

Stepwise Injection Photometric Determination of Nitrogen Oxides in Atmospheric Air

Andrey Bulatov^{1,*}, Kseniia Medinskaia¹, Andrey Ipatov², Aleksey Moskvina¹ and Leonid Moskvina¹

¹ Department of Chemistry, Saint-Petersburg State University, Universitsky pr., 26, Saint-Petersburg, 198504, Russia

² The National Microelectronics Center (Centro Nacional de Microelectrónica - CNM), Campus UAB, Bellaterra, Barcelona, 08193, Spain

Abstract

The automated technique of photometric determination of nitrogen oxides in atmospheric air is developed. This technique includes liquid nitrogen oxides absorption from air into borate buffer solution directly in the standard units of the hydraulic scheme of the stepwise injection analyzer with further determination according to the reaction with Griess reagent. The range of nitrogen oxides concentration which are determined is from 0.03 to 0.75 mg·m⁻³ in terms of NO₂, the sample volume is 2 L. The analysis time is 20 min.

Keywords: Stepwise injection analysis, nitrogen oxides, air

1. Introduction

One of the most important ecological tasks of atmospheric air monitoring is the determination of nitrogen oxides in it. Nitrogen oxides are related to so-called “acid gases” which interact with water vapours in the atmosphere and causes acid rains and smogs which change acid-base balance in atmosphere and cause the poisoning of hydro- and lithosphere. Their appearance in atmosphere is conditioned by burning of fossil fuel types biomass and by fertilizers usage [1].

Taking into account the fact that the determination of oxides concerns to the number of analyses which are carried out regularly, the automated techniques with the application of flow techniques are preferable.

The automated techniques for determination of nitrogen oxides in atmospheric air are known in variants of flow-injection analysis (FIA) [2-4] and sequential injection analysis (SIA) [5, 6]. The proposed automated techniques have a range of substantial limitations which are attributed directly with fundamental principles of FIA and SIA. The “controlled dispersion” principle of analyte zones in hydraulic channels which is built into these techniques leads to desensitization of the flow analyses automated techniques in comparison with their static analogues [7]. Furthermore, in case FIA and SIA it is difficult to gain the optimal sensitivity because of multistage kinetically delays reactions formation of analytical form which include the formation of azo-compounds which are the base of photometrical determination of nitrogen oxides.

Therefore, the search of methodological and instrumental solutions which could allow to automate determination of nitrogen oxides in the air static techniques and retain their sensitivity during the adaptation to the flow analysis conditions is urgent. The general methodological solution, which is the most appropriate to the stated problem is stepwise injection analysis (SWIA) [7, 8]. There is no lacks the sample dispersion in hydraulic channels in SWIA, analytical signal measuring in conditions when it gains the maximal value for this technique

and creates favorable conditions which eliminate the “memory” effect.

2. Experimental

2.1. Reagents

Acid and alkaline solutions of nitrite-ions were prepared by sequential diluting of 1 g·L⁻¹ NaNO₂ solution with citrate or borate buffer solution, respectively.

Citrate buffer solution was prepared by diluting of 20 g citric acid (C₆H₈O₇·H₂O) and 8 g NaOH in 1 L of distilled water with sequential addition of 1 M HCl to pH over the range 3.5 to 4.0.

Borate buffer solution (pH=9) was prepared by heating of 30 g NH₄Cl and 10 g Na₂B₄O₇·10H₂O in 1 L of distilled water. pH of borate buffer solution was being corrected by adding 1 M HCl or 1 M NaOH.

To generate the gas mixture which contains NO_x, 5 ml acidized solution of nitrit-ion (1 mg·L⁻¹) was placed into a glass bubbler vessel (capacity is 15 ml) and nitrogen was run through at rate of 0.4 L·min⁻¹.

Griess reagent was prepared directly before the experiment by mixing 10 g·L⁻¹ solution of sulfanil acid and 1 g·L⁻¹ solution of 1-naphtilamin in medium of acetic acid, half-and-half.

