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Stepwise Injection Photometric Determination of Phenol in Air

Andrey Bulatov*, Michael Soloviev, Anastasia Petrova, Aleksey Moskvin, Leonid Moskvin

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

Abstract

An automated method for the photometric determination of phenol in air has been developed. This method includes liquid-absorption isolation of phenol from a gas phase. The isolation proceeds directly in a reaction vessel by a hydraulic scheme of a stepwise injection analyzer with subsequent generation of an analytical form reacted with 4-aminoantipyrine. The determination concentration range is from 10 to 200 μg m^{-3} at the sample volume of 4.8 L and time of concentration of phenol is 6 min. Time for analysis is 10 min.

Keywords Stepwise injection analysis, photometry, air, phenol

1. Introduction

The content of phenols refers to number of hard normalized quality coefficients of air, because phenols are able to influence negatively on men's health and environment [1]. The method used for photometric determination of phenols in air in analytical practice bases on liquid-absorption isolation of phenols from gas phase into liquid phase with sequent determination by photometric reaction with 4-aminoantipyrine [2]. Disadvantages of this method are big expense of time and reagents at performance of analyses. The important problem is search of instrumental solutions, that allows to automate known method of photometric determination of phenols in air. The solution of already formulated problem is automation of given method in conditions of stepwise injection analysis (**SWIA**) [3]. Presence of reaction vessel communicated with atmosphere in scheme of SWIA provides isolation and concentration possibility of analytes from gas phase into liquid solutions, mechanical solution's mixture of reagents by gases flow and maximal unification of hydraulic schemes.

The purpose of given research is development of an automation method for the photometric determination of phenol in air by stepwise injection analysis.

2. Experimental

2.1. Reagents and solutions

A 0,1 g L^{-1} phenol solution was prepared by dissolving of proper reagent's shot in distilled water. Obtained solution was standardized by iodometric titration. 10 mL of a 0.1 g L^{-1} phenol solution, 15 mL of bromate-bromide mixture, 10 mL of a 1 M H_2SO_4 were added into a flask, mixed, closed and left for about 30 min. Then 1g of potassium iodide was added and flask was closed again. Through 5 min liberated iodine was titrated by a 0.01 M sodium thiosulfate solution in presence of starch as an indicator (1 ml of 1 g L^{-1} solution). For determination of quantity of the liberated bromine blank titration carried out.

For preparing bromate-bromide mixture 0.3 g of potassium bromate and 1.2 g of potassium bromide were dissolved in 500 mL of distilled water.

Phenol solutions for calibration were prepared by subsequent dilution of the standard solution by borate buffer solution (pH=10).

In order to prepare a borate buffer solution (pH=10), 20 g of sodium tetraborate was dissolved in 1 L of distilled water. The pH buffer solution was then corrected by 1 M HCl and 1 M NaOH.

0.2 g L^{-1} solution of 4-aminoantipyrine and 1 g L^{-1} solution of potassium ferricyanide were prepared directly before the experiment.

Gases mixtures of analyte were prepared by passing nitrogen with velocity of 0.8 L min^{-1} through 20 ml of a phenol solution in distilled water (5, 10, 20 mg L^{-1}) in glass bubbler.

All reagents used were of analytical reagent grade ("Reactive", Saint-Petersburg, Russia).

2.2. Apparatus

The scheme for the determination of phenol in air was created on a base of the stepwise injection analyzer "SWIA-1" (St.

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*Corresponding author

E-mail: bulatov_andrey@mail.ru

Petersburg State University, Russia). Photometric detector (λ=500 nm, length of optical way 50 nm); peristaltic pump, that provides backspacing of flow's direction; six-ways valve (polytetrafluoroethylene), reaction vessel – monolithic cell from acryl (height 50 mm, inside diameter 10 mm) filled with granules (polytetrafluoroethylene, diameter 0.5 mm) were used in this work. The analyzer was operated by the computer.

The SWIA scheme that includes absorption of phenol from air into absorbing solution is shown on Fig. 1.

