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Quantitative Analysis of The Inorganic Content in Aqueous Solutions Based on Selective Membrane Dialysis and Electric Current Measurement

Anastas Dimitrov Dakashev, Krasimira Angelova Stancheva

Department of Inorganic and Analytical Chemistry, Prof. Dr. Assen Zlatarov University, 8010 Bourgas, Bulgaria

Abstract

Quantitative chemical analysis of ion species in aqueous solutions is performed. It is based on dialysis in an aqueous solution with ion exchange membranes and indication of the dialysis process by galvanic current created in a dialysis cell having one or two membranes. An analyte solution is set on one side of the membrane(s) and water on the other side of the membrane(s). A standard solution of the species under investigation is added to a measured volume of the water in a stepwise manner. Thus a solution with known concentration is created after every single addition of the standard solution. Different concentration gradients of analyte species form across the membrane(s) in this way. The analyte concentration is determined by finding graphically the standard solution volume corresponding to the zero concentration gradient. Five different modifications of the method are developed allowing analysis of concentrated solutions, fast or more accurate and precise determination, as well as pH determination. The method can be applied to the analysis of mineral content in sea water, mineral water and sylvenite.

Keywords: Selective membrane dialysis; electric current indication; quantitative analysis in aqueous solutions.

1. Introduction

Important applications of dialysis with ion selective membranes are removal of inorganic ion pollutants from water [1–3] and recovery of valuable metals from diluted solutions, e.g. rinse waters after metal plating [4]. The analytical implementation of dialysis is mainly for sample pretreatment in Flow injection analysis [5, 6]. The process is a useful technique for preconcentration and separation of metal ions [7]. Recently an unusual method of titration using selective membranes was developed in our laboratory [8]. The titrant is added continuously to the analyte by means of electrodialysis. In the present work, a method of analysis is proposed in

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which a dialysis process with selective membranes and a current created in this process are employed to determine an electrolyte concentration in aqueous solutions.

2. Principle of the method

When dialysis is carried out with a dialyzer as shown in Fig. 1, consisting of one or two ion-exchange membranes (cation exchange or/and anion exchange), a selective transport of ions with identical charges (positive or negative) occurs.

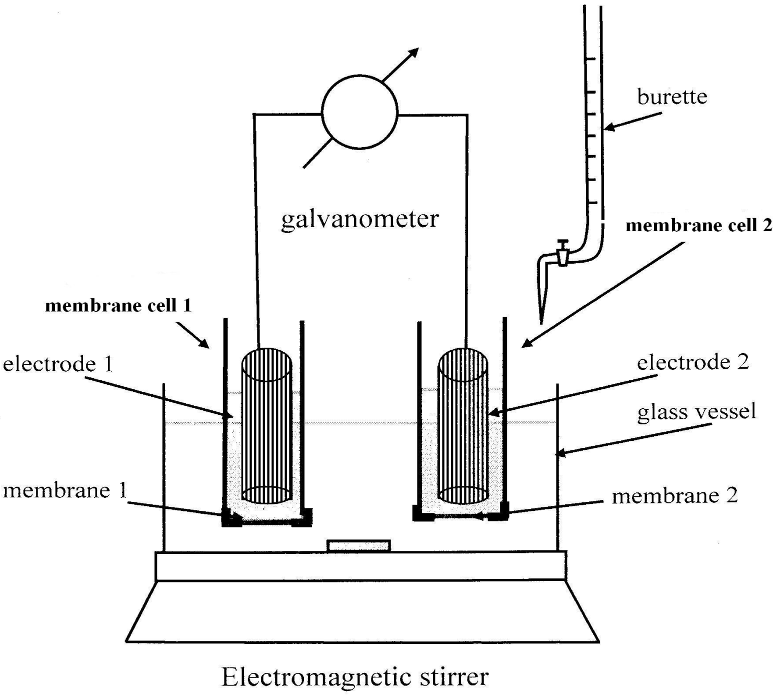


Fig.1. Experimental setup for Dialysis amperometry.

