Stepwise Injection Photometric Determination of Hydrogen Sulfide in Natural Gas

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Abstract

The new approach to automate stationary techniques to analyze gas using a stepwise injection analysis (SWIA) is revealed and determination of hydrogen sulfide in natural gas using SWIA is described. The determination is based on absorption of hydrogen sulfide into open to the air reaction tube with 2% zinc acetate solution, stepwise injection of the reagents to the reaction tube to form a methylene blue and subsequent measurement of the downstream colored product at 670 nm. The open to the air reaction tube is a part of hydraulic system and has PTFE granules to increase a surface area during the gas sample bubbling. Nitrogen was purged to the reaction tube for enhanced mixing. All experimental manipulations were controlled by software.

The absorbing solution has an absorption efficiency of >98% at a sampling flow rate of 0.3 l/min. This method provides a linear working range of 0.5 to 20 mg/m^3 with a relative standard deviation of 2.5 % (n=10) at the 5 mg/m^3 level for 3 liters of gas sample and concentration time of 10 min. The determination limit of 0.1 mg/m^3 was achieved using 3 liters of gas sample and time of one cycle of 18.5 min.

Key words: Stepwise injection analysis (SWIA); Hydrogen Sulfide; Natural gas.

Introduction

Till now problems of automation of the chemical analysis mainly were solved using flow injection analysis (FIA) [1] or sequential injection analysis (SIA) [2]. Sequential injection analysis, the second generation of traditional FIA, was introduced to further reduce reagent consumption and to make the technique more compatible with computer automation. While conventional FIA requires the physical rearrangement of the flow manifold to perform different assays, SIA methodology allows for all experimental stages to be altered by software control [3]. However both methods obligated by use of additional connectors, diffusion cells or manual interaction in case allocation of absorbed analyte [4,5]. Dispersion of analytical signal is a significant drawback of FIA, SIA and lab-on-valve (LOV) technique [7] due the volume minimization of the sample path and not sufficient mixing. The differences between flow velocities of adjacent streamlines, flow reversals and flow acceleration are the only factors that promote mixing. In many cases dispersion minimized by increase the magnitude of the flow reversal and the distance traveled [8], accomplished mixing is gained by stopping the flow [9] that elongates the time of analysis.

Stepwise injection analysis (SWIA) is a new variant of the flow methods helps to avoid the drawbacks described above [10]. The scheme of SWIA assumes reproduction of all stages of the analysis as if it was for stationary techniques (sampling; analyte preparation; reagents adding; complete mixing of a solution to eliminate the dispersion of an analytical signal; thermostat control; a pause to achieve the maximal values of an analytical signal; measurement of an analytical signal).

SWIA as well as SIA usually consists of three basic executive elements: a single-channel bi-directional pump, a multiposition valve in which several inputs switch to the one output and a flow through detector. In comparison with FIA and SIA or LOV stepwise injection analysis scheme doesn't contain a reaction coil neither holding coil; instead the open to the air cylindrical reaction tube with a funneled output is used. In addition one of the inputs of the multiposition valve incorporates with an atmosphere or with inert gas, providing intensive mixing in the reaction tube therefore the dispersion of an analytical signal is eliminated. SWIA allows concentrating analyte from a gas phase to water solution in reaction tube within the analysis scheme that does not require application of additional connectors and simplifies the design of the analysis.

The present work is devoted to experimental verifying of an opportunity for the automation of the environmental monitoring gas quality using SWIA to determine H$_2$S in natural gas.

Due to high sensitivity (molar absorptivity is 3×10^4 liter·mol^{-1}·cm^{-1}) and selectivity [9] described in numerous papers the methylene blue (MB) method was chosen for photometric determination of H$_2$S. Effect of interfering mercaptans [10] on determination hydrogen sulfide was eliminated by choosing 2% Zn(CH$_3$COO)$_2$ as an absorbing solution [11]. Zinc acetate is widely used as a trapping solution for H$_2$S and does not require any precaution to prevent the photo-oxidation of fixed sulfide [12].

