

Research Article

Spectrophotometric Determination of Carbon Disulphide in the Workplace Air

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This paper describes a simple method of carbon disulphide determination in the air of working environment in the chemical companies and plants after its absorption into aprotic *N,N*-dimethylformamide solvent. Carbon disulphide absorbed into aprotic solvent was transformed by using ammonium hydroxide on sulphides which were determined by spectrophotometry. 5,5'-Dithiobis(2-nitrobenzoic acid) and blue tetrazolium chloride were used as chromogenic sensing reagents. Colour-reducing products were measured at the wavelength of 500, respectively 520 nm. Detection limits for determination of carbon disulphide in the air are 0.2, respectively 0.4 mg·m⁻³.

1. Introduction

Carbon disulphide (CS₂) is a strong neurotoxic poison with broad toxic influence on the human organism [1]. It belongs among important industrial chemical compounds. Enormous amount of CS₂ is produced annually for synthetic fibres, rubber-making chemical compounds, or pesticides. CS₂ is commonly present in oil industry. Significant part of CS₂ is released into the working environment and contaminates it. Determination of CS₂ in the working environment of chemical companies and plants is therefore one of the basic conditions for the health protection of workers and population.

Recently series of strongly powerful instrumental techniques have been applied in analytics using chromatographic separation methods [2–4]. Additionally traditional methods based on coloured reactions keep their relevancy. The oldest colorimetric and spectrophotometric methods are based on the reaction of CS₂ with alcohols transformed on yellow copper xanthates [5]. Coloured dithiocarbamates have the most important relevance, which results from the reaction of CS₂ with the primary and secondary amines and usually with ion of copper and nickel [6–9]. Other methods were described as well. One of the selection methods is based on the reaction of CS₂, phloroglucinol, and nickel with

production of the red salt of 2,4,6-trihydroxydithiobenzoic acid [10]. Reactions with thiols were used for spectrophotometric determination of CS₂, for instance, benzyl thiol, which in the presence of potassium hydroxide reacts on yellow potassium benzyl-trithiocarbonate [11]. Spectrophotometric kinetic iodide-azide method was also used for the sensitive determination of carbon disulphide [12]. Indirect determination of CS₂ with reagent of bis[4(4'-nitrophenyl)azo-2-nitrophenyl] disulphide is also known [13].

Determination methods of CS₂ in the air are based mostly on its consumption of solid sorbent [14] or amine solutions, for instance, triethanolamine [15]. Based on previous experiments [16], a determination method of CS₂ in the air was proposed and based on absorption of CS₂ in aprotic solvent and its transformation to sulphides. Determination of sulphides was performed using 5,5'-dithiobis(2-nitrobenzoic acid) or blue tetrazolium chloride, which are reduced to typical colouring products.

2. Experimental

2.1. Chemicals and Apparatuses. The following chemicals were used for experiments: carbon disulphide (Riedel-de Haën), 5,5'-dithiobis(2-nitrobenzoic acid) (DTNB,

Ellman's reagent), blue tetrazolium chloride (BTC), that is, 3,3'-((3,3'-dimethoxy-4,4'-biphenylene)-bis(2,5-diphenyl-2H-tetrazolium chloride)), N,N-dimethylformamide (DMFA), ammonium hydroxide 28%, and ethanol anhydrous (all from Sigma-Aldrich-Fluka). All chemicals were analytically pure. Water was distilled twice.

Two analytical reagents (A and B) were prepared.

Analytical reagent A was prepared in the 100 mL volumetric flask by weighing 0.01 g of DTNB, then 0.2 mL ammonium hydroxide (28%) was added using pipette, and DMFA was added up to the mark.

Analytical reagent B was prepared by solving 0.1 BTC in the mixture which contained 2 mL of ammonium hydroxide (28%) and 2 mL anhydrous ethanol and DMFA was added to the volume of 100 mL.

Reagents must be fresh (8 hours). Under alkaline conditions, DTNB or BTC is already transformed into the colour product without any reactant.

Measurements of absorbance were done on UV-VIS spectrophotometer Helios Alpha (Thermo Electron). The pump AirCheck 2000 (SKC) with flow meter was used for the air sampling.

