Simple *in situ* Visual and Tristimulus Colorimetric Determination of Sulfur Dioxide in Air

VLADIMÍR PITSCHMANN[1*], ZBYNĚK KOBLIHA[2], EMIL HALÁMEK[2], IVANA TUŠAROVÁ[1]

[1]Oritest spol s r.o., Staropramenná 17, 150 00 Prague, Czech Republic
[2] NBC Defence Institute, University of Defence, Víta Nejedlého 691, 682 01 Vyškov, Czech Republic
pitschmann@oritest.cz

Abstract

A simple *in situ* visual and tristimulus colorimetric method of determination of the trace amount of sulfur dioxide in air has been developed. Tristimulus colorimetry is based on application of three-dimensional colour space L*a*b* according to CIE (Commission Internationale de l'Éclairage). L* represents lightness and a* and b* represent chromaticity. The analytical method is based on drawing the harmful pollutants through a filter made of modified cotton fabric, which is planted on a special extension piece. The filter is saturated with chromogenic reagent based on 5,5'-dithio-bis(2-nitrobenzoic acid) in the mixture of *N,N*-dimethylformamide – dimethyl sulfoxide (1 : 1). On the filter the orange colour appears; the intensity of the colour is assessed visually and/or by a tristimulus colorimeter (LMG 173, Lange, Germany). The detection limit is 0.01 mg.m^{-3}. Interferences of reduction (especially hydrogen sulfide), oxidation, alkaline and acid agents have been describes.

Keywords: tristimulus colorimetry, sulfur dioxide, *in situ* analysis of air, 5,5'-dithio-bis(2-nitrobenzoic acid).

Introduction

Sulfur dioxide (SO_2) is a significant industrial harmful pollutant and an important factor of hygienic environment suitability and an indicator of its overall pollution. A whole series of analytical methods and technical means based on physical, physically chemical or chemical principles [1-2] are used for detection of SO_2 presence in air. In the system of these means the colorimetric and spectrophotometric methods, which are based on assessment of colour reactions of SO_2 with various chromogenic reagents also have their place [3]. The most often used method uses the SO_2 reaction with the chromogenic reagent on the basis of HCHO/pararosaniline with spectrophotometric assessment of the intensity of the arisen colour [4, 5]. Other colorimetric and spectrophotometric methods of SO_2 detection use for example a reaction with 1,3,5-trinitrobenzene [6], reaction with Fe^{3+} under the presence of 1,10-phenanthroline [7], or reactions with some aromatic disulfides which provide

colour thiols in consequence of reduction splitting of the disulfidic bonds. The reactions of SO_2 with aromatic disulfides are irreversible. One of the most favourite reagents of this type is Ellman's reagent [8], chemically 5,5'-dithio-bis(2-nitrobenzoic acid), which was applied for spectrophotometric detection in water [9] and in air through the mediation of detection tubes [10]. The reagent provides yellow 3-carboxy-4-nitrophenylthioate according to the reaction Figure 1. The reaction appears in the water-ethanol solution in a pH range of 6 to 9. The reaction product at that conditions is measurable at wavelength $\lambda_{max} = 412$ nm. The reaction is quite rapid and complete.

In industry tristimulus colorimetry is used in quality control of various colour materials. This method has also been used in analytical chemistry recently, e.g. in determination of iron, cobalt and nickel [11], arsenic [12] phosphates [13] or

residual chlorine [14]. The aim of this article is to describe simple visual and tristimulus colorimetric method of SO_2 determination in air, which is based on gas withdrawal on a filter of cotton fabric impregnated with the chromogenic Ellman's reagent dissolved in the mixture of *N,N*-dimethylformamide – dimethyl sulfoxide.
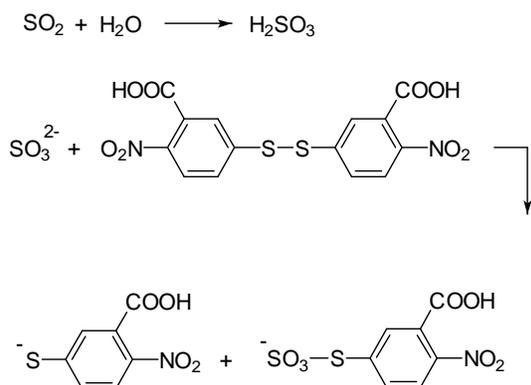
$$SO_2 + H_2O \longrightarrow H_2SO_3$$

Fig. 1. Reaction of SO_2 with 5,5'-dithio-bis(2-nitrobenzoic acid)

Experimental

Chemicals and equipments

5,5'-dithio-bis(2-nitro-benzoic acid), *N,N*-dimethylformamide (DMFA) and dimethyl sulfoxide (DMSO), all of them Sigma-Aldrich, purity p.a. at minimum, were used for preparation of the chromogenic reagent. The chromogenic reagent was prepared by dissolving 0.4 g of 5,5'-dithio-bis(2-nitrobenzoic acid) in 100 mL of the mixture of DMFA and DMSO (1:1).