The kinetic movement of the ions tends to drive them through the membrane in the direction of the lower concentration. A cation exchange membrane permits only positive ions to pass through it. An anion exchange membrane permits only passage of negatively charged ions. The rate of movement of any species through the ion-exchange membrane is proportional to the concentration gradient across the membrane according to the Fick's law of diffusion. As a result of the dialysis process, a charge potential forms on each side of the membrane. Actually, the dialyzer becomes a galvanic cell. The low intensity current, which appears in this cell, is suitable for indicating the dialysis process. In order to determine the concentration of an electrolyte, concentration gradient across the membrane(s) is formed as the analyte solution is set on one side of the membrane(s), and on the other side of the membrane(s) a solution of the same electrolyte is created and its concentration changes. Various concentrations for this solution are achieved as different volumes of a standard solution of the electrolyte are consecutively added to a measured volume of distilled water. Thus the concentration of this solution is known after every single volume of the standard solution added. An increase of the concentration of this solution causes a decrease of the concentration gradient. When the concentrations of the solutions on the two sides of the membrane(s) become equal, the concentration gradient is zero. Further increase of the electrolyte concentration causes at this point a growth of the concentration gradient but the dialysis process gets in the opposite direction. The current also turns its course. By following current readout, the zero concentration gradient point can be found and that allows the concentration to be determined.

3. Experimental

3.1. Reagents and solutions

Analytical-reagent grade reagents were used throughout. Distilled and doubly distilled water were used for preparing the solutions. The stock standard solutions were prepared directly by weighing the solid reagents, dissolving and diluting to the corresponding volumes with distilled water. Working standard solutions were prepared by suitable dilution of the stock solutions with distilled or doubly distilled water.

3.2. Membranes

Use was made of cation exchange membrane MK 40 (Russia) and anion exchange membrane MA 40 (Russia). The ion-exchange membranes were soaked for 2h in the solutions that passed through the membranes by the time of performing the dialysis.

3.3. Apparatus

The selective membrane dialysis of the ions under investigation is performed with a laboratory-built dialyzer, shown in Figure 1. It includes a glass vessel, two platinum gauze electrodes, galvanometer (Model VEB Geophysikalischer Geraetebau Brieseland, Germany) connected in series with the electrodes and two membrane cells. The membrane cell is made from a glass tube. Its lower end is sealed with epoxy glue to the piece of tubing taken from the upper part of the screw-capped polyethylene bottle. An ion-exchange membrane is mounted on the edge of the polyethylene tubing by the cup, in which a hole is drilled to expose a membrane area of about 12.6 cm^2. An electromagnetic stirrer is applied for stirring the solution in the glass vessel. The dialyzer is provided with a burette by which the standard solution is added.

4. Analysis procedures

4.1. Zero concentration gradient method (basic method)

The membrane cell(s) is filled up with about 60 cm^3 of a solution to be analyzed. In the glass vessel, 200 cm^3 distilled or doubly distilled water are added, measured with a pipette. The platinum electrodes are dipped. The electric stirrer and galvanometer are switched on and standard solution of the species under investigation is added from a burette in a stepwise manner. The current is reported when a minute elapses after each volume of the standard solution added. A current versus standard solution volume curve is plotted. The standard solution volume corresponding to the zero concentration gradient is found from the plot (see Fig.2). Actually, it is the point where the current begins to change its course (see Fig. 2). The analyte concentration C_a is calculated by the equation: $C_a = C_{st} V^0_{st} / (V_w + V^0_{st})$, (mol/dm^3), where C_{st}, (mol/dm^3), is the standard solution concentration, V^0_{st}, (cm^3), is the standard solution volume, corresponding to the zero concentration gradient point, and V_w, (cm^3), is the water volume in the glass vessel.

In the case of an automatic analysis, the concentration C_a is calculated by the following equation: $C_a = C_{st}(\omega_1 t_1 + \omega_2 t_z) / (V_w + \omega_1 t_1 + \omega_2 t_2)$, (mol/dm^3), where ω_1 and ω_2, (cm^3/s), are two different flow rates of the standard solution added ($\omega_1 > \omega_2$), t_1 is the time (*in s*) for adding the standard solution with a flow rate ω_1, and t_z is the time (*in s*) in which a zero concentration gradient is attained delivering standard solution with flow rate ω_2 (see Fig.5).