Experimental

Apparatus

The stepwise injection manifold for automated determination of H$_2$S is shown in Fig. 1. A main part of the hydraulic system is the flow-injection analyzer PIACON-30-1 (Rosanalyt, St. Petersburg, Russia) with flow through photometric detector (λ = 670 nm, light path length 10 mm), a bi-directional pump (silicon 1 mm i.d.), six-way and two-way valves. An open to the air glass reaction tube (height 200 mm, 15 mm i.d.) was filled with PTFE granules of 2-3 mm in diameter to maximize surface area. Flow tubes were made of PTFE (0.5 mm i.d.). Instrumental control, signal evaluation, and determination of analyte concentration with integrated calibration were performed using software package with standard RS232C interfaces. To set the process order and time of the analysis stage a special matrix was used. This matrix was a part of the program that provided full computer control of the SWIA. Each line in this matrix corresponded to a certain stage and columns corresponded with the position of each operated element. The matrix for the developed technique is presented in Table 1.

Reagents

All chemicals used in this experiment were of analytical reagent grade quality and purchased from Ecros Chemical Co., (St. Petersburg, Russia). Solutions were prepared with distilled

Table 1 Conditions for the determination of hydrogen sulfide in natural gas.

Time, s	Six-way valve position	Double valve position	The direction of pump rotation (-1;0;1)[*]	Measurement (0;1)[**]	Comment
50	a	II	+1	0	Absorbing solution flow in RT
10	b	II	+1	0	N,N-dimethyl-*p*-phenylenediamine solution flow in RT
10	c	II	+1	0	Fe(III) solution flow in RT
30	d	II	+1	0	N_2 flow in RT
100	f	II	-1	1	Solution flow through temperature-controlled coil to detector
50	a	II	+1	0	Absorbing solution flow in RT
600	a	I	0	0	Sample flow in RT
10	b	II	+1	0	N,N-dimethyl-*p*-phenylenediamine solution flow in RT
10	c	II	+1	0	Fe(III) solution flow in RT
30	d	II	+1	0	N_2 flow in RT
100	f	II	-1	1	Solution flow through temperature-controlled coil to detector
50	e	II	+1	0	Water flow in RT
60	f	II	-1	0	Washing liquid waste from RT and detector

*-1 – rotation of the pump clockwise

0 – a stop of the pump

+1 – rotation of the pump counter clockwise

**0 – measurements are not made

1 – registration of a signal from the detector

RT – reaction tube

Rates of stream of water and gas phases are $5 \cdot 10^{-3}$ and 0.3 l/min accordingly

water, which was boiled prior to preparation of the set of standards and reagents to make it free from dissolved oxygen.

The sulfide standard solution (ca. 0.01 M) was prepared daily by dissolving 2.4 g of $Na_2S \cdot 9H_2O$ in 10 ml of a 1 M NaOH solution and was diluted to 1000 ml with oxygen-free water. The final solution was standardized daily iodimetrically [13]. Working solutions were prepared by dilution of the standard solution with oxygen-free water.

The N,N-dimethyl-*p*-phenylenediamine of 0.25, 0.65, 1.0, 1.5, 2.5 g/l was prepared daily by dissolving stock solution in 4.5 M HCl.

The Fe (III) solution (ca. 3 g/l) was prepared daily by dissolving 15 g of $FeCl_3 \cdot 6H_2O$ in 100 ml of a 4.5 M HCl solution. The Fe (III) ions solution was standardized daily complexonometry [14].

To prepare 2% $Zn(CH_3COO)_2$ solution, 2 g of $Zn(CH_3COO)_2$ was dissolved in 50 ml water, 1 ml concentrated acetic acid was added and then was diluted to 100 ml with water.

0.2 M H_2SO_4 solution was purchased from Ecros Chemical Co., (St. Petersburg, Russia).

Generation of the H_2S standard gas mixtures

To prepare the H_2S standard gas mixtures, 3, 30, 60, 90 and 120 mg/l of working solutions were used. 0.5 ml of working solution S^{2-} ions and 0.5 ml of 0.2 M H_2SO_4 solution were placed into a glass bubbler (8) and nitrogen (9) was passed through with the flow rate of 0.3 l/min (Fig .1). Quantity of H_2S in gas phase (m_i) was calculated using the equation: $m_i = C_i \cdot V$, where C_i – S^{2-} ion concentration in the working solution, g/l; V- the volume of S^{2-} ion solution in bubbler (0.5 ml).

Calibration graph

The calibration of the standard gas mixtures using SWIA was carried out before the analysis of natural gas (Fig. 1). SWIA method excludes bubbles in the flowing stream and eliminates the dispersion of analytical signal due the completion of analytical reaction in the open to the air reaction tube (3).