2.2. Construction of Calibration Graph. Working solution was prepared by dissolving 0.1 mL CS₂ in DMFA to a total volume of 100 mL. Cleanliness of CS₂ was controlled by iodine-metric titration [17]. 4 mL of analytic reagent was measured off into a set of test tubes; using pipette 0 up to 100 μ L base solution of CS₂ was added and levelled with DMFA up to 20 mL. Absorbance values were measured against pure DMFA after 30 minutes of reaction time.

2.3. Determination of Carbon Disulphide in the Air. Steam-air mixture with CS₂ prepared in testing chamber was absorbed into 15 mL of DMFA in the washing apparatus. Speed of air flow was 200 mL·min⁻¹. After sampling, 4 mL of analytical reagent (A or B) was added to the absorbed substance and levelled with DMFA to 20 mL. Absorbance values were measured against pure DMFA after 30 minutes of reaction time.

Concentration of CS₂ in the air (c_{air}) was calculated according the following formula:

$$c_{\text{air}} = \frac{c_{\text{abs}} \cdot V_{\text{abs}}}{V_{\text{air}}}, \quad (1)$$

where c_{abs} is the concentration of CS₂ in the absorbed substance ($\mu\text{g}\cdot\text{mL}^{-1}$), V_{abs} is the volume of absorbed substance (mL), and V_{air} is the volume of air sample (L).

3. Results and Discussion

3.1. Reaction Mechanism. In the presence of ammonium hydroxide, CS₂ reacts with ammonium dithiocarbamate,

which with excess ammonium hydroxide is transformed into ammonium sulphide and ammonium thiocyanate. Sulphides reduced DTNB or BTC to coloured products suitable for spectrophotometric measurements. The course of chemical reaction for the case of DTNB reagent is displayed in Figure 1. Chemical structure of coloured product of reduction of BTC is presented in Figure 2. Value of λ_{max} 500 nm, respectively 520 nm, was read from the course of dependence of absorbance on wavelength (Figure 3). Aprotic solvent influences intensification of colouring of thiol (reaction product of sulphides with DTNB) from yellow (ethanol, $\lambda_{\text{max}} = 412$ nm) into red. Shift of λ_{max} was not observed with violet-coloured product during reaction with BTC.

3.2. Reaction Conditions. Ammonium hydroxide was used for transformation of CS₂ to sulphides, but other compounds with ammonium ions (e.g., ammonium acetate) are suitable also. Reaction is progressing in the significant surplus of ammonium ions. Dependence of absorbance on concentration of ammonium ions, described as ratio of molar concentration of NH₄⁺ and reagent (DTNB, BTC), is shown in Figure 4.

Transformation of CS₂ to sulphides is progressing very quickly and with a good yield in aprotic solvents. This report describes application of DMFA, but it is also possible to use dimethyl sulfoxide (DMSO). Since DMSO solidifies at the temperature of 18°C, in the field and unfavourable climate conditions it is advantageous to use the mixture of DMFA/DMSO (1 : 1).

Stability of reaction balance is achieved for both methods within 30 minutes. The start of colouring is quicker with the DTNB method. One-half of the maximal absorbance at wavelength λ_{max} was achieved after 2 minutes and with the BTC method after 9 minutes.

One of the limiting factors of CS₂ determination in the air is the effectiveness of its absorption in aprotic solvent. Effectiveness of absorption is mainly dependent on the speed of air flow during sampling. It is valid that the lower the speed of air flow, the higher the effectiveness of absorption. In practice the optimal time of the air sampling must also be taken into account, as not to exceed the acceptable limit. Air sampling with the speed of air flow 200 mL·min⁻¹ for 50 minutes seems to be optimal. It corresponds with air sampling with the total volume of 10 L.

3.3. Analytical Characteristics. Basic parameters of determination of CS₂ in the absorbed substance (molar absorptivity, detection limit, determination limit, Sandell's sensitivity, and parameters of linear regression) are presented in Table 1. Sandell's sensitivity was calculated for $A = 0.05$. Detection limit was calculated from the formula $3\sigma/b$ and determination limit from the ratio $10\sigma/b$, where σ is a standard deviation of blind attempt and b is the slope of calibration line.