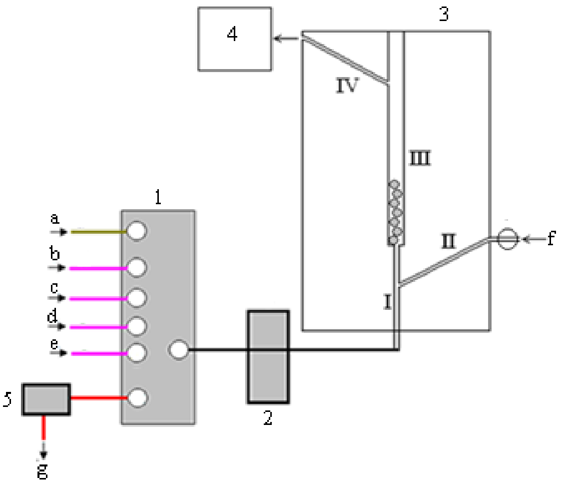

Fig. 1 SWIA scheme for phenol's determination in air: multi-way valve (1); reverse pump (2); reaction vessel (3) (channels for absorbing solution (I), gas sample (II), channels for absorption of analyte (III) and waste (IV); aspirator (4); detector (5); channels for entering: borate buffer solution (a), 4-aminoantipyrine solution (b), potassium ferricyanide solution (c), nitrogen (d), distilled water (e), gas sample (f); waste (g).

3. Results and discussion

3.1. The choice of conditions for liquid-absorption of phenol isolation in reacting vessel

At first the influence of gating rate of gas phase through absorbing solution in reaction vessel with polytetrafluoroethylene's granules on efficiency of liquid-absorption phenol's isolation from gases phase was studied. Borate buffer solution was used as an absorbing solution. It provides phenol's isolation into liquid phase and reaction with 4-aminoantipyrine. Granules were used for increasing of phase's contact area in a process of gas's bubbling through reacting vessel.

The bubbler (2), that is intended for generation of gas mixtures, was connected with two sequentially joined equal reaction vessels 3 and 4 (Fig. 2). In every reaction vessel 0.5 mL of borate buffer solution was added. The gas mixture, generated in bubbler, was passed with fixed rate (from 0.2 to 2 mL min^{-1}) through reaction vessels (3 and 4) during 5 min. After that reaction vessels were cut, then one by one were connected in SWIA scheme (Fig. 1) and phenol's determination was carried out. Through multi-way valve (1) by means of pump (2) 60 µL of 0.5 g L^{-1} of 4-aminoantipyrine solution were added into reaction vessel (3) with rate 2 mL min^{-1}. After that operations solution were mixed by nitrogen (d). Then 60 µL of 2 g L^{-1} of potassium ferricyanide solution and nitrogen for mixing (d) were added into reaction vessel by means of pump (2) through valve (1) with rate of 2 mL min^{-1}. After injection of each reagent's batch 0.25 mL of borate buffer solution (a) were added for services cleaning. Then colored solution from reaction vessel (3) was directed into detector (5) to measure the absorbance.

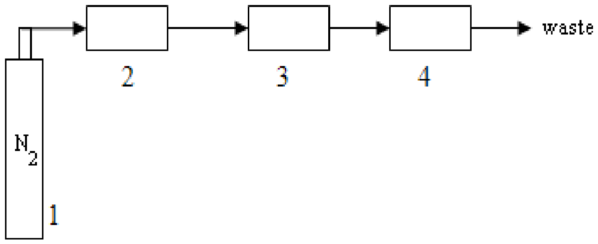

Fig. 2. The scheme of isolation of phenol from gas phase: 1 – balloon with nitrogen; 2 – bubbler for generation of gas mixture; 3 and 4 – reaction vessels with absorbing solution.

It was found up, till gating rate of gas phase – 0.8 L min^{-1}, effective absorption of phenols takes place in first reaction vessel (Fig. 3), which was chosen as optimal for further experiments.

