

PHOTOMETRIC FLOW INJECTION DETERMINATION OF FORMALDEHYDE IN ATMOSPHERIC AIR USING CHROMATOMEMBRANE ABSORPTION

O.V.Rodinkov¹, L.N.Moskvin¹, E.A.Vaskova^{1*}

¹St.-Petersburg State University, Department of Chemistry, University prospect, 26, Petrodvorets, 198504, St. Petersburg, Russia

Abstract

The photometric flow injection technique using the chromatomembrane preconcentration method was developed to determine the trace amounts of formaldehyde in a stream of air. It is based on chromatomembrane absorption of formaldehyde from the air to a microvolume of distilled water followed by the determination of the product formed upon the reaction of formaldehyde with acetylacetone in the carrier stream under the heating at 90°C. The detection limit of formaldehyde decreased proportionally to the time period of absorption and was 10 µg/m³ after 6 minutes at air flow rate 500 ml/min. Temperature dependence of the partition coefficient of formaldehyde in the system of air/water was established and the technique for generating the modeling gas mixtures with the given concentration of the formaldehyde was offered by the passing nitrogen gas through the water solution of formaldehyde.

Keywords Formaldehyde, air, photometric determination, absorption, acetylacetone, chromatomembrane cell

Introduction

The determination of formaldehyde in atmospheric and indoor air requires the effective methods of preliminary concentration [1,2]. The main disadvantage of the traditional absorption technique based on bubbling air through the absorbent is the low rate of interphase exchange that causes hourly sample preparation [3,4]. Fluorometric flow injection analysis of formaldehyde in the atmosphere was developed [5] where industry air samples were aspirated during 40 min in advance using conventional impinger and the LOD of the method was 0.9 ppb. Other problems with the bubbling technique are the restricted opportunity for decreasing the detection limits and difficulty in creating an automated system. In the last years different investigations using the gas diffusion scrubbers were carried out, Toda et al. developed the portable system for sensitive and near-real time measurement of formaldehyde in the air using parallel diffusion scrubbers [6]. But the application of standard gas mixtures for graduation of the analyzer results in the rigid control of the temperature and the analyzed air rate in order to receive the correct data. The more effective chromatomembrane absorption opens new prospects in the methods of concentration [7]. Chromatomembrane preconcentration allows for a time reduction in the absorption process and also allows to graduate the analyzer using solutions because of the complete chromatomembrane absorption of analyzed gas. The main principles and advantages of the chromatomembrane mass exchange processes are given in a number of works [8, 9]. The chromatomembrane preconcentration of the formaldehyde carried out [10] but adsorptive polarographic determination makes it inappropriate for flow injection analysis.

Chromatomembrane absorption easily allows automating an absorption stage of substances from a stream of air to the liquid absorbent. In a combination to the subsequent automated flow injection analysis it creates favorable preconditions for the development of the automated universal gas analyzers for the monitoring of harmful organic substances in atmospheric and workplace air.

As shown in the previous papers [11-13] the most specific reagent for photometric and also fluorometric determination of formaldehyde is acetylacetone. However, photometric determination was chosen because it is more economical. Formaldehyde reacts with acetylacetone in the presence of ammonium acetate to form 3,5-diacetyl-1,4-dihydrolutidine (DDL) that absorbs the electromagnetic radiation at 420 nm.

The purpose of the investigation was to develop an automated scheme for the realization of express flow injection determination of formaldehyde with chromatomembrane absorption preconcentration in the atmospheric air.

Experimental

Chromatomembrane cells (CMC) were made of PTFE and manufactured by researchers at St. Petersburg State University's Chemistry Facility. Aspirator M - 822 («Krasnii viborzhec», Saint Petersburg, Russia) and flow injection analyzer PIKON-02 ("Rosanalyt", Saint Petersburg, Russia) with the photometric detector were used for realization of chromatomembrane absorption of formaldehyde from a gas phase and photometric flow injection determination in the absorbent. Details of CMC application in the flow injection analysis are given earlier [14, 15].

