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Stepwise Injection Potentiometric Determination of Ammonium-Ions in Water

Andrey V. Bulatov*, Polina A. Ivasenko, Alexey L. Moskvin, Leonid N. Moskvin

St. Petersburg State University, Department of Chemistry, pr. Universitetskij 26, 198504
St. Petersburg, Russia

Abstract

An automatized technique of stepwise injection potentiometric determination of ammonium-ions in water is developed. The technique includes consecutive stages of evolution of ammonium-ions in the form of ammonia and its liquid absorption into water phase. The determination range is of 5 to 2000 µg/l and efficiency of 7 determinations per hour.

Key words Stepwise injection analysis, ammonium-ions, water.

1. Introduction

One of the important tasks of eco-analytical control and ecological monitoring of water is the observation of the level of compounds of biogenic elements contained in the water, one of such biogenic elements being ammonium nitrogen, which plays an important role in the metabolism of animal and plant organisms, which inhabit the water bodies [1].

At present the most wide-spread method of determination of ammonium-ions in water is the photometric method which employs the Nessler reagent [2]. However the use of this method in analysis of water with increased mineralization and hardness is limited and is not applicable for analysis of waters containing organic compounds, reacting with Nessler reagent (spirits, ketones, aldehydes and amines). Apart from this, the Nessler reagent contains highly toxic mercury chloride (II), which makes it necessary to collect and recycle the waste, created in the process of analysis performance.

Automatized methods of ammonium-ions detection under the conditions of flow-injection analysis (FIA) [3] and sequential injection analysis (SIA) [4, 5], have also been developed. They include the stage of evolution and concentration of ammonium-ions in the form of ammonia. The suggested automatized methods have a number of considerable limitations, directly connected with the principles of the used methods (FIA and SIA). The principle of "controlled dispersion" of analyte zones in hydraulic traces underlying the FIA and SIA methods results in decrease of sensitivity of the methods of flow analysis in comparison with automatized statistic analogs. Apart from this the schemes of FIA and SIA are limited in the possibilities of optimization of conditions of evolution and concentration of the analytes that create volatile analytical forms and they demand that special devices for evolution of the volatile compounds from the water solutions are incorporated in the hydraulic schemes.

The suggested method of stepwise injection analysis (SWIA) that we develop allows us to overcome the above-described limitations [6]. SWIA assumes the strict reproduction of all stages of the analysis, that the stationary techniques characterized: taking a portion of a sample; the sample preparation, including, if it is necessary, preconcentration, conversion of analyte into the chemical form that is convenient for determination; additions of solutions of reagents to a solution of sample; mixing the solutions by a stream of gas up to the establishment of balance in system; thermostating (if necessary); pauses for achievement of the maximal value of an analytical signal (if necessary) and measurements of an analytical signal. In certain sense SWIA can be considered as a return to the initial scheme of automation of the chemical analysis based on reproduction of manual operations, carried out by chemists-analysts with the automated mechanical devices, but with use of the experience

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*Corresponding author

E-mail: bulatov_andrey@mail.ru

which has been acquired during development of flow methods of the analysis.

In this case the process of evolution of ammonium-ions in the form of ammonia from water solutions can be executed directly in the standard reaction vessel of the hydraulic SWIA scheme.

The purpose of the present work was the development of the technique of stepwise injection potentiometric determination of ammonium-ions in water, including the stage of evolution and concentration of ammonium-ions in the form of ammonia.

2. Experimental

The operational solutions of ammonium-ions were prepared through the consecutive dilution of the standard solution with concentration parameter 1g/l, which was prepared through dissolution of NH_4Cl. 1 M solution of NaOH was used as a working solution. All chemicals were of analytical reagent grade quality.

The hydraulic schemes of SWIA for the potentiometric determination of ammonium-ions in water were assembled on the base of module flow analyzer (Rosanalit St. Petersburg) with a potentiometric detector. A muli-way valve (titanium); a peristaltic pump, providing the reverse of the flow direction (speed of the flow 6 ml/min) were used in the course of work. As opposed to the regular scheme of SWIA [6] the reaction vessel used for the implementation of the analytical reaction was structurally united with the potentiometric cell to detect the analyte according to the change of the pH level of the absorber solution. Two schemes of commutation of the reaction vessel (RV) with the potentiometric cell (PC) were considered (Fig. 1).