A portable tristimulus colorimeter (reflectance spectrophotometer LMG 173, Dr. Lange, BRD) was used for measuring the intensity of coloured stains. The laboratory gas tempered chamber at the volume of 617 dm^3 (Lamon, Czech Republic) was used for preparing the SO_2 samples. Other used equipment: chemical detector CHP-5 (electrical pump, Oritest, Czech Republic), a suction pump XDS-10C (BOC Edwards, UK) with connected flowmeter and UV/Vis spectrophotometer Helios-α (Thermo Electron, UK).

Procedure of the filter preparation

The fabric based on a web of cotton threads 0.31 – 0.33 mm thick was used for the filter preparation. This cotton fabric was modified by impregnation with the solution which contained 0.3 g of $Na_2B_4O_7.10\,H_2O$, 0.45 g of H_3BO_3, 0.1g NaCl, 2.5 g of silica gel (fraction up to 5 µm) and 3.0 g of dextran per 100 ml of water. The impregnated fabric was dried freely in the air and drying was finished in a dessicator above solid sodium hydroxide. After drying it was formed in a shape of circle with 45 mm in diameter.

Sample preparation and checking its concentration

In the laboratory chamber various SO_2 concentration were prepared by action of the sulfuric acid on the sodium sulfite. The real SO_2 concentration in the laboratory gas chamber was determined by a spectrophotometric method modified for HCHO/pararosaniline [4]. The air temperature was kept at 24 ± 2 °C and the relative humidity at 60 ± 15 % in the laboratory chamber.

The procedure of determination by the proposed method

The apparatus which is shown in Figure 2 was used for determining the SO_2 concentration. The filter was fixed in the extension piece with a supply hose connected with the chemical detector CHP-5 (electrical pump). A 50 µl of the chromogenic reagent was dosed to the middle of the filter. The gas sample was suck through the activated filter through the mediation of the chemical detector CHP-5 (electrical pump) with the velocity of 1 L/min for the period of 3 minutes. The appeared colour was assessed 1 minute after the sample withdrawal. Because the reaction system is irreversible a new filter saturated with chromogenic reagent was always used. Measuring the analytic signal was performed in three-dimensional colour system CIE-L*a*b*, with the neutral brightness line (axis) (L*), chromatic green-red axis (a*) and chromatic blue-yellow axis (b*). The obtained values represent the arithmetic average of three measurements. The colour deviation ΔE is defined on the basis of differences between the individual coordinates of comparing objects according to the equation
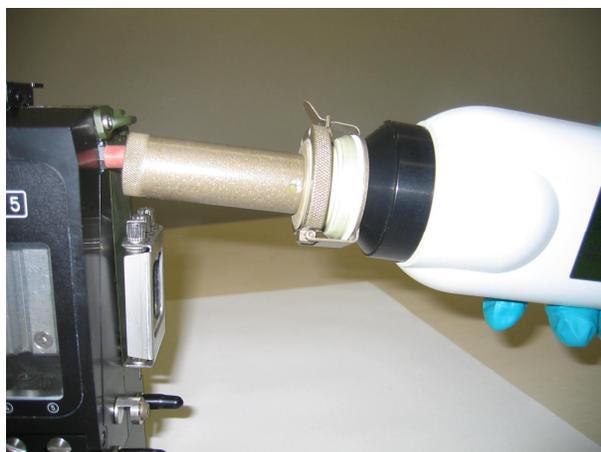$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}.$$

Fig. 2. Apparatus for determining the SO₂ concentration: chemical detector CHP-5 (electrical pump), filter with the extension piece and the tristimulus colorimeter Lange LMG 173

Results and discussion

Colour effect and its stability

In contact of SO₂ with the chromogenic reagent, the orange colour appears on the cotton filter immediately in fact; this orange colour has a characteristic reflection curve which shows the dependence of light reflection (reflection factor) on the wavelength (Figure 3). All of the measured parameters of the tristimulus colorimetry (L^*, a^*, b^*) are stabile in a long time interval (Table 1).
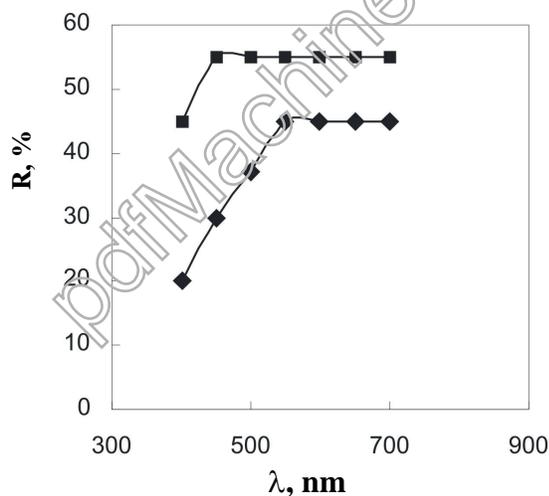