Calibration line (Figure 5) was constructed on the basis of absorbance dependence on CS₂ concentration in the air. Detection limit of CS₂ in the air by the proposed procedure is 0.2, respectively 0.4 mg·m⁻³ (calculated according to the

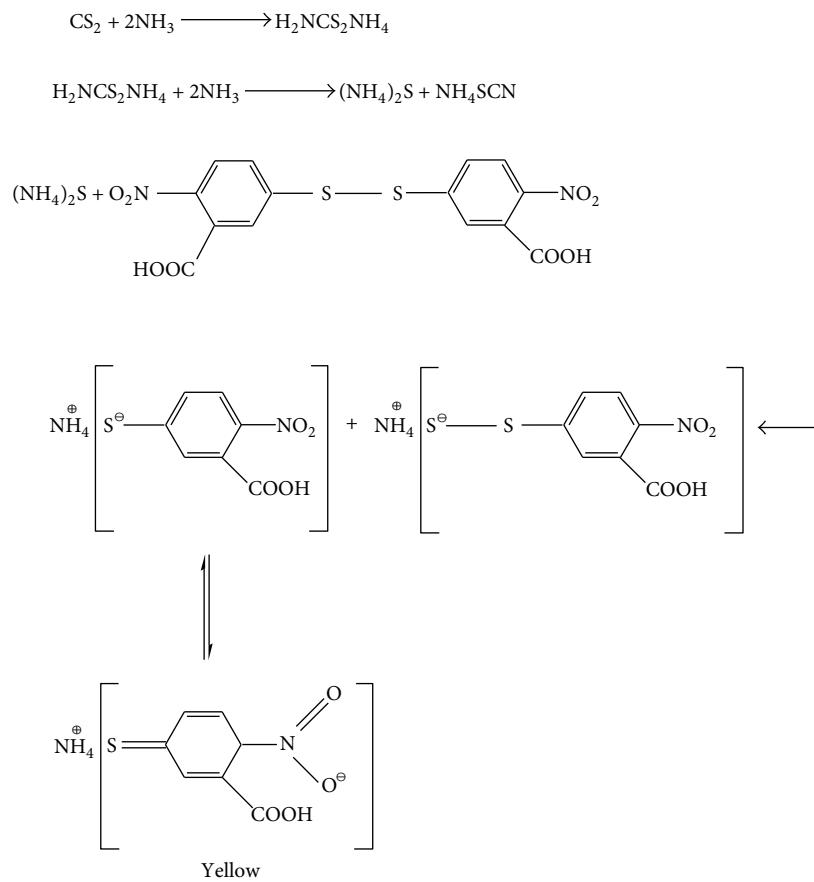


FIGURE 1: Scheme of analytical reaction (with DTNB).

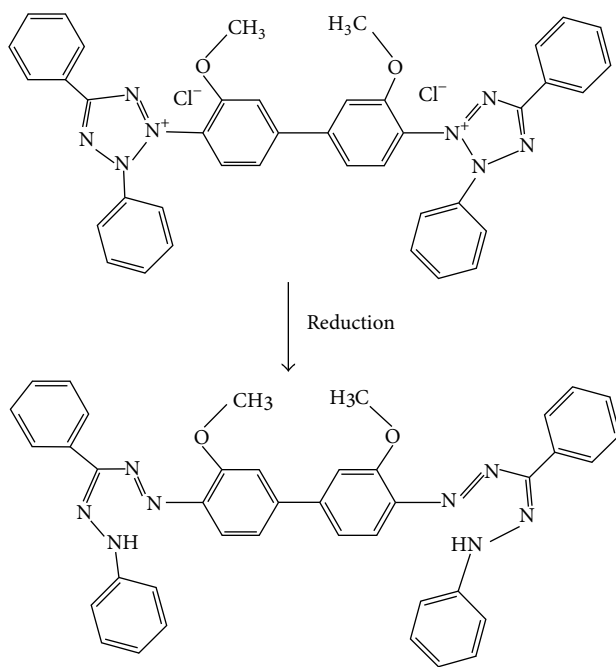


FIGURE 2: Reduction of BTC.

formula c_{air}). In practice, with this procedure it is possible to determine CS_2 (without dissolving the absorption solution) up to the concentration of $4.8 \text{ mg}\cdot\text{m}^{-3}$. It is fully acceptable for the requirements of hygienic control of the air in the working environment (e.g., in the Czech Republic PEL = $10 \text{ mg}\cdot\text{m}^{-3}$, NPK-P = $20 \text{ mg}\cdot\text{m}^{-3}$). Correctness of determination was verified by the method “inserted-found”, (see Table 2). Determination error is not higher than 20%.