The stainless steel tubes usually used in gas chromatography as conjunctive lines contained following alloy components: 12%Cr, 18%Ni and 10%Ti. The tubes with inner diameter of 1 mm and a wall thickness of 0.5 mm were used.

* Corresponding author:
e-mail: e_vaskova@yahoo.com

To prepare a standard solution of formaldehyde a volumetric weight method was used: 2.7 mL of formaldehyde (37 %, "Himreaktiv", Saint-Petersburg, Russia) was dissolved in 100 mL of distilled water to prepare a 1 % of formaldehyde solution which was standardized by iodometry. The solution was diluted 10000-fold to prepare a working solution of formaldehyde with a concentration of 1ppm.

Modeling gas mixtures (MGM) of formaldehyde were made by the pressurization of nitrogen through water solutions with known concentrations of formaldehyde. For the determination of formaldehyde concentration in generated mixture C_G , the stream of gas was pressurized through an absorber with a porous plate. The absorber was filled up with 10 mL of distilled water (V_L) that provided the full absorption of formaldehyde. By photometric determination of the formaldehyde concentration in water C_L and using the volume of pressurized gas V_G , the concentration of formaldehyde in the stream of gas was found:

$$C_G = C_L V_L / V_G \quad (1)$$

Therefore after the formaldehyde concentration was determined in the modeling gas mixture, the partition coefficient K between water and gas phases was found using the following equation:

$$K = C_L^0 / C_G \quad (2)$$

where C_L^0 is the known concentration for formaldehyde in a water solution through which a stream of nitrogen was passed while generating a modeling gas mixture.

The flow injection manifold for determining formaldehyde in the air is shown in Fig. 1. A main part of the arrangement was the hydraulic system of analyzer PIAKON-02 that included a switching valve (1), peristaltic pump (7), warmed reaction coil (8), cooled coil (9) and photometric flowing detector (10). In the first step (the switching valve (1) was in the position drawn by thin lines) absorption of formaldehyde from a stream of air sample (3) into 0.25 mL of distilled water which was introduced from (2) was carried out in CMC (4) by using electroaspirator (5). In the second step, after switching the position of valve (1), the concentrated formaldehyde solution was eluted to a warmed reaction coil (8) where it mixed with a stream of a reagent solution (6) (1:1). Further, after cooling off in the cooled coil (9), a stream of an analyzed solution went to the photometric flow detector (10, $\lambda = 420$ nm). The cycle of the analysis continued in an automatic mode without refreshing the CMC before next sample injection.

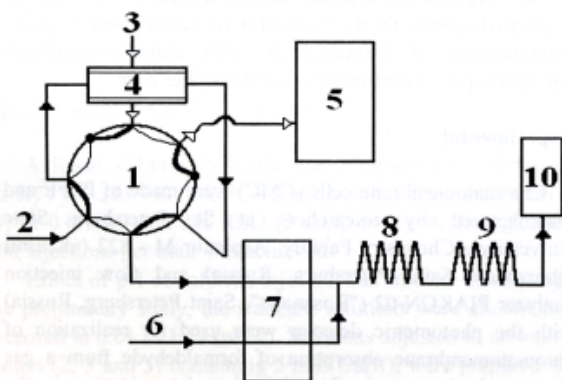


Fig 1. Scheme of flow injection system for determination of formaldehyde from the air using chromatomembrane absorption: 1, switching valve; 2, input of water absorbent; 3, input of analyzed air; 4, CMC; 5, electroaspirator; 6, input of reagent carrier; 7, peristaltic pump; 8, warmed reaction coil; 9, cooled reaction coil; 10, flow photometric detector.

Results and Discussion

The first stage of the experiment consisted of selecting optimal conditions for the flow injection determination of formaldehyde in water solutions. Therefore instead of CMC a sampling loop 0.25 mL was used. The loop was filled with a water solution of formaldehyde that was dosed into the analyzer. At the second stage optimal conditions for chromatomembrane absorption of formaldehyde were carried out and the technique for determination in air was developed.

The effect of pH and studies of different ranges of component concentrations showed that for photometric determining of formaldehyde in water samples, following component concentrations in a reagent stream were the best for receiving the strongest analytical signal (absorbance): acetylacetone, 1.2 g/L; acetate of ammonium, 140 g/L; acetic acid, 2 g/L, pH = 6.2. The effect of warmed stainless steel coil length shown in Fig. 2.