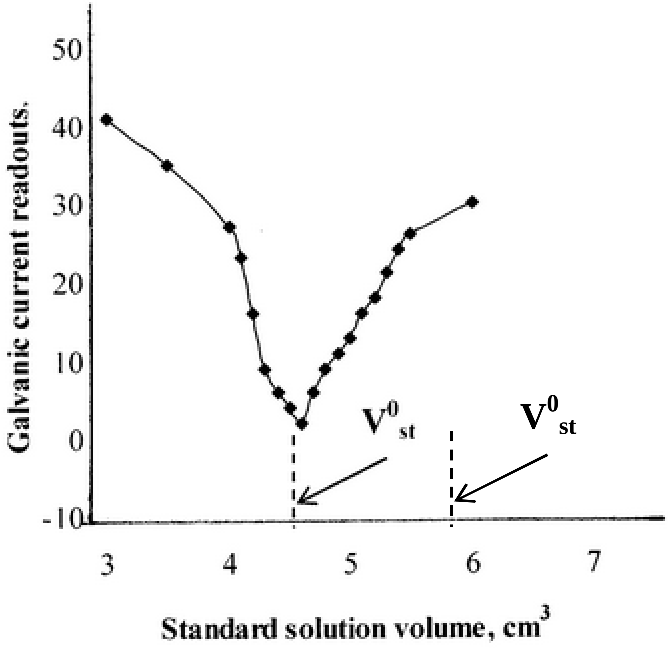


Fig.2. Typical graph for evaluating the zero concentration gradient when 0.1009 mol/dm^3 K^+ is analyzed by Zero concentration gradient method (basic version).

4.2. Zero concentration gradient method for analyzing concentrated solutions

The membrane cell(s) is filled up with about 60 cm^3 of a standard solution of the species to be analyzed. In the glass vessel, 200 cm^3 distilled water are added, measured with a pipette. The platinum electrodes are dipped. The electric stirrer and galvanometer are switched on. The analyte solution is added to the water stepwise. The current is reported when a minute elapses after each volume of the standard solution added. A current versus standard solution volume curve is plotted and the standard solution volume, corresponding to the zero concentration gradient, is found from the plot (see Fig.2). The zero concentration gradient point is the point where the current begins to change its course. The analyte concentration is calculated by the equation: $C_a = C_{st} (V_w + V^0_a) / V^0_a$, (mol/dm^3), where V_w, (cm^3), is the water volume in the glass vessel, V^0_a, (cm^3), is the added volume of the analyte, corresponding to the zero concentration gradient, and C_{st}, (mol/dm^3), is the concentration of the standard solution in the membrane cell(s).

4.3. Zero concentration gradient method of diluting an analyte solution

The membrane cell(s) is filled up with about 60 cm^3 of the solution to be analyzed. About 100 cm^3 of the same analyte solution is placed in the glass vessel. A suitable volume of distilled water, measured with a pipette, is added to the analyte solution in the glass vessel. The platinum electrodes are dipped. The electric stirrer and galvanometer are switched on and the standard solution of the species to be determined is added from a burette in a stepwise manner. The current is reported when 30 seconds elapses after each volume of the standard solution added. A current versus standard solution volume curve is plotted and the standard solution volume, corresponding to the zero concentration gradient V^0_{st}, (cm^3), is found from the plot (see Fig.3).