3.4. Effect of Foreign Components. Reducing components present in the controlled air disturb determination of CS_2 by the proposed method. Hydrogen sulphide reacts mostly with DTNB or BTC, which can originate for instance like a byproduct of synthesis of CS_2 with methane and sulphur. To eliminate hydrogen sulphide, we can use filtration insert produced by impregnation of filtration paper or filtration materials from glass fibres by the solution of salts from certain heavy metals, for instance, lead, copper, or bismuth. This filtration insert is placed in the form of tube in front of the container with absorptive liquid. Sulphur dioxide (a result of pyrolysis of CS_2) and volatile aliphatic triplets have significant disturbing influence. Overview of the selected the disturbing influences, which with DTNB and BTC produce the coloured reduction products, is in Table 3.

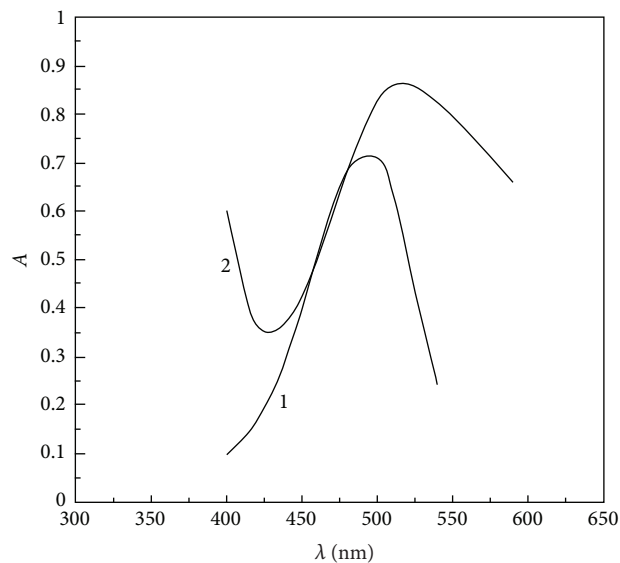


FIGURE 3: Simple absorption spectra; 1: DTNB method, 2: BTC method.

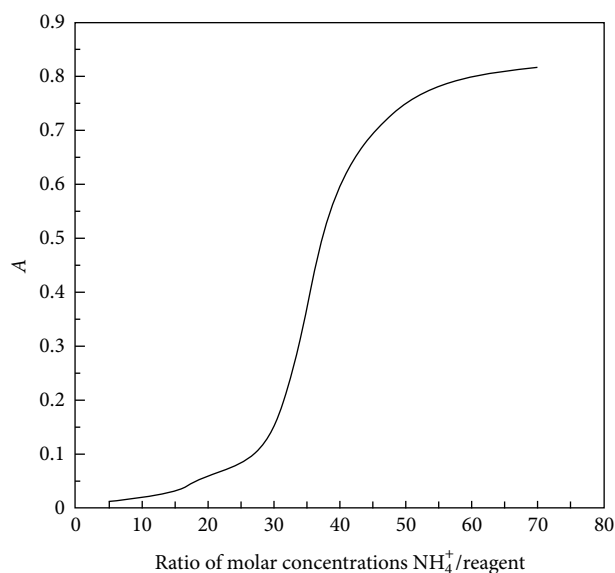


FIGURE 4: Dependence of absorbance on the ratio of molar concentrations of NH_4^+ and reagent.