Initially, all the reagents used in the methylene blue (MB) method with absorbing solution were pumped into the reaction tube (3) at flow rate of 5 ml/min using bi-directional pump (1) and the six-way valve (2). Baseline was achieved by measuring the absorption of the solution from reaction tube (3) without H_2S. Solution from the open to the air cylindrical glass tube (3) was pumped through the temperature-controlled coil, 20 cm at 40 ^{o}C (4) to the flow photometric detector (6). Flow time was established by software Table 1 so that no air bubbles get into the flow system. Analytical signal was measured at 670 nm, light path length 10 mm.

To record maximum absorbance – plateau level, for different concentration of H_2S, 0.5 ml of each working solution was mixed with 0.5 ml of 0.2 M H_2SO_4 solution in the glass bubbler (8). Double valve (5) was switched into the position (I) so that H_2S was purged to the absorbing solution of 2 % zinc acetate in the reaction tube (3) by bubbling nitrogen through glass bubbler (8) at flow rate of 0.3 ml/min. After absorbing 3 liters of the sample, two-way valve was switched back to the position (II) and using the six-way valve (2) and bi-directional pump (1), 1.5 g/l N,N-dimethyl-*p*-phenylenediamine
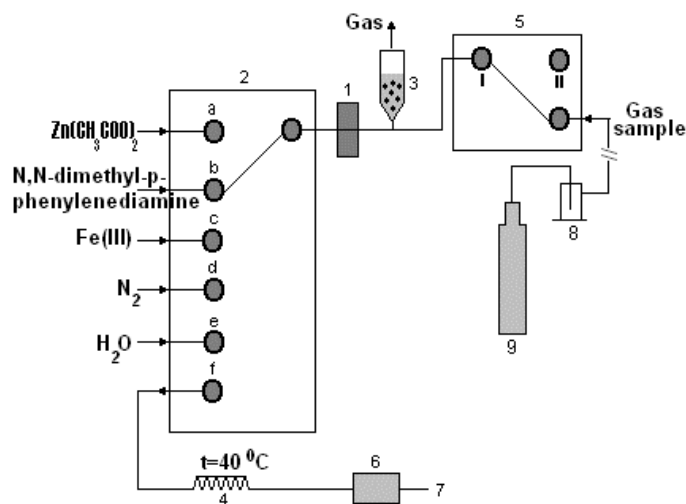
Fig. 1. Manifold of SWIA system for the determination of H_2S: 1 –bi-directional pump; 2 – six-way valve (position a, b, c, d, e, f); 3 – reaction tube; 4 –thermo coil; 5 – double-way valve (position I, II); 6 – flow detector; 7 – waste; 8 –glass bubbler for generation of the H_2S standard gas mixtures; 9 – tank with nitrogen.

solution (b), 0.2 g/l Fe(III) solution (c) and nitrogen (d) were pumped into the open to the air cylindrical glass tube (3) where hydrogen sulfide was already absorbed. After switching the valve (2) into position (f), the MB was eluted through the temperature-controlled coil (4) to the photometric detector (6). The difference between baseline and plateau level is taken as analytical signal.

The calibration graphs were linear in the range of 0.5 to 20 mg/m^3, the RSD (n=10) is less than 2.5 % for 5 mg/m^3 for 3 liters of the gas sample and concentration time of 10 min. LOD (S/N=3) was 0.1 mg/m^3 using 3 liters of the gas sample and 18.5 min time of analysis.

Sampling procedure

As shown in Fig.1, at the first stage of the analysis with a flow rate of 5 ml/min, the absorbing solution of 2 % Zn(CH$_3$COO)$_2$ (a), 1.5 g/l N,N-dimethyl-p-phenylenediamine solution (b), 0.2 g/l Fe(III) solution (c) and nitrogen (d) were pumped into the open to the air reaction glass tube (3) using six-way valve (2) and reversible pump (1). Nitrogen provided better integration in the reaction tube. Later the valve was switched to the position (f) and the solution flowed from the reaction tube (3) through the temperature-controlled coil at 40 °C (4) to the photometric detector (6) at the same time the baseline signal appeared on the monitor. At the next stage of analysis the valve (2) returns to the position (a) and the absorbing solution flows into reaction tube (3). After that the double valve (5) was switched into the position (I) and the flow of natural gas from the tank was passed into the reaction tube (3) with the flow rate of 0.3 l/min, thus analyte preconcentration into the absorbing solution occurred. Then the two-way valve was switched to the position (II) and N, N-dimethyl-*p*-phenylenediamine (b), Fe (III) ions (c) and nitrogen (d) were pumped into the reaction tube. Finally the six-way valve (2) was switched to the position (f) and the mixture flowed from the reaction tube (3) through the temperature-controlled coil at 40 °C (4) to the flow photometric detector (6). The analytical signal was measured simultaneously.