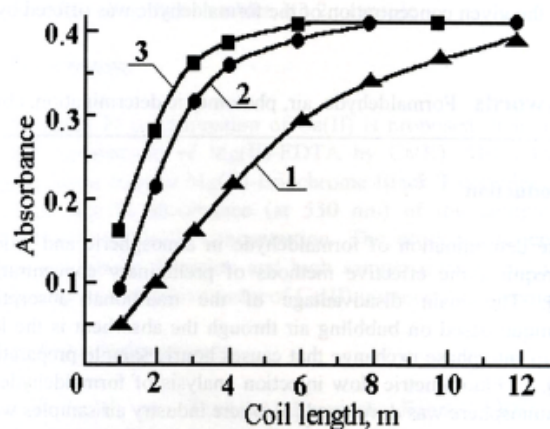


Fig.2. Effect of warmed coil length at different temperatures on formaldehyde absorbance. 1, 85 °C; 2, 90 °C; 3, 95 °C. Carrier flow rate was 4.4 mL/min.

Due to the received results a warmed coil with the length of 3 m and a temperature of 90 °C were chosen. The cooling coil length was 0.5 m and temperature was 15 °C. According to the total flow rate of 4.4 mL/min of the reagent mixture through the mixing coil the time flow through the warmed coil was 40-50 seconds.

Under the chosen conditions the value of the detection limit of formaldehyde in the water solution was 40 µg/l and the time of flow injection determination was 90-100 seconds. The calibration graph with aqueous formaldehyde solution showed a straight line through the origin up to 0.5 µg. Using the method of least squares the slope Z was calculated.

Experiment results showed that at room temperature the partition coefficient of formaldehyde between water and gas phases exceeds 10^5 . The following equation shows the dependence of the partition coefficient from temperature T in the range of (15-30) °C with relative error less than 5%:

$$\log K = 883.3/T + 2.2 \quad (3)$$

According to the results, it was evident to use distilled water for absorption of formaldehyde from the air.

To estimate the effectiveness of chromatomembrane absorption the mass of formaldehyde in a stream of air was determined upon the output of CMC. Fig. 3 details the dependency of formaldehyde breakthrough volume (with 95%

extraction of formaldehyde from air) on the air flow rate. The effectiveness of chromatomembrane absorption slightly depends on the velocity of the air flow. Thus the maximal air flow rate was up to 500 mL/min that allowed decreasing duration of the absorption stage.

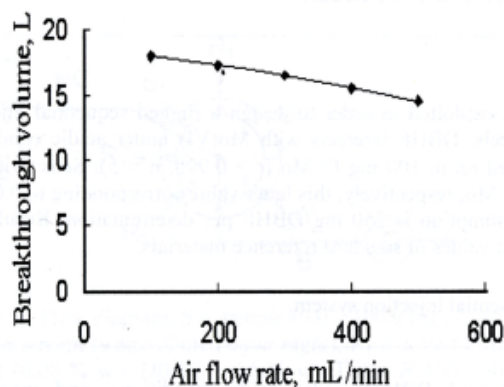


Fig. 3. Effect of air flow rate passed through the CMC on the breakthrough volume with 95% extraction of formaldehyde.

The amount of the absorbed formaldehyde rises up in a direct ratio with the volume of analyzed air passed through CMC (Fig.4). It allows the determination of the formaldehyde concentration (C) in the analyzed air using the formula:

$$C = AZ/V \quad (4)$$

Where A is the absorbance; Z is the slope calculated from a graduation stage of the analyzer; V is the volume of air passed through CMC.