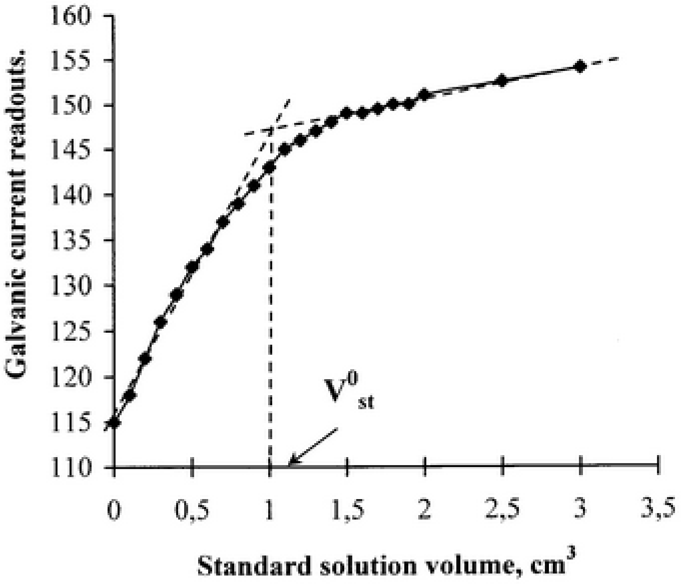


Fig.3. Typical graph for determining the zero concentration gradient point by curve extrapolation for the analyte dilution version of the Zero concentration gradient method. Analysis of 0.1000 mol/dm^3 K^+.

The analyte concentration C_a, (mol/dm^3), is calculated by the equation: $C_a = C_{st}V^0_{st} / (V_w+V^0_{st})$, where C_{st}, (mol/dm^3), is a standard solution concentration, V_w, (cm^3), is the water volume added with a pipette.

4.4. Zero concentration gradient method with improved analytical characteristics

The membrane cell(s) is filled up with about 60 cm^3 of the solution to be analyzed. In the glass vessel, 100 cm^3 of distilled or doubly distilled water is placed, measured with a pipette. A volume of a standard solution of the species to be determined is added to the water. This solution is 10 to 20 times more concentrated than the analyte one. The added solution has to be in such a volume that the analysis to be taken to a stage immediately before the zero concentration gradient point. This can be achieved if the analyte concentration is approximately known, or if a preliminarily analysis by the basic variant of the Zero concentration gradient method is made. The platinum electrodes are dipped. The electric stirrer and galvanometer are switched on. Then a second standard solution of the species to be determined is added from the burette in a stepwise manner. The concentration of this standard solution is ten times lower than the previous one. The current is reported when 30 seconds elapse after each volume of the standard solution is added. A graph of current versus volume of the second standard solution is plotted. The volume of the second standard solution, V^0_{st2}, (cm^3), corresponding to the zero concentration gradient point, is established from the plot. The analyte concentration is determined by the equation: $C_a = C_{st1}V_{st1} / (V_w+V_{st1}) + C_{st2}\,V^0_{st2} / (V_w + V_{st1} + V^0_{st2})$, (mol/dm^3), where C_{st1} and C_{st2}, (mol/dm^3), are the concentrations of the first (more concentrated) and the second (more diluted) standard solutions; V_w and V_{st1}, (cm^3), are the volumes of the water and the first standard solution, respectively.

4.5. Zero concentration gradient method for determining pH

A dialyzer with a cation exchange membrane is used. About 60 cm^3 of the test solution is set in the membrane cell. A buffer mixture is selected according to the expected pH value. In the glass vessel, 50 cm^3 (measured with a pipette) of one of the two buffer mixture solutions, is placed. The platinum electrodes are dipped. The electric stirrer and galvanometer are switched on. The second buffer mixture solution is added to the first one in a stepwise manner. The current is reported when a minute elapses after each volume of the second buffer mixture solution is added. The second buffer solution volume, corresponding to the zero concentration gradient, is found from a graph of the current versus second buffer solution volume. Common logarithm is taken from the mol ratio of the first and second buffer solutions, $lg\ C_1V_1/C_2V_2$, where C_1 and C_2 are concentrations, (mol/dm^3), of the first and second buffer solutions, respectively, V_1, (cm^3), is the volume of the first buffer solution and V_2, (cm^3), is the volume of the second buffer solution, corresponding to the zero concentration gradient. Test solution pH value is determined using mol ratio data and respective to those data pH values for the particular buffer. Such data are available in the specialized reference books.

5. Results and discussion

A dialysis process and electric current are included in order to carry out the analysis, so we generally named the method “Dialysis amperometry” (DA). As the method is based on zero concentration gradient determination, it is particularly called “Zero concentration gradient method”.

