration curves obtained for ISE containing Zr(IV)[TPP]Cl_2 as ionophore. Measurements in 0.1 M Gly buffer, pH 3.0.

ISE containing Zr(IV)[TPP]Cl_2 as ionophore are presented in Fig. 2. Linear response towards carboxylic acids was observed in the concentration range of 10^{-4} to 10^{-2} mol dm^{-3}, with the slopes in the range of -110 to -150 mV dec^{-1} (for acetate$^-$ and butyrate$^-$, respectively). Selectivity of tested membranes, was evaluated using separate solutions method (SSM). The following values of selectivity coefficients for inorganic interfering anions (given as log $K^{pot}_{Ac^-,Y^-}$) were obtained: -4.6 ($Y = Cl^-$), -2.9 (NO_3^-), -0.3 (SCN^-), -0.1 (ClO_4^-), 0.6 (F^-) [12]. Cross sensitivity for tested carboxylic acid anions, calculated according to SSM, log $K^{pot}_{Ac^-,Y^-}$, are as follows: 0.6 (Y = propionate$^-$), 1.2 (Y = butyrate$^-$). It should be mentioned that the values of all selectivity coefficients should be treated as approximate, due to super-Nernstian slopes of calibration curves towards acetate (also for propionate$^-$ and butyrate$^-$), recorded for electrodes with tested membranes.

Differences in sensor responses towards various aliphatic carboxylic acid anions arise from differences in liphophilicity of these anions. *n*-Octanol/water partition coefficients calculated in ALOGPS 2.1 program using artificial neural networks are as follows: -0.20, 0.49, 1.16 for sodium acetate, sodium propionate and sodium butyrate, respectively [16–18].

Determination of aliphatic carboxylic acids has been carried out in flow-injection system (FIA). The experimental setup for FIA measurements is presented in Fig. 3. ISEs discussed above have been used in this system as detectors. Each electrode was placed in wall-jet cap, directing the buffer solution stream directly towards the sensing membrane. 0.1 M glycine (Gly) buffer solution (pH 3.0) was used, as it is the most favorable for obtaining potentiometric response porphyrin-based electrodes.

First, proposed system was used to evaluate the possibility of total VFAs concentration determination in artificial samples. Solutions of VFAs with different total concentrations of anions (acetate$^-$, propionate$^-$, butyrate$^-$), as well as different ratios of these anions were prepared. Example of dynamic response towards

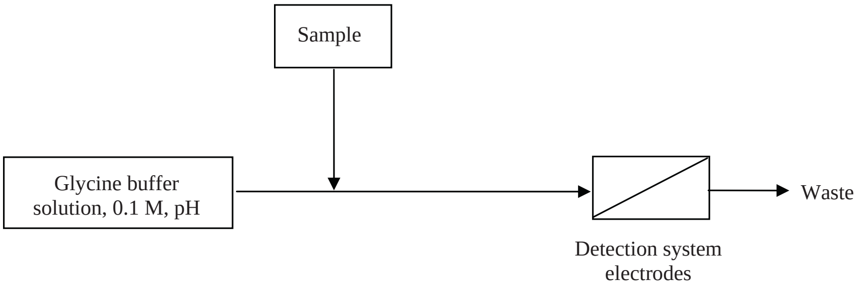

Fig. 3. Measurement setup for flow-injection analysis (FIA) of aliphatic carboxylic acids, used in this work.

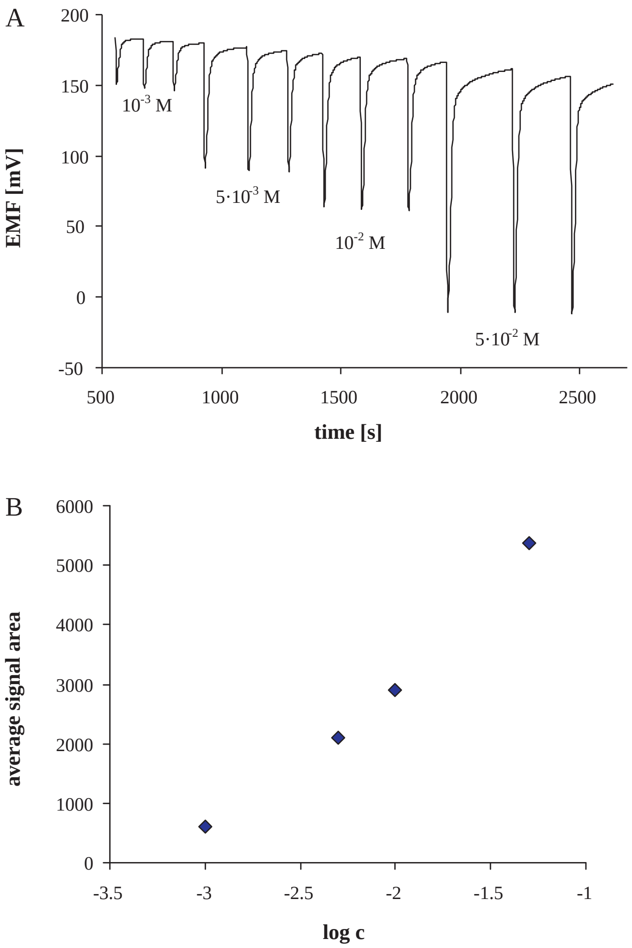

Fig. 4. Dynamic response towards aliphatic acids anions mixture. (acetate^{-}:propionate^{-}:butyrate^{-} 3:1:1) solutions (concentrations given in the figure) – A; and corresponding calibration curve obtained for ISE containing Zr(IV)[TPP]Cl_2 as ionophore measured in 0.1 M Gly buffer, pH 3.0 – B.

