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A simple *in situ* visual and tristimulus colorimetric method for the determination of diphosgene in air

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Abstract: A simple visual and tristimulus colorimetric method (three-dimensional system CIE–$L^*a^*b^*$) for the determination of trace amounts of diphosgene in air has been developed. The method is based on the suction of diphosgene vapors through a modified cotton fabric filter fixed in a special adapter. Prior to analysis, the filter is saturated with a chromogenic reagent based on 4-(*p*-nitrobenzyl)pyridine. The optimal composition of the reagent is 2 g of 4-(*p*-nitrobenzyl)pyridine and 4 g of *N*-phenylbenzylamine in 100 ml of