When analysis is performed with a dialyzer having two membranes, a cation and an anion exchange membrane, both the cation and the anion analyte compositions are simultaneously determined. When one ion exchange membrane (a cation or an anion) is used, the cation or anion analyte composition is determined, respectively.

A specific behavior of the galvanic current is observed. When the electric circuit of the dialyzer is closed or the concentration of the solution from one side of the membrane(s) is changed (for example, after an addition of a standard solution), an intense current appears. Then the current diminishes, at first rapidly, followed by a slow calming down. Good results for the analysis are reached if current readouts are taken after a minute’s delay.

The proposed method resembles an amperometric titration. Similar appliances are used (see Fig. 1), a standard solution is added and the current measured is of the same magnitude. The zero concentration gradient is determined in the same way as it is done for an end point evaluation (see Figs. 2 and 3). No voltage is applied and no chemical reaction takes place. It is experimentally found that the current indication is an excellent way of establishing the zero concentration gradient point.

It is important for this method that the concentration gradient only of an analyzed ion can vary while all the other identically charged ions, present in the solution, do not change their gradients. This is achieved by adding a standard solution of the species under investigation. It becomes possible for an ion to be determined in the presence of other identically charged ions and for a compound to be analyzed in the presence of other ones. It seems that there are not any interferences at all. It is confirmed by analysis of Na^+ in the presence of K^+, and K^+ in the presence of Na^+, and also by analysis of every single salt in the mixture of four soluble salts (Table 1).

Table 1 Analysis results by different variants of the Zero concentration gradient method of Dialysis amperometry

Compounds, ions or pH of buffers to be determined	Concomitant compounds or ions	Introduced (mol/dm^3)	Found by DA $\bar{x} \pm tS / \sqrt{n}$, (mol/dm^3)	Relative standard deviation S_r=$(S/\bar{x})\ 100$, (%)	Method of analysis
Na^+		0.1022	0.1020 ± 0.0006	0.49	Basic method
Na^+	K^+	0.1048	0.1046 ± 0.0010	0.74	Basic method
Na^+		0.1000	0.0991 ± 0.0015	1.20	Basic method (automated)
Na^+		1.003×10^{-5}	$(0.980 \pm 0.020) \times 10^{-5}$	0.62	Basic method
K^+	Na^+	0.1009	0.1013 ± 0.0011	0.88	Basic method
Cl^-		0.1003	0.1001 ± 0.0010	0.77	Basic method
Cl^-		1.003×10^{-5}	$(0.982 \pm 0.013) \times 10^{-5}$	1.04	Basic method
Cl^-		0.1000	0.0994 ± 0.0039	3.20	Basic method (automated)
NaCl	KNO_3; $CaCl_2$; $Mg(CH_3COO)_2$	0.1000	0.0998 ± 0.0011	0.89	Basic method
KNO_3	NaCl; $CaCl_2$; $Mg(CH_3COO)_2$	0.1003	0.1000 ± 0.0011	0.90	Basic method
$CaCl_2$	NaCl; KNO_3; $Mg(CH_3COO)_2$;	0.0970	0.0975 ± 0.0066		Basic method
$Mg(CH_3COO)_2$	NaCl; KNO_3; $CaCl_2$	0.1014	0.1013 ± 0.0007	0.56	Basic method
Na^+		2.6539	2.66 ± 0.02	0.76	Method for concentrated solutions
K^+		2.0194	2.02 ± 0.02	0.80	Method for concentrated solutions
Cl^-		2.0020	2.0073 ± 0.0008	0.75	Method for concentrated solutions
Na^+		0.1000	0.1001 ± 0.0002	0.19	Method with improved analytical characteristics
K^+		0.1000	0.0997 ± 0.0002	0.16	Method with improved analytical characteristics
HCO_3^-		0.1001	0.1002 ± 0.0002	0.20	Method with improved analytical characteristics
HCO_3^-		1.0007×10^{-5}	$1.0011 \pm 0.0030) \times 10^{-5}$	0.24	Method with improved analytical characteristics