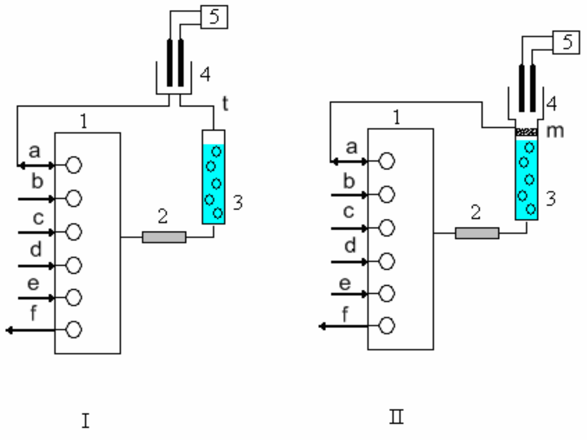

Fig. 1. Schemes of the stepwise injection determination of ammonium-ions in waters: 1 – multi-way valve (positions a, b, c, d, e, f); 2 – reverse pump; 3 – reaction vessel; 4 – potentiometric cell; 5 – potentiometric detector; t – connecting tube; m – gas-permeable membrane.

The first scheme of SWIA (Fig. 1) presupposed transfer of the ammonia sample created in alkaline solution by gas-extractant (atmosphere air) from the reaction vessel (polypropylene tube, diameter 10 mm, height 20 mm) (3) through a connecting pipe (t) into the potentiometric cell (polypropylene tube, diameter 10 mm, height 20 mm) (4). The second scheme (Fig. 1. II) presupposed transfer of the ammonia from the reaction vessel (polypropylene tube, diameter 10 mm, height 20 mm) (3) into the potentiometric cell (polypropylene tube, diameter 9 mm, height 20 mm) (4) through a gas-permeable membrane (m) (polytetrafloretylene). The membrane (m) was pressed on the joint of the upper part of the reaction vessel (3) and the lower part of the potentiometric cell. In both cases the body of PC was filled with 0.1 M solution of KCl, used to absorb the ammonia.

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3. Results and discussion

On the preliminary stage we made a choice of the optimal scheme of the evolution of ammonium-ions in the form of ammonia with its subsequent liquid absorption in the condition of SWIA. Two above-mentioned schemes of the SWIA that do not demand special devices for evolution of analyte were checked for this purpose (Fig. 1).

It was determined that, in the use of the scheme 1 (Fig. 1, I), a considerable reproducibility of determination, caused by droplet liquid entrainment while gas-extactant is being transmissed through it, was demonstrated.

No such problem arises in use of the SWIA system with the transfer of the ammonia through a gas permeable membrane (Fig. 1, II). That is why this scheme was chosen for further study. To optimize the conditions of the evolution of ammonium-ions in the form of ammonia in the conditions of the chosen scheme of SWIA the influence of the time of transfusion of the gas phase through the alkaline solutions of the analyte in the reaction vessel on the value of the analytical signal was studied. For this purpose the reaction vessel (3) was filled with 1 ml of 0.1 M solution of KC1 (b) with the help of a reverse pump (2), after that by switching the valve (1) the absorbing solution was directed along the channel (a) into potentiometric cell (PC) (4) and the potential difference corresponding to the background solution (E_1) was measured. After that the reaction vessel (3) was filled with 1 ml of the sample (c), 1 ml of 1 M solution of NaOH (d) and the flow of the atmospheric air (e). With that a gas extracted emission of the ammonia formed in the RV through a gas-permeable membrane (m) with its subsequent absorption from the gas phase into the solution located in PC (4), took place. The time of transmission of air was varied from 1 to 10 minutes under fixed speed of air – 6 ml/min. After the flow of the atmospheric air was stopped the potential difference was measured, corresponding to the sample (E_2), after that the solution PC и RV were emptied and the communication systems were rinsed with 0.1 M solution of KCl.

As an analytical signal corresponding to the presence of ammonium ions in the sample, we used the difference $\Delta E = E_1 - E_2$. As seen from the received results (Fig. 2) starting from 6 minutes independently of the concentration of the analytes in the sample the value of the analytical signal is stabilized which allowed us to take 6 minutes period as an optimal duration of the process of gas extraction.

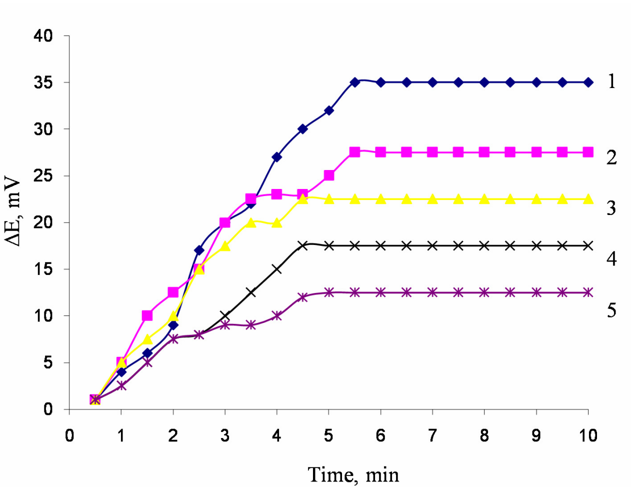

Fig. 2. Dependence of the analytical signal (ΔE) from the time of the gas phase transmission (t) through the alkaline solutions with ammonium-ions concentration: 1 – 2 mg/l, 2 – 0,2 mg/l, 3 – 20 µg/l, 4 – 10 µg/l, 5 – 5 µg/l. The speed of the gas phase flow – 6 ml/min.