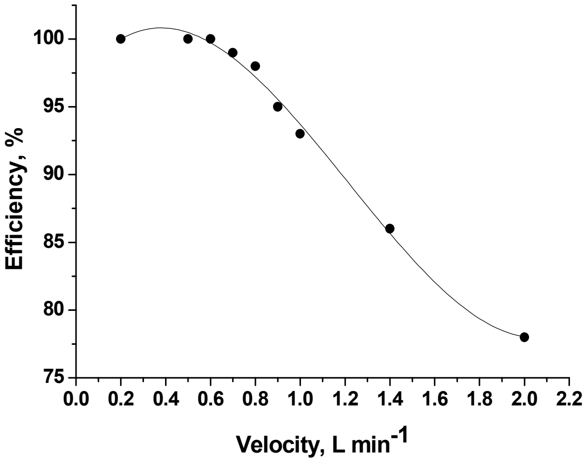

Fig. 3. The influence of gating rate of gas phase on effectuality of phenols absorption.

3.2. The choice of concentrations of 4-aminoantipyrine and potassium ferricyanide

Then the influence of concentration of 4-aminoantipyrine on absorbance of analytical form solution was studied. For that 0.5 mL of 0.8 mg L^{-1} of phenol's solution in borate buffer solution (a), 60 μL of 4-aminoantipyrine solution (b) was added through valve (1) (Fig. 1) by means of pump (2) into reaction vessel (3). The concentration of photometric reagent was changed from 0.05 to 0.5 g L^{-1}. After that the solution in reaction vessel was mixed by the nitrogen stream (d). Then 60 μL of 2 g L^{-1} of potassium ferricyanide solution (c) with rate of 2 mL min^{-1} and nitrogen for mixing were added into the reaction vessel. After injection of each portions of reagent's solutions 0.25 mL borate buffer solution (a) was added. Then colored solution from reaction vessel (3) was directed into detector (5) for measuring of absorbance.

According to received data (Fig. 4) maximal magnitude of absorbance achieves from concentration of 4-aminoantipyrine in injected solution 0.2 g L^{-1}. It was chosen as an optimal concentration.

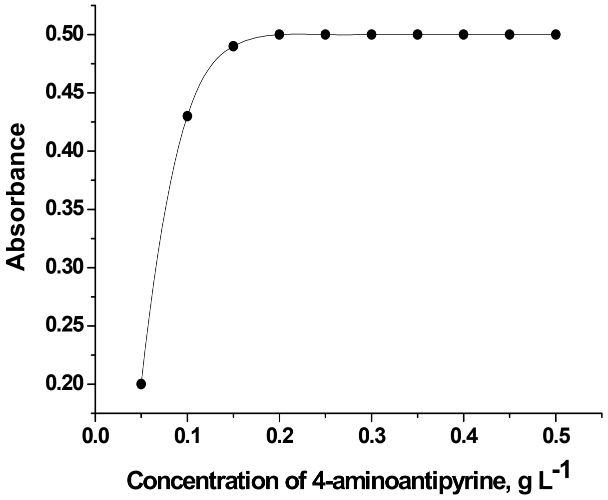

Fig. 4. The concentration's influence of 4-aminoantipyrine on absorbance (phenol's concentration – 0.8 mg L^{-1}).

Then the influence of concentration of potassium ferricyanide on the magnitude of absorbance was studied. The experiment was carried out by above mentioned scheme. Here concentration of 4-aminoantipyrine was equal to 0.2 g L^{-1} and concentration of potassium ferricyanide was varied from 0.5 to 5 g L^{-1}.

From received data (Fig. 5) optimal concentration of potassium ferricyanide has been chosen equal to 1 g L^{-1}.

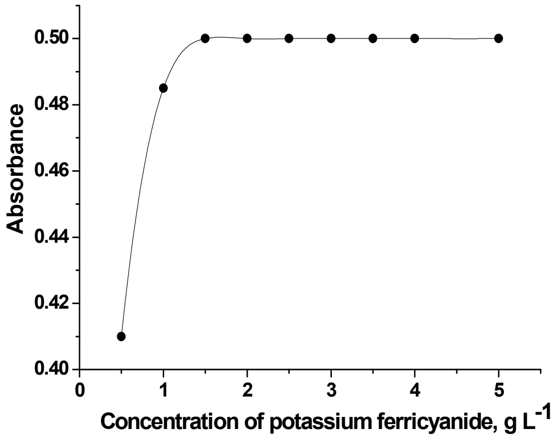

Fig. 5. The concentration's influence of potassium ferricyanide on absorbance (phenol's concentration – 0.8 mg L^{-1}).

3.3. Stepwise injection photometric determination of phenols in air

Developed method for determination of phenols in air includes two steps. At first through multi-way valve (1) by means of pump (2) into reaction vessel (3) (Fig. 1) 0.5 mL of borate buffer solution (a) was added. Then with help of aspirator (4) sample of air has been passed through absorbing solution during 6 min with rate of 0.8 L min^{-1} and isolation of analyte took place into liquid phase too. Chosen analyte's time isolation allows to perform the determination of phenols at the level of maximum permissible concentration in the ambient air (30 μg m^{-3}). If it's necessary, time of concentration can be increase without constitutive loss of analyte.

On the next step through valve (1) (Fig. 1) by means of pump (2) into reaction vessel (3) 60 μL of 0.2 g L^{-1} of 4-aminoantipyrine solution and 0.25 mL of borate buffer solution (a) and nitrogen for mixing (d) were added. Then colored solution from reaction vessel (3) was directed into detector (5) for measuring of absorbance (A_1).

At the close of process distilled water (e) was injected into system for cleaning communications and background signal (A_2) was measured.

Difference A_1-A_2 is used as magnitude of absorbance corresponding to the content of phenols.

For setting the order of mixing and amounts of reagents and also the order and emission's time of analyte program was created. It allows to set states of controlled elements of device in each time as a matrix. Each row in this matrix corresponds to certain stage, while columns reply to position of each controlled element. The matrix for developed method is shown in Table 1.

Table 1. Conditions of phenol's determination in the SWIA variant.

Time, s	Valve position	The direction of pump rotation (+1;0;-1)*	Measurement (0;1)**	Comments
15	a	+1	0	Injection of buffer solution
360	f	0	0	Injection of sample
2	b	+1	0	Injection of 4-aminoantipyrine solution
8	a	+1	0	Injection of buffer solution
30	d	+1	0	Injection of nitrogen
2	c	+1	0	Injection of potassium ferricyanide solution
8	a	+1	0	Injection of buffer solution
30	d	+1	0	Injection of nitrogen
30	g	-1	0	Injection of sample solution into detector
10	g	0	1	Measurement of absorbance
20	e	+1	0	Injection of distilled water
30	d	+1	0	Injection of nitrogen
30	g	-1	0	Injection of distilled water into detector
10	g	0	1	Measurement of background signal
20	g	-1	0	Waste

*+1 – rotation of the pump clockwise, 0 – stop of the pump, -1 – rotation of the pump counter clockwise; ** 0 – measurements are not made, 1 – registration of a signal from the detector; the velocity of flows of liquid and gases phases – 2 and 800 mL min^{-1}, directly.

Table 2. The results of phenol's determination in gases mixtures and in the air (n=4, P=0.95).

Sample	Added *, μg m^{-3}	Found, μg m^{-3}
Gas mixture «I»	9±1	11±2
Gas mixture «II»	18±2	15±4
Gas mixture «III»	36±4	37±2
Air from organic chemistry laboratory	-	<LOD
Air from organic chemistry laboratory	-	21±4

*concentration of phenol (C, μg m^{-3}) generated in gas phase was calculated from distribution coefficient (K_d=(1,8±0,2)·10^5), $C = C_0 K_d^{-1}$, where C_0 – concentration of phenol in water solution (5, 10, 20 mg L^{-1}).

The calibration of SWIA by standard water solutions of phenol in borate buffer solution, which were approached through channel (1), was used during carrying out analysis.

The developed method was tested in analysis of air by method «added-found». In this method known amount of analyte was added into sample of gas by above-mentioned method of generating of standard gas mixtures. Added and found amounts of phenol are nearly equal (Table 2).

The calibration is linear in the range from 10 to 200 μg m^{-3} of phenols. The detection limit of phenols is 3 μg m^{-3} (3σ) in the sample's volume 4.8 L and time of analysis 10 min.

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