2.2. Apparatus

Aerohydraulic scheme for determination of nitrogen oxides was put together on the basis of the modular stepwise injection analyzer “SWIA-1” (Rosanalyt, Russia). The main constituent parts of analyzer are: fibre-optical spectrophotometer (Ocean Optics, USB-2000) (the optical way length is 50 mm, the wavelength is 485 nm); a six-way valve, a reaction vessel (a glass tube, which height is 50 mm and inner diameter is 10 mm, which is placed into the thermostat); auxiliary vessel (a monolithic acrylic cell, which height is 60 mm and inner diameter is 10 mm, filled with polytetrafluorethylene granules 2-3 mm over) (Fig. 1). The polytetrafluorethylene tubes the inner diameter of which is 0.5 mm were used for commutation of analyzer units. The analyzer is run automatically by the instrumentality of computer. The scheme of stepwise injection analysis which includes nitrogen oxides absorption from the air

*Corresponding author.

E-mail: bulatov_andrey@mail.ru

into the absorption solution is shown in Fig. 1.

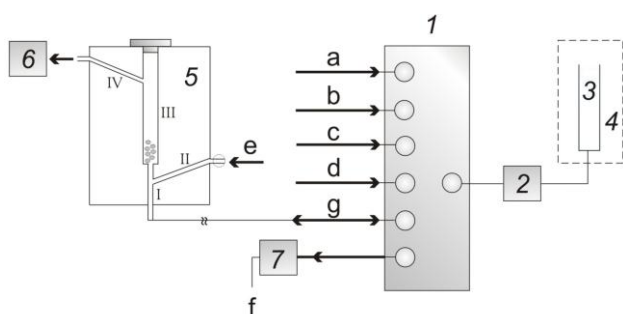


Fig. 1. SWIA scheme for determination of nitrogen oxides in air: 1 – six-way valve; 2 – reverse pump; 3 – reaction vessel; 4 – thermostat; 5 – auxiliary vessel (I – channel for supplying absorbing solution, II – channel for supplying air, III – channel for absorbing of analyte, IV – waste); 6 – aspirator; 7 – detector; a – nitrite-ions solution; b – Griess reagent solution; c – nitrogen; d – borate buffer solution; e – air; f – waste.

3. Results and Discussion

3.1. The temperature and thermostatic time influence on the absorbance.

At the preliminary stage, the influence of temperature range from 20 to 90 °C was investigated on basis of alkaline water solution of nitrite-ions, according to the scheme which is shown in Fig. 1. To perform it 1 ml 0.25 g·L⁻¹ of alkaline solution of nitrite-ions (a) and 0.5 ml of Griess reagent solution were input through the multi-way valve (1) by bidirectional pump (2) into the thermostated reaction vessel (3). After that the solution in the reaction vessel was being mixed by the nitrogen stream (c) for 15 min. Then dyed solution from the reaction vessel (3) was transferred into the photometrical detector (7) to measure absorbance.

At the second stage, the scrubbing of the scheme communications was done by borate buffer solution (d) in the same temperature range and the background signal was measured in the detector which was filled by distilled water.

As the obtained results show (Fig. 2), the maximal absorbance value of the standard solution does not changed practically beginning with the temperature of 70 °C. Therefore, the temperature of 70 °C was chosen as optimum.

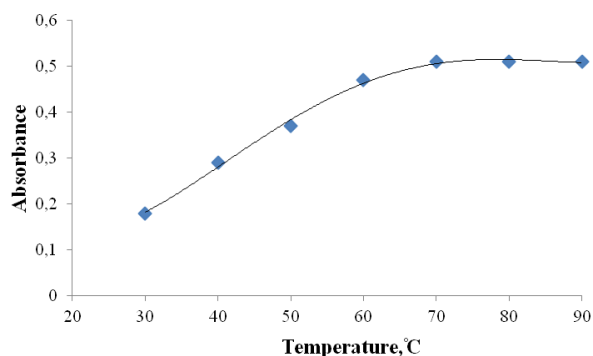


Fig. 2. Influence of temperature on absorbance (C_{NO₂}=0.5 mg·L⁻¹).