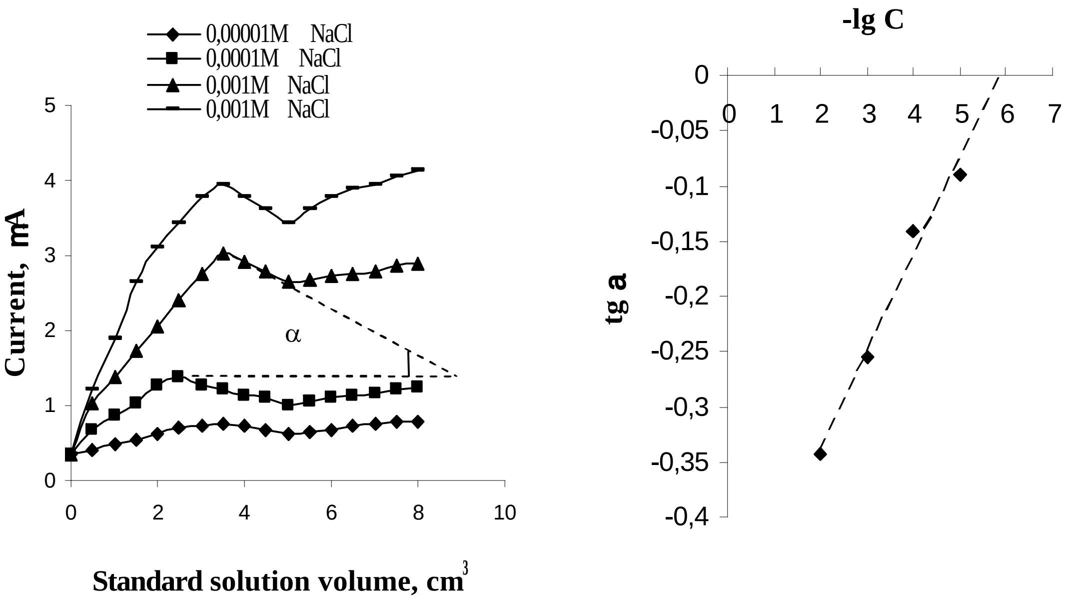
(Table 1 continued)

Compounds, ions or pH of buffers to be determined	Concomitant compounds or ions	Introduced (mol/dm^3)	Found by DA $\bar{x} \pm tS / \sqrt{n}$, (mol/dm^3)	Relative standard deviation Sr=(S/ $\bar{x}$) 100, (%)	Method of analysis
Na^+		0.1002	0.0999 ± 0.0011	0.87	Method of diluting the analyte solution
K^+		0.1000	0.1035 ± 0.0036	2.84	Method of diluting the analyte solution
pH of (1M CH_3COOH+ 1M HCl)		1.4	1.41 ± 0.01	0.61	Method for determining pH
pH of (1/15M KH_2PO_4 + 1/15M Na_2HPO_4)		6.5	6.47 ± 0.01	0.18	Method for determining pH
pH of (0.05M Na_2HPO_4 + 0.1M NaOH)		11.6	11.59 ± 0.02	0.14	Method for determining pH
distilled water		6.50*	6.50 ± 0.02	0.20	Method for determining pH

Number of determinations n, 5; t, Student's t-value at 95% probability; S, standard deviation;` x an average
*The value is determined potentiometrically with glass pH electrode.

Concentrations as low as 10^{-6} mol/dm^3 can be analyzed by the Zero concentration gradient method. Figure 4 illustrates how the lowest analyzed concentration can be predicted.

In order to permit the analysis of concentrated solutions without preliminary dilution, a variation of the Zero concentration gradient method of Dialysis amperometry was developed. There is no other method in the analytical practice for direct analysis of concentrated solutions. Currently a sample of the analyte solution is diluted and then an aliquot of this solution is analyzed. This complicates analysis and it is a source of errors as well. The distinction between the method discussed here and the fundamental one is in the analysis procedure. In this variant the standard solution of the species under investigation is placed in membrane cell(s) and the analyte solution is added from a burette to the water. The method requires the standard solution concentration to be 10 to 20 times lower than the analyte one, which is easy to achieve. Standard solution concentration of about 0.1 mol/dm^3 is appropriate for analysis of concentrated solutions.