aliphatic acid anions mixture (acetate^{-}:propionate^{-}:butyrate^{-} 3:1:1) solutions obtained in flow system for ISE containing Zr(IV)[TPP]Cl_2 as ionophore are presented in Fig. 4. Electrode response is repeatable and EMF signal is linearly dependent on the total concentration of volatile organic acids. In Table 2, final system responses – ΔEMF, are presented. Responses of both ISEs towards anion mixtures with different ratios of acetate^{-}, propionate^{-} and butyrate^{-} (Ac^{-}, Pr^{-}, Bu^{-}, respectively) are compared. Combination of two detector electrodes enables significant decrease of differences between responses to mixtures of various compositions, as compared to the results obtained with porphyrin-based ISE only.

Total VFAs concentration measurements in samples from methane fermentation process.

To verify the usefulness of presented system, the determination of total concentration of VFAs in samples from methane fermentation process has been performed.

Anaerobic digestion is a complex biochemical process which can be divided up to four main phases of organic substrate degradation, namely hydrolysis, acidogenesis, acetogenesis and methanogenesis. Each of these individual phases is carried out by different group of microorganisms which has different environmental requirements [19].

The complex microbial population responsible for biogas production exist in a dynamic equilibrium. The process is sensitive to many chemical and physical factors. An increase in volatile fatty acids concentration, for example, and decrease in the pH of bulk

Table 2
Comparison of final system responses – ΔEMF for both ISEs towards anion mixtures with different ratios of acetate^{-}, propionate^{-} and butyrate^{-} (Ac^{-}, Pr^{-}, Bu^{-}, respectively).

VFAs mixture solution composition (total anions concentration: 0.01 M)	Acetate^{-}	Propionate^{-}	Butyrate^{-}	Ac^{-}/Pr^{-}/Bu^{-} 1-1-1	Ac^{-}/Pr^{-}/Bu^{-} 3-1-1	Ac^{-}/Pr^{-}/Bu^{-} 1-3-1	Ac^{-}/Pr^{-}/Bu^{-} 1-1-3	Ac^{-}/Pr^{-}/Bu^{-} 1-2-2	Ac^{-}/Pr^{-}/Bu^{-} 2-1-2	Ac^{-}/Pr^{-}/Bu^{-} 2-2-1
Porphyrin-based membrane electrode average peak area	857.5 ± 9.2 $n = 4$	902.3 ± 5.2 $n = 4$	1106.1 ± 10.9 $n = 4$	987.4 ± 12.3 $n = 4$	903.5 ± 12.2 $n = 4$	987.2 ± 12.3 $n = 4$	1095.4 ± 12.9 $n = 4$	1061.6 ± 7.7 $n = 4$	1017.8 ± 8.2 $n = 4$	937.1 ± 9.1 $n = 4$
Ion exchanger-based membrane electrode average peak area	25.5 ± 0.6 $n = 4$	79.8 ± 1.1 $n = 4$	256.5 ± 0.1 $n = 4$	125.5 ± 0.7 $n = 4$	80.6 ± 1.1 $n = 4$	103.0 ± 0.8 $n = 4$	169.8 ± 1.1 $n = 4$	122.9 ± 1.2 $n = 4$	124.8 ± 1.1 $n = 4$	90.2 ± 1.1 $n = 4$
ΔEMF	832.0	822.6	849.6	862.0	822.9	884.2	925.6	938.7	893.0	846.9

Table 3
The results of VFAs total concentration measurements in samples from methane fermentation reactor using potentiometric detection system and colorimetric Nanocolor LKT 3000 reference method.

Sample no.	Nanocolor LKT 300	Potentiometric flow-injection system
1	4.32×10^{-3} M	4.03×10^{-3} M
2	1.47×10^{-3} M	1.83×10^{-3} M
3	1.17×10^{-3} M	1.08×10^{-3} M

solution, subsequently inhibits the methanogensis step and leads to process failure. The interdependence of the different microbial groups involved in anaerobic digestion is the main cause of the process instability [20].

Sample solutions, prepared as described above, were injected into the system. Measurements with colorimetric commercial reference method (Nanocolor LKT 3000 test tubes) were carried out on the same day. Results, compiled with those obtained with the use of reference method, are presented in Table 3. The results of VFAs – determination with presented potentiometric flow-injection system are in good agreement with results obtained using Nanocolor LKT 3000 commercial method. This confirms the usefulness of proposed system and method for real-life applications.

5. Conclusions

Based on the data presented above, it can be summarized that presented flow-injection system with potentiometric detection dedicated to determination of aliphatic carboxylic acids total concentration can be successfully used in real-life samples analysis. In the contrary to optical methods, sample turbidity and color does not pose any difficulties. Because of the reduction of sample pretreatment and the use of ISE in flow-through system, there is a possibility of system automation and on-line analysis. Additional advantage of proposed system is its relatively low cost, especially in comparison to chromatographic methods.

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