To define a minimal time interval which is necessary for the reaction of formation azo-compound in the reaction vessel of the SWIA scheme (Fig. 1), a number of similar experiments was

carried out at different times of solution thermostating in the reaction vessel with the fixed temperature of 70 °C and fixed flow rate of nitrogen (2 ml·min⁻¹) for mixing.

The results of the time study behavior of analytical reaction in reaction vessel which influences on the analytical signal are shown in Fig. 3. As the obtained results indicate the minimal time which is necessary for the complete photometrical reaction in the reaction vessel is 10 min.

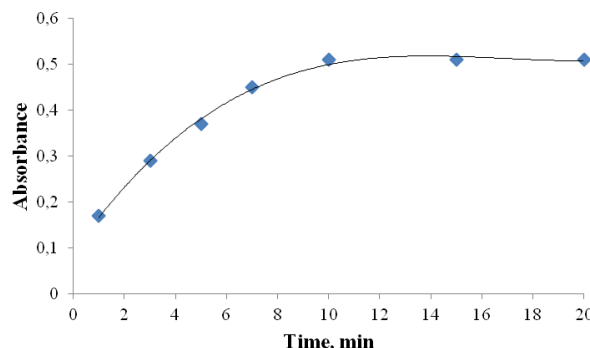


Fig. 3. Influence of thermostating time on absorbance (C_{NO₂}=0.5 mg·L⁻¹).

3.2. The gas flow rate influence on the absorbance.

The influence of the gas phase flow rate though the absorption solution in the reaction vessel with polytetrafluorethylene granules on the efficiency of nitrogen oxides absorption from air. The borate buffer solution (pH=9) was used as an absorbing solution. The borate buffer solution provides the release of nitrogen oxides into water phase and the behavior photometrical reaction with Griess reagent [5]. Polytetrafluorethylene granules were used to increase the contact area of phases during the barbotage of the gas though the reaction vessel.

To generate the gas mixture into the bubbler vessel (2) (Fig. 4) 5 ml of 0.5 mg·L⁻¹ NO₂⁻ solution was placed into the bubbler vessel and the nitrogen stream was let through it. Then the bubbler vessel was connected sequentially with two similar auxiliary vessels (3 and 4). 1 ml of absorbing solution was placed into each auxiliary vessel. The gas mixture which being generated in the bubbler vessel was being let through the auxiliary vessels at the fixed flow rate from 0.2 to 1 L·min⁻¹ during 5 min.

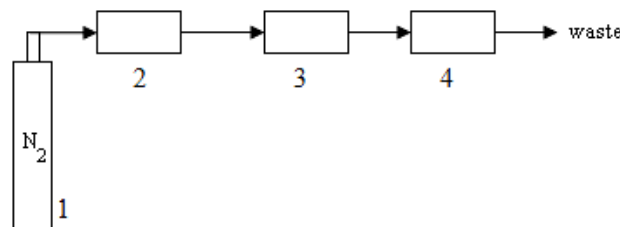


Fig. 4. Scheme of nitrogen oxides absorption from gaseous phase: 1 – nitrogen tank; 2 – bubbler for gas mixtures; 3, 4 – auxiliary vessels with absorbing solutions.

After that the vessels were detached, they were included into SWIA (Fig. 1) in turn through the line (g) and nitrite-ions were determined according to the reaction of Griess reagent. To perform it, 1 ml of absorbing solution was taken through the multiway valve (1) by bidirectional pump (2) from auxiliary vessel into the thermostated (70 °C) reaction vessel (2), 0.5 ml of Griess reagent solution was transferred, then the solution was

being mixed by nitrogen (c) during 10 min. Further, the dyed solution was transferred from reaction vessel into the detector (7) to measure the absorbance of the solution. In the end the hydraulic scheme was scrubbing with borate buffer solution (d).

It was found out that the effective extraction of nitrogen oxides occurs in the first reaction vessel up to the gas phase running of $0.4 \text{ L}\cdot\text{min}^{-1}$ (Fig. 5). This rate was chosen as optimum for the further experiments. The efficiency (R) was calculated as the ratio of difference of optical densities of solutions in the first (A_1) and second (A_2) bubbler vessels and the absorbance in the first (A_1) bubbler vessel.