A **B**

Fig. 4. Graphs illustrating the way to find the lowest concentration determined by the Zero concentration gradient method. (A) Graphs for determining the zero concentration gradient point for different sodium chloride concentrations. (B) The concentration dependence of the curve slope in the vicinity (before) the zero concentration gradient point. The minimal concentration to be determined is found as the cross point of the curve extrapolation with the abscissa. The standard solutions added have concentrations about 50 times higher than the respective analyzed solution concentrations.

Another version of the Zero concentration gradient method was developed in order to reduce analysis duration. This method is also distinguished from the basic method by the procedure used. Here the analyte solution is put on both sides of the membrane(s). A concentration gradient is created by adding small volume of water to the analyte solution located on one side of the membrane(s). Then the standard solution is added to the diluted analyte solution. The graph for the zero gradient point evaluation is somehow different, more rounded (Fig.3). It is due to the low concentration gradient that is formed by this method. The best results of analysis are reached if the dilution is minimal.

The aim of the next version of Zero concentration gradient method is to improve the analytical characteristics of the analysis. Generally, the overall error of this method is accumulated from errors of the standard solution preparation, the volume measurement, as well as the zero concentration gradient evaluation. The latter is the main contributor to the overall error. Accuracy and precision of the method are improved by more precise determining of the zero gradient point. In the beginning, a big portion of a standard solution is added. The concentration of this solution is 10 to 20 times higher than the analyte concentration that takes analysis to a stage near to the zero gradient point, but before it. Then the second standard solution is added. The concentration of this solution is the same as the analyte concentration. The second standard solution volumes added are as small as they can be measured by the burette. The galvanic current is measured as sensitively as possible. As it can be seen in Table 1, the results of this modified method with two standard solutions are more favorable than those obtained by the basic method.

pH determination can also be done by the Zero concentration gradient method. This unusual application of the method is realized as tested solution is placed on one side of a cation exchange membrane and on the other side is set one of the two solutions that a standard buffer mixture consists of. The second component of the buffer mixture is then added to the first one. Thus the pH of the buffer mixture so created is determined from the volume of the second buffer component added, and has the pH value corresponding to this volume. Such data are available in the specialized reference books. In zero gradient point, pH of the test solution is equal to the pH of the buffer mixture. The method is confirmed by determining pH of standard buffer solutions (Table 1).

Table 2 Results for analysis by Zero concentration gradient method (basic version) of the Black sea water, the bay of Bourgas, north beach

Ions to be determined	Concentration by literature data [9] (g/dm^3)	Found by DA $\bar{x} \pm tS/\sqrt{n}$, (g/dm^3)	Relative standard deviation $S_r=(S/\bar{x})\,100$, (%)
Na^+	6.8	6.85 ± 0.13	1.54
K^+	0.25	0.23 ± 0.10	2.41
Mg^{2+}	0.68	0.62 ± 0.02	2.65
Ca^{2+}	0.24	0.22 ± 0.01	2.19
Cl^-	13	13.7 ± 0.47	2.74
SO_4^{2-}	1.42	1.27 ± 0.04	3.49
CO_3^{2-}	1.96×10^{-2}	$(2.06 \pm 0.09)\times10^{-2}$	2.17
pH	8.15*	8.19 ± 0.02	0.18

Number of determinations n, 5; t, Student's t-value at 95% probability; S, standard deviation; $\bar{x}$, an average

* The value is determined potentiometrically with glass pH electrode

The Zero concentration gradient method is easy for automation. In the work an automatic analysis is performed by adding continuously the standard solution with a peristaltic pump, and measuring and recording the current by a polarograph. Improved results of analysis are achieved if standard solution delivery is delayed in the vicinity of the zero concentration gradient point (Fig. 5).