To guarantee the chosen order and duration of all the stages of analysis a matrix allowing to set the state of the function elements of the analyzer in each moment of time was designed. Each line in this matrix corresponds to a certain stage and columns suit to the position of each executive element. The matrix for the developed technique is demonstrated in Table 1.

In analysis performance a standard procedure of ammonium-ions solution calibration of the instrument was used. The solutions of ammonium-ions were delivered along the test portion channel (c) of the designed SWIA scheme (Fig. 1. II). The obtained calibration curve is linear in the ammonium ion concentration range from 5 to 2000 µg/l ($y = 5.8 \cdot \lg c(NH_4^+) + 40.1$) (Fig. 3).

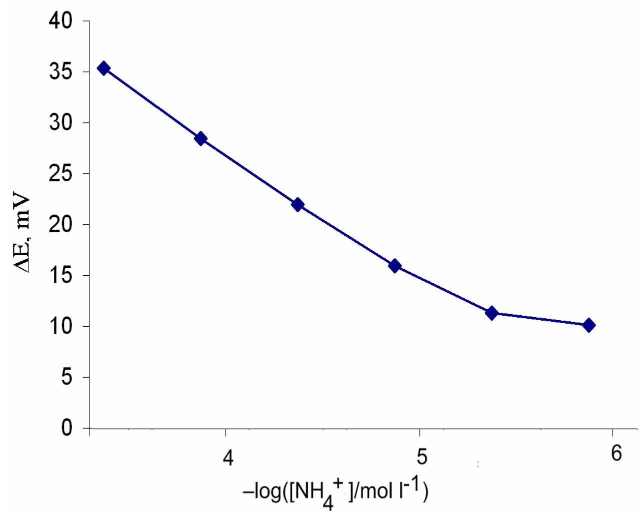

Fig. 3. Calibration curve for ammonium ion determination.

4. Conclusion

The developed technique was tested on natural water samples. The obtained results are demonstrated in the Table 2. The accuracy of the results obtained though the use of the designed technique was verified by spiking samples and checking recoveries. As can be seen from the Table 2 the entered and found quantities of the analyte practically coincide.

The designed technique provides the 3 µg/l determination limit of ammonium-ions in 1 ml volume of the sample. The productivity in the chosen optimal conditions of the evolution and concentration of ammonium ions in the form of ammonia amounted to 7 determinations per hour.

Table 1. Conditions of stepwise injection ammonium-ions determination in waters.

Time, s	Valve position	The direction of pump rotation	Measurement	Comments
10	b	-1	A	0.1 M solution of KCl flow in RV
10	a	+1	A	0.1 M solution of KCl flow in PC
10	c	-1	B	Sample flow in RV
10	d	-1	B	1 M solution of NaOH flow in RV
360	e	-1	A	Air flow in RV
30	e	0	B	Measurement of ammonium ion concentration in absorption solution in PC
10	a	+1	A	Discharge of solution from PC
25	f	+1	A	Discharge of solution from RV
10	b	-1	A	0.1 M solution of KCl flow in RV
10	f	+1	A	Discharge of washing liquid from RV
10	b	-1	A	0.1 M solution of KCl flow in RV
10	a	+1	A	0.1 M solution of KCl flow in PC
10	a	-1	A	Discharge of washing liquid from PC to RV
15	f	+1	A	Discharge of washing liquid from RV
-1 – rotation of the pump clockwise, 0 – a stop of the pump, +1 – rotation of the pump counter clockwise, A – measurements are not made, B – registration of a signal from the detector, RV– reaction vessel, PC – potentiometric cell				

Table 2. The results of ammonium-ions determination in waters (n=3, P=0.95).

Sample	Added, µg/l	Found, µg/l
Gulf of Finland	- 15	15 ± 1 30 ± 2
Neva river	- 9	9 ± 1 17 ± 2
Moika river	- 10	10 ± 2 18 ± 2
Fountain river	- 8	8 ± 2 15 ± 2

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