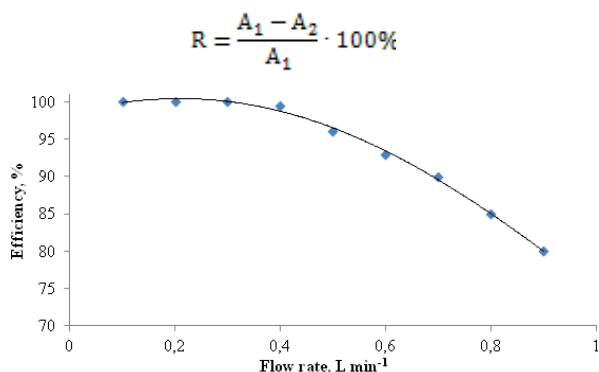
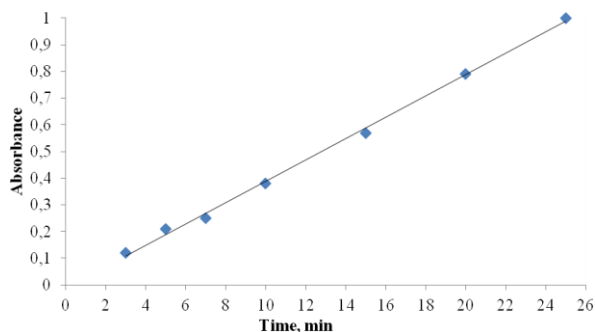


Fig. 5. Influence of gas flow rate on NO_x absorption in solution.

In addition, the influence of the gas mixture running through the absorbing solution in the auxiliary vessel with granules on the value of analytical signal was studied. As follows from the obtained relation (Fig. 6), the time of extraction and concentration of nitrogen oxides from the air and the sample volume respectively can be varied without significant waste of analyte.

Fig. 6 Absorbance dependence from blowing off through the acid nitrite-ions solution (gaseous phase flow rate is $0.4 \text{ L}\cdot\text{min}^{-1}$,



pH=3.7, $C_{\text{NO}_2} = 1 \text{ mg}\cdot\text{L}^{-1}$).

3.3. The technique of stepwise injection determination of nitrogen oxides in atmospheric air.

At the preliminary stage the nitrogen oxides absorption from atmospheric air into the absorbing solution is performed. For this purpose 1 ml of alkaline buffer solution is given through the multiway valve (1) by bidirectional pump (2) into the reaction vessel (3). Then the buffer solution is transferred into the

auxiliary vessel (5).

Further an air sample (e) is run by the aspirator through the absorbing solution at rate of $0.5 \text{ L}\cdot\text{min}^{-1}$ during 5 min. While the extraction of analyte into the water phase takes place. The chosen value of running time allows to determine nitrogen oxides at the level of maximum permissible concentration (MPC) in atmospheric air ($40 \mu\text{g}\cdot\text{m}^{-3}$). If it is necessary the time of concentration of analyte can be increased without significant waste of analyte.

At the next stage the absorbing solution from auxiliary vessel, 1 ml of buffer solution (d) and 0.5 ml of Griess reagent solution (b) are transferred through the multiway valve (1) by bidirectional pump (2) into the thermostated (70°C) reaction vessel. The solution is being mixed by the stream of nitrogen (c) during 10 min, the formation of analytical form is occurring. Then the solution of analytical form runs into flow detector (7) where the absorbance is measured (A_1).

At the final stage the scrubbing of system communication is done with the buffer solution (d) and the analytical signal (A_0) is measured when the detector (7) is filled with the buffer solution (d).

The difference $\Delta A_a = A_1 - A_0$ is used as the value of absorbance which corresponds with the concentration of nitrite-ions in the sample.

To provide the order of mixing, the amount of samples and solutions of reagents, the sequence and duration of all the stages of the analysis, the matrix (Table 1) which allows to run the analyzer and actuator components state in each time period was made. Each line in the matrix corresponds the definite stage while columns are responsible for the position of each actuator component.

When the analyses was being carried out, the SWIA graduation according to the standard solutions of nitrite-ions was used. Calibration curve ($A = 0.535 \cdot C + 0.093$) is linear in the range from 0.03 to $0.75 \text{ mg}\cdot\text{m}^{-3}$ in terms of NO_2 , the volume of sample is 2 L.