4. Conclusion

The proposed method allows spectrophotometric determination of CS_2 in the workplace air of chemical companies and plants. This method is based on transfer of CS_2 with the help of ammonium ions to sulphides, which react further with DTNB or BTC to the characteristically coloured reaction products. Reactions are in progress in the medium of aprotic solvent, with advantage in DMFA. The method is simple and easy to instrumentation and technique. The sensitivity method, detection limits, and the range of use are comparable

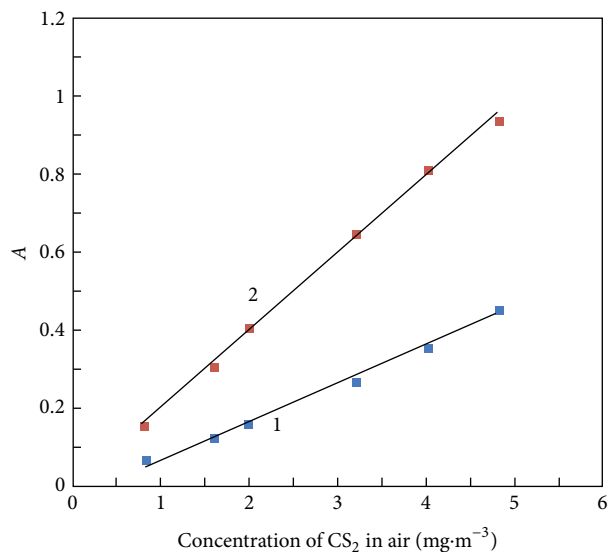


FIGURE 5: Calibration curves obtained for the determination of CS_2 in the air by the DTNB method (1) and BTC method (2).

TABLE 1: Base parameters of CS_2 determination (in the absorbed substance).

Parameter	Method A (DTNB)	Method B (BTC)
Molar absorptivity ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$)	$2.4\cdot 10^4$	$2.0\cdot 10^4$
Detection limit ($\mu\text{g}\cdot\text{mL}^{-1}$)	0.1	0.2
Determination limit ($\mu\text{g}\cdot\text{mL}^{-1}$)	0.2	0.6
Sandell's sensitivity ($\mu\text{g}\cdot\text{cm}^{-2}$)	0.002	0.004
Standard deviation σ	0.007	0.015
Linear regression ($y = bx + a$)		
Slope b	0.3138	-0.2639
Intercept a	0.2318	-0.1435
Correlation coefficient r	0.9884	0.9983

TABLE 2: Verifying of correctness of CS_2 determination in the air.

CS_2 inserted, $\text{mg}\cdot\text{m}^{-3}$	CS_2 found, $\text{mg}\cdot\text{m}^{-3}$	
	Method A (DTNB)	Method B (BTC)
1	0.8 ± 0.2	0.8 ± 0.2
5	4.5 ± 0.9	4.3 ± 0.8
10	8.8 ± 1.1	8.1 ± 1.1
25	21.9 ± 2.1	20.5 ± 2.4
50	47.5 ± 3.3	47.8 ± 3.9

with other spectrophotometric methods described in the literature [9, 14, 15].

The advantage of the proposed analytical process (based on transfer of CS_2 to sulphides) is in the opening of new development possibilities of colorimetric and spectrophotometric methods for CS_2 determination. Interconnection of CS_2 and sulphides analysis allows using and modifying a

TABLE 3: Concentration limit of foreign components which with reagents produce coloured products.

Component	Concentration limit, $\text{mg}\cdot\text{m}^{-3}$	
	Method A (DTNB)	Method B (BTC)
Hydrogen sulphide	0.2	0.2
Sulphur dioxide	2.0	—
Hydrogen cyanide	0.4	—
2-Sulfanyethane-1-ol	0.2	0.2


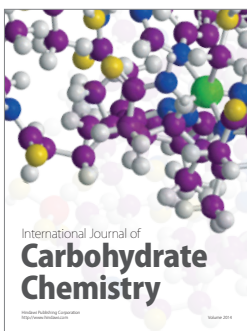
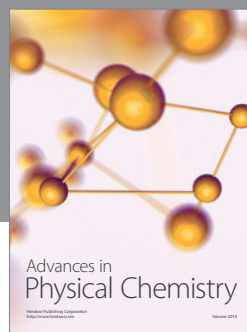
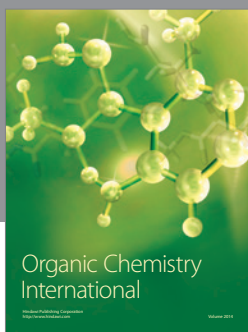
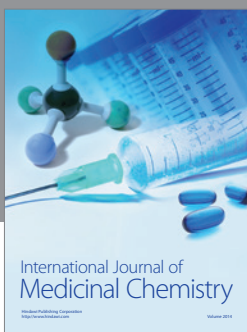
relatively significant number of standard methods for determination of sulphides (hydrogen sulphide) with regard to concrete conditions and determined objectives.