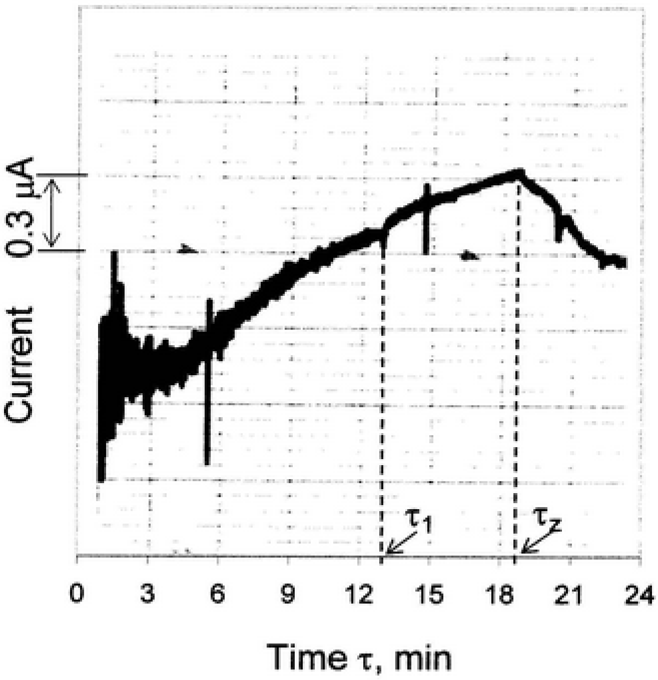


Fig.5. Typical record for an automatic analysis of 0.1000 mol/dm^3 Na$^+$ by Zero concentration gradient method (basic version). Flow rate of the standard solution added is ω_1=0.652 cm^3/min from 0 to point τ_1, and ω_2=0.328 cm^3/min from point τ_1 to point t $_z$, the time corresponding to zero concentration gradient.

Methods developed in the work are implemented for environmental analysis. Ingredients of sea water, natural mineral water and Sylvinite are analyzed (Tables 2-4).

Table 3 Results for analysis of Hissar mineral water by the Zero concentration gradient method (basic version) of Dialysis amperometry

Ions to be determined	Concentration by the producer certificate (mg/dm^3)	Found by DA $\bar{x} \pm tS/\sqrt{n}$, (mg/dm^3)	Relative standard deviation $S_r=(S/\bar{x})\,100$, (%)
Na$^+$	74.3	74.4 ± 1.1	1.24
K$^+$	2.1	2.2 ± 0.1	5.29
Ca^{2+}	7.3	9.3 ± 0.9	4.27
F$^-$	3.4	3.2 ± 0.2	4.91
Cl$^-$	12.7	12.6 ± 0.4	2.65
SO$_4^{2-}$	36.0	32.1 ± 1.8	4.02
CO$_3^{2-}$	12.0	11.9 ± 0.3	2.25
HCO$_3^-$	119.0	117.4 ±6.3	4.30
pH	8.35	8.36 ± 0.04	0.34

Number of determinations n, 5; t, Student's t-value at 95% probability; S, standard deviation;` $\bar{x}$ an average

Table 4 Results of the analysis of Sylvinite by the Zero concentration gradient method (basic version) of Dialysis amperometry

Compound to be determined	Concentration by a certificate (%)	Found by DA $\bar{x} \pm tS / \sqrt{n}$, (%)	Relative standard deviation $S_r = (S / \bar{x})\ 100$, (%)
NaCl	67-76	70.01 ± 0.98	1.13
KCl	22-31	26.25 ± 0.31	0.93
$MgCl_2$	0.25	0.32 ± 0.11	1.28
$CaSO_4$*	1.81	1.77 ± 0.12	0.57

Number of determinations n, 5; t, Student's t-value at 95% probability; S, standard deviation;` $\bar{x}$ an average

* The analysis of $CaSO_4$ is performed with a standard solution of $CaCl_2$ instead of a solution of $CaSO_4$

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Corresponding author: Anastas Dimitrov Dakashev

Address: Department of Inorganic and Analytical Chemistry, Prof. Dr. Assen Zlatarov University, 8010 Bourgas, Bulgaria

Phone: (359) - 56-858-337

Fax: (+359) 56 880 249

E-mail: adakashev@btu.bg