At the end of the analysis all flow system tubes were washed with distilled water (e).

Results and discussion

Evaluation of absorbing solution

At first stage the evaluation of the trapping solution was carried out. To estimate the effectiveness of H_2S absorbance into the 2 % Zn(CH$_3$COO)$_2$ solution, the absorption depending on gas flow rate was examined and illustrated on Fig.2. To increase contact surface area during bubbling, the open to the air reaction tube was filled with PTFE granules of 2-3 mm i.d. Thus the extraction of H_2S from the working solution of 7.5 mg/m^3 was 98% at the nitrogen flow rate of 0.3 l/min. Therefore gas flow rate was chosen 0.3 l/min for effective absorbency of H_2S in the trapping solution.
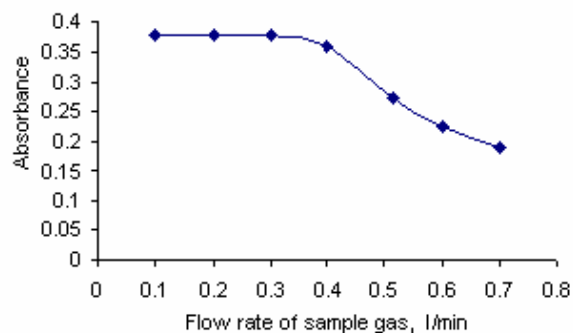

Fig. 2. Absorption efficiency of H_2S in Zn(CH$_3$COO)$_2$ solution in reaction tube depending on the flow rate of the gas sample. C(H_2S)=7.5 mg/m^3.

Absorption of analytical signal

Hydrogen sulfide reacted with N,N-dimethyl-*p*-phenylenediamine in presence of Fe(III) to form methylene blue (MB) in acidic medium. The derivatization reaction is shown in Scheme 1.

Effect of N, N-dimethyl-p-phenylenediamine and Fe (III) concentration

Using SWIA Fig. 1, the effect of N,N-dimethyl-*p*-phenylenediamine concentration in the range of 0.25 – 2.5 g/l was studied. According to the result optimum concentration
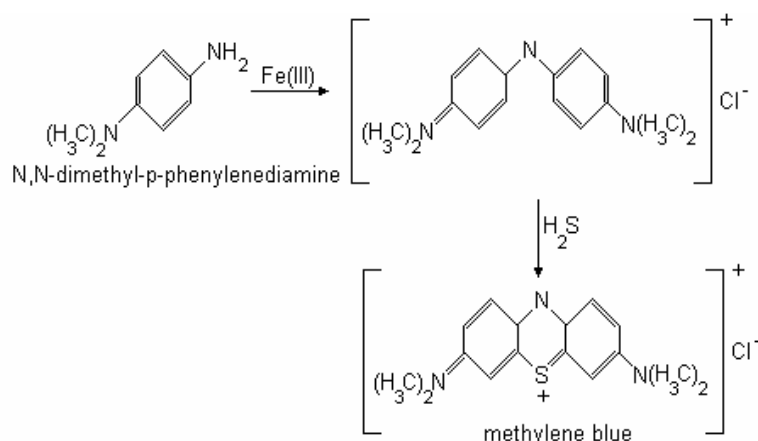
Scheme 1. Formation of methylene blue.

was chosen of 1.5 g/l (Fig. 2) where the maximum of absorbance was achieved, as shown in Fig. 3.