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References

- [1] H. P. Gelbke, T. Göen, M. Mäurer, and S. I. Sulsky, "A review of health effects of carbon disulfide in viscose industry and a proposal for an occupational exposure limit," *Critical Reviews in Toxicology*, vol. 39, no. 2, pp. 1–126, 2009.
- [2] A. R. Bandy, B. J. Tucker, and P. J. Maroulis, "Determination of part-per-trillion by volume levels of atmospheric carbon disulfide by gas chromatography/mass spectrometry," *Analytical Chemistry*, vol. 57, no. 7, pp. 1310–1314, 1985.
- [3] K. H. Kim and M. O. Andreae, "Determination of carbon disulfide in natural waters by adsorbent preconcentration and gas chromatography with flame photometric detection," *Analytical Chemistry*, vol. 59, no. 22, pp. 2670–2673, 1987.
- [4] W. M. Valentine, H. L. Valentine, K. Amarnath, and V. Amarnath, "Toluene-3,4-dithiol analysis of blood for assessing carbon disulfide exposure," *Toxicological Sciences*, vol. 50, no. 2, pp. 155–163, 1999.
- [5] G. A. Gaparsadonian, *Gigiena i Sanitariia*, vol. 31, pp. 53–54, 1966.
- [6] E. C. Hunt, W. A. McNally, and A. F. Smith, "A modified field test for the determination of carbon disulphide vapour in air," *The Analyst*, vol. 98, no. 1169, pp. 585–592, 1973.
- [7] W. Schwack and S. Nyanzi, "Simultaneous UV-spectrophotometric determination of CS_2 and COS using the piperidine, pyrrolidine, ethylenediamine or morpholine reagent," *Fresenius' Journal of Analytical Chemistry*, vol. 345, no. 11, pp. 705–711, 1993.
- [8] K. Hayashi, Y. Sasaki, S. Tagashira, and K. Hirata, "Spectrophotometric determination of copper(II) with carbon disulfide, a secondary amine and triton X-100," *Analytica Chimica Acta*, vol. 198, pp. 271–275, 1987.
- [9] S. A. Sagalakov and S. V. Kachin, *Journal of Siberian Federal University*, vol. 2, pp. 193–199, 2010.
- [10] A. Niewiadomy and B. Macik-Baranska, *Chemical Analysis*, vol. 28, pp. 603–609, 1983.
- [11] B. C. Verma, R. K. Sood, and H. S. Sidhu, "A new colorimetric method for the determination of carbon disulphide and its application to the analysis of some dithiocarbamate fungicides," *Talanta*, vol. 30, no. 10, pp. 787–788, 1983.
- [12] A. A. Ensafi, H. R. Mansour, and R. Majlesi, "Determination of trace amount of carbon disulfide in water by the spectrophotometric reaction-rate method," *Analytical Sciences*, vol. 19, no. 12, pp. 1679–1681, 2003.
- [13] K. V. Veksler, E. N. Volkova, N. S. Vol'berg et al., "Spectrophotometric determination of carbon disulfide using bis(4-(4'-nitrophenyl)azo-2-nitrophenyl) disulfide," *Journal of Analytical Chemistry*, vol. 58, no. 12, pp. 1108–1113, 2003.
- [14] T. Göen, J. Müller, J. Angerer, and H. Drexler, "Determination of carbon disulfide at the workplace by sampling on charcoal tubes—problems and solutions," *American Industrial Hygiene Association Journal*, vol. 63, no. 5, pp. 659–663, 2002.
- [15] S. P. Chattopadhyay and A. K. Das, *Indian Journal of Chemistry*, vol. 25A, pp. 1069–1070, 1986.
- [16] V. Pitschmann and Z. Koblíha, *Sborník VVS PV Vyškov*, pp. 157–164, 2002.
- [17] M. Walkman and M. Vaněček, *Annals of Occupational Hygiene*, vol. 25, pp. 5–15, 1982.



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