Fig. 3. Dependence of the reflection factor R on the wavelength λ for SO₂ (♦) and a blind sample (■)

Table 1. Dependence of colouring on time (as a sample: 30 μl 0.01% of the Na₂SO₃ solution)

Time, min	L^*	a*	b*
Immediately	71.68	-5.57	20.17
1	71.71	-5.40	19.56
2	72.06	-5.28	19.08
3	72.26	-5.23	18.98
5	72.49	-5.18	19.14
10	72.79	-5.14	20.18
15	73.02	-5.08	21.44

The mixed dissolvent of the chromogenic reagent DMFA / DMSO secures suitable reaction conditions and shifts the spectrum to the area with higher wavelengths (from the usual yellow to the orange or red colour, Figure 4). Besides that, presence of DMSO has a positive effect on capturing SO₂ on the cotton filter and DMFA increases the resistance of the chromogenic reagent towards low temperatures, and therefore it makes its usability in the real field conditions easier.
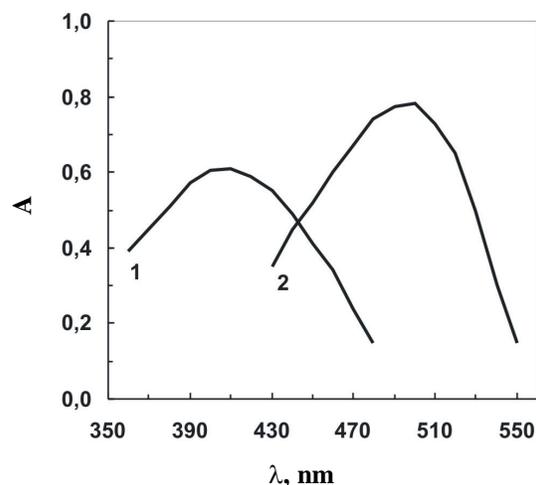

Fig. 4. Absorption spectrum of reaction products: (1) water/ethanol solution, (2) DMFA/DMSO solution

Effect of the exposition time

The optimum time of SO₂ exposition also has influence on the correctness and accuracy of the results. Dependence of the filter colouring (parameters L^*, a^*, b^*) on the time of sucking the gas is documented in Table 2. It is noticeable from

the measured data that the dependence of the parameter b* on the exposition time is approximately linear in the interval 1 to 5 minutes.

Table 2. Dependence of the colouring on the time of sucking the air (SO$_2$ concentration = 1.31 mg.m^{-3}, velocity of the air flow 1 dm^3.min^{-1})

Parameter	1 min.	2 min.	3 min.	5 min.
L*	61.89	63.67	62.78	63.90
a*	-0.82	1.62	-1.85	-0.78
b*	9.23	14.05	19.24	26.41

Effect of the flow rate

As it is shown in Table 3, the intensity of the filter colouring does not increase with the flow velocity higher than 0.5 L/min. These higher flow velocities do not provide effective capturing SO$_2$ on the filter and the quantitative course of the colour chemical reaction any more. Lower flow velocities then increase the time necessary for performing the analysis disproportionately. It appears that the chemical detector CHP-5 (electrical pump) which is set for the standard flow velocity of 1 L/min^{-1} can be used for practical measuring with an advantage.

Table 3. Dependence of colouring on the flow velocity (SO$_2$ concentration =1.31 mg.m^{-3}, exposition 3 minutes)

Parameter	0,5 dm^3.min^{-1}	1,0 dm^3.min^{-1}	2,0 dm^3.min^{-1}
L*	63.08	62.78	64.92
a*	-1.37	-1.85	-1.37
b*	22.08	19.24	19.87

Calibration graph

The characteristic course of the dependence of the analytic signal on SO$_2$ concentration is shown in Figure 5. The taken values of Δb*, which characterize the chromatic blue-yellow axis, were used as an analytical signal. The limit of SO$_2$ detection by the proposed method is lower than