The developed technique was tested on the analysis of the air according to the known technique of photometrical determination [9]. As follows from the Table 2, the data which were obtained from these techniques are coincides satisfactorily. To generate gas mixtures A and B, 5 mL ($0.5 \text{ mg}\cdot\text{L}^{-1}$) of NO_2^- solution were placed into the bubbler vessel (2) (Fig.4) and the nitrogen stream was being run for 3 and 7 min, respectively.

LOD is $0.01 \text{ mg}\cdot\text{m}^{-3}$ (3σ) in terms of NO_2 was attained, the sample volume is 2 L and the time of one analysis is 20 min.

4. Acknowledgement

The authors thank the Russian Foundation for Fundamental Researches (Grant № 10-03-0007-a) and the Government of Russia (Grant MK-550.2010.3) for financial support.

Table 1. Conditions of stepwise injection determination of nitrogen oxides in atmospheric air.

Time, sec	Valve position	Direction	Measurement (0;1) ^b	Comment
		of pump rotation (+1;0;-1) ^a		
12	D	+1	0	Supply of buffer solution into RV ^c
20	G	-1	0	Transfer of buffer solution from RV into AV ^d
300	E	-1	0	Supply of air into AV
20	G	+1	0	Transfer of gas absorbed buffer solution into RV
6	D	+1	0	Supply of buffer solution into RV
8	B	+1	0	Supply of the Griess reagent into RV
600	C	+1	0	Supply of nitrogen stream into RV
30	F	-1	0	Transfer the developed dye from RV into detector
10	F	0	1	Analytical signal measurement
30	F	-1	0	Waste
30	D	+1	0	Supply of buffer solution into RV
10	G	-1	0	Transfer of buffer solution from RV into AV
10	f	1	0	Waste
30	F	-1	0	Waste
20	D	1	0	Supply of buffer solution into RV
20	f	-1	0	Transfer buffer solution from RV into detector
10	f	0	1	Background signal
20	f	-1	0	Waste

Total time: 20 min

- a. +1 – clockwise pump rotation, 0 – pump is stopped, 1 – anticlockwise pump rotation;
b. 0 – measurement is not carried out, 1 – measurement is carried out.
c. RV – reaction vessel
d. AV – auxiliary vessel

Table 2. Results of nitrogen oxides determination (n=3, P=0.95).

Analysis object	Found NO _x , µg·m ⁻³	
	SWIA	Known method [8]
Gas mixture «A»	114±7	110±6
Gas mixture «B»	265±5	263±4
Air in chemistry laboratory	30±2	30±1
Air in chemistry laboratory	<LOD	<LOD

5. References

- [1] A.C. Stern. Air Pollution, Vol. VI, Academic Press. New York, 1986. 206 P.
[2] Y. Wei, M. Oshima, J. Simon, S. Motomizu. *Talanta*, 2002, **57**, 355.
[3] Y. Wei, M. Oshima, J. Simon, L.N. Moskvina, S. Motomizu, *Talanta*, 2002, **58**, 1343.
[4] H. Erxleben, L.N. Moskvina, T.G. Nikitina, J. Simon, *Fresenius J Anal. Chem.*, 1998, **361**, 324.
[5] Y. Wang, S. Fan, S. Wang. *Anal. Chim. Acta*, 2005, **541**, 131.
[6] K. Toda, Y. Hato, K. Mori, S. Ohira, T. Namihira, *Talanta*, 2007, **71**, 1652.
[7] A.V. Bulatov, A.L. Moskvina, L.N. Moskvina, A.V. Mozhuhin, *J. Flow Injection Anal.*, 2010. **27**, 13.
[8] A. Bulatov, M. Soloviev, A. Petrova, A. Moskvina, L. Moskvina, *J. Flow Injection Anal.*, 2010. **27**, 158.
[9] ISO 6768:1998. Ambient air – Determination of mass concentration of nitrogen dioxide – Modified Griess-Saltsman method.

(Received November 1, 2011)

(Accepted November 22, 2011)