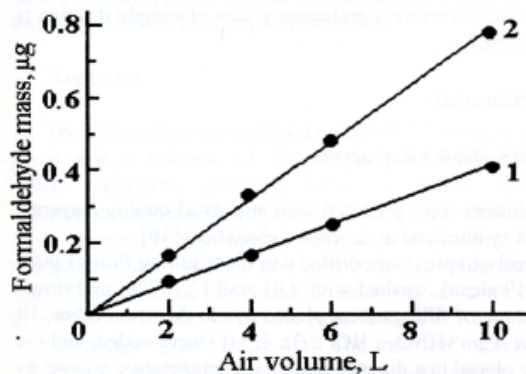


Fig. 4. Effect of the model air mixture volume pressurized through the CMC on the absorbed formaldehyde mass. Concentration of formaldehyde: 1, 35 µg/m³; 2, 70 µg/m³.

Detection limit of formaldehyde was 10 µg/m³ with six-minutes of absorption and decreased in the direct ratio with the time of absorption. The response of the analyzer for the modeling gas mixture with a concentration of formaldehyde of 35 µg/m³ and 70 µg/m³ is illustrated in Fig.5. The duration of formaldehyde absorption was 6 minutes; the air flow rate was 500 mL / minutes.

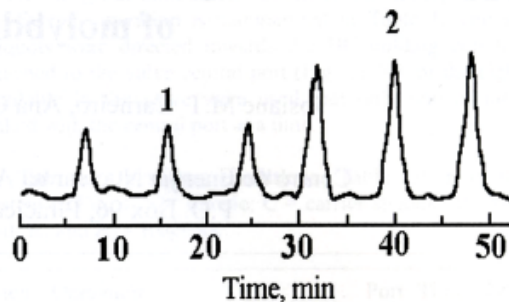


Fig. 5. Analytical response of the flow injection analyzer in time for analysis of model gas mixtures with known formaldehyde concentration. 1, 35 µg/m³; 2, 70 µg/m³.

Conclusions

The combination of chromatomembrane absorption with the subsequent flow injection analysis of absorbable substance allowed the automation of formaldehyde determination in the air at low levels of the most rigid sanitary-and-hygienic standards. The detection limit decreased proportionally to the absorption time and was 10 µg/m³ after 6 minutes at air flow rate 500 ml/min. Due to the chromatomembrane variant of absorption it was possible to limit the duration of a preconcentration stage of formaldehyde from the air in comparison to the conventional air-lifting process.

Acknowledgments

Authors express gratitude to the Russian Fund of Basic Researches (the grant 03-03-32328) and to the Ministry of Education and Sciences of Russia (grant E-02-5-135).

References

- [1] Q. Fan, P.K. Dasgupta, *Anal. Chem.*, **66**, 551 (1994).
- [2] M. Possanzini, V.Di Palo, *Atmos. Environ.*, **30**, 3757 (1996).
- [3] L. Salas, H. Singh, *Atmos. Environ.*, **20**, 1301 (1986).
- [4] S.M. Correa, E.M. Martins, *Atmos. Environ.*, **37**, 23 (2003).
- [5] T. Sakai; S. Tanaka, *Talanta*, **58**, 1271 (2002).
- [6] K. Toda, K. Yoshioka, *Anal. Chim. Acta*, **531**, 41 (2005).
- [7] L.N. Moskvina, *J. Chromatogr. A*, **669**, 81 (1994).
- [8] O.V. Rodinkov, L.N. Moskvina, *Russian J. Phys. Chem.*, **75**, 272 (2001).
- [9] L.N. Moskvina, A.L. Moskvina, *LRA*, **10**, 3 (1998).
- [10] Z. Qi; Z. Hong; G. He, *Talanta*, **57**, 317 (2002).
- [11] B.J. Compton, W.C. Purdy, *Anal. Chim. Acta.*, **119**, 349 (1980).
- [12] H. Tsuchiya, S. Ohtani, et al., *Analyst*, **119**, 1413, (1994).
- [13] O. Largiuni, R. Udasti, *Intern. J. Environ. Anal. Chem.*, **82**, 97, (2002).
- [14] Y. Wei, M. Oshima, J. Simon, L.N. Moskvina, S. Motomizu, *Talanta*, **58**, 1343 (2002).
- [15] H. Erxleben, J. Simon, L.N. Moskvina, et al., *Fresenius J. Anal. Chem.* **366**, 332 (2000).

(Received March 30)

(Accepted May 26)