0.01 mg/m^3. In this concentration, the value of Δb* = 2.6 and the colour is still visible.
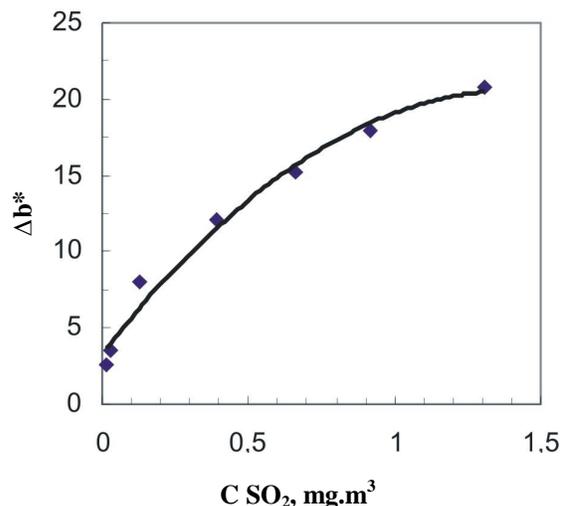
Fig. 5. Dependence of Δb* on SO$_2$ concentration in the air, time of suction 3 minutes, air flow velocity 1 L/min^{-1}, temperature in the chamber 25 °C, relative air humidity 45 %

Interference

The presence of reduction agents leads to serious interferences. Hydrogen sulfide, thiols and hydrogen cyanide, to which the chromogenic reagent is also very sensitive, give the same or similar colour effect. At flow rate 1 L/min and sampling for 2 minutes, the following average values have been found at hydrogen sulfide concentration of 1 mg/m^3: L* = 62.63, a* = -1.18, b* = 16.61. The affect of the hydrogen sulfide may be eliminated or depressed by a series cotton filter which is impregnated with the solution of the lead acetate and which is perfectly dried.

The positive colour effect may appear also in presence of higher concentrations of ammonia and volatile amines. These agents increase pH value and can decompose the reagent.

Oxidants (chlorine, ozone, nitrogen dioxide) that can oxidize 3-carboxy-4-nitrophenylthioate or sulfite also interfere. However their influence to SO$_2$ determination appears only at concentration of 10 mg/m^3 and high.

Presence of acid gases and vapours (hydrogen chloride, carbon dioxide) decreases the determination sensitivity. These agents decrease

pH of the reaction medium and limit chromogenic reagent ability to redox reactions.

Application for the field analysis

The proposed method is advantageous for application on the field conditions where especially its simplicity and speed approve itself. Furthermore, the method is sensitive enough, and it enables to set the SO_2 concentration in the air on the level of hygienic limits (0.01 mg/m^3).

The dry modified filter is very stable. If stored in hermetically closed packaging, it does not lose its properties for several years. It was verified experimentally that the solution of chromogenic reagents for application on the filter are usable for several days. After 72 hours, decrease in the value Δb* was measured and it was 87 % at maximum. It can be advantageous to use the set of agents which contains two components: 5,5'-dithio-bis(2-nitrobenzoic acid) at the amount dosed in advance and the mixture of DMSO / DMFA. The chromogenic reagent is prepared by mixing both components as needed before the analysis.

References

1. E. Smolková - Keulemanová and L. Feltl, *Analysis of Substances in the Gaseous Phase*, Elsevier, Amsterdam, (1991).

2. R. H. Harrison and R. Perry, *Handbook of Air Pollution Analysis*, Chapman & Hall, New York, (1986).

3. P. Luis and C. P. Carducci, *Microchim. Acta*, 62 (1974) 839.

4. P. W. West and G. C. Gaeke, *Anal. Chem.*, 28 (1956) 1816.

5. S. K. Goyal, *J. Environ. Monit.*, 3 (2001) 666.

6. Y. Suzuki and S. Imai. *Anal. Chem.*, 58 (1986) 3271.

7. V. Raman, M. Singh and D. C. Parashar, *Microchem. J.*, 33 (1986) 223.

8. G. E. Ellman, *Arch. Biochem. Biophys.*, 82 (1959) 70.

9. P. MacLaurin, K.S. Parker, A. Townshend, P,J. Worsfold, N.W. Barnett and M. Crane, *Anal. Chim. Acta*, 238 (1990) 171.

10. V. Pitschmann, E. Halámek and Z. Kobliha, *Chem. Listy*, 98 (2004) 923.

11. F. Yokota and S. Abe, *Anal. Commun.*, 34 (1997) 111.

12. M. Rahman, K. Fujinaga, Y. Seike and M. Okumura, *Anal. Sci.*, 20 (2004) 165.

13. I. Kasahara, A. Fujinawa, N. Hata and S. Taguchi, *J. Ion Exchange*, 14 (Supplement) (2003) 317.

14. Y. Suzuki, M. Endo, J. Jin, K. Iwase and M. Iwatsuki, *Anal. Sci.*, 22 (2006) 411.