The derivatization of MB occurs only in the presence of Fe (III) (Scheme 1.) so the influence of Fe(III) ions concentration on absorbance was explored. The results are shown in Fig. 4. Due to the received result the concentration of 0.2 g/l Fe(III) ions in the injection solution was chosen.
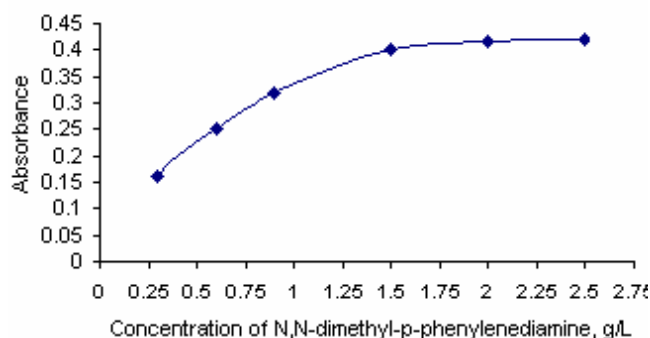

Fig. 3. Effect of N, N-dimethyl-*p*-phenylenediamine concentration on the absorbance. $C(H_2S)$=7.5 mg/m^3.

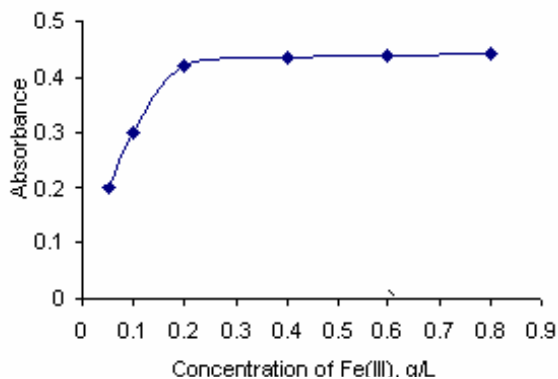Fig. 4. Effect of the Fe(III) ions concentration on the absorbance. $C(H_2S)$=7.5 mg/m^3.

Effect of temperature on the formation of methylene blue

The effect of temperature on the formation of derivative with hydrogen sulfide was studied in the range 20 – 65 ^{o}C. Thermostat control took place in 20 cm thermo coil (4), Fig. 1. The temperature was controlled by flow thermometer and was placed between thermo coil (4) and flow through detector (6). According to the online analysis of temperature effect, the maximum value of absorbance was obtained at 35-40 ^{o}C (Fig. 4). The temperature range 35-40 ^{o}C is the optimum range to form methylene blue. At lower temperature longer time for MB formation was observed meanwhile at higher temperature the formation of methylene red occurred and maximum absorbance was shifted from 670 nm to 730 nm.
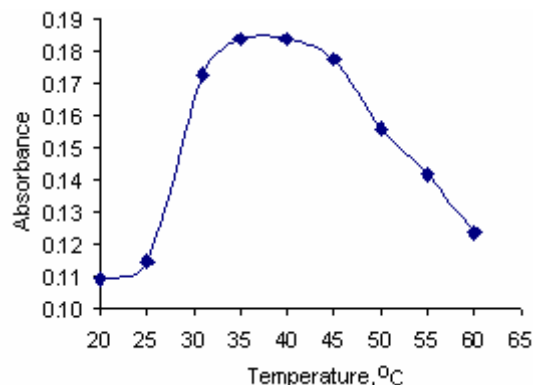

Fig. 5. Effect of the temperature on the absorbance. $C(H_2S)$=3.5 mg/m^3.

Conclusion

The present work introduces the stepwise injection analysis SWIA technique into environmental monitoring natural gas quality and demonstrates the advantage of absorbing gas into open to the air reaction tube of hydraulic SWIA scheme without physical reconfiguration. New opportunity of SWIA method allows automation of different steps of analysis without dispersion of analytical signal.

SWIA manifold provides robust method with simplicity in absorbing hydrogen sulfide and consequent analysis within the

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Table 2. Stepwise injection determination of H_2S (n=5, P= 0.95) in the natural gas.

H_2S added, mg/m^3	H_2S found, mg/m^3
0	<Cmin
0.8	0.7±0.1
2.0	1.9±0.2
6.0	5.8±0.2

automated manifold. SWIA was successfully applied for the determination of hydrogen sulfide at low level in the natural gas. According the "added-found" from Table 2 it appears that added and found quantities of H_2S in close coincide. Under optimized conditions, the developed method can be used to determine as low as 0.1 mg/m^3 of hydrogen sulfide spending 18.5 min on one cycle and 3 liters of gas sample.

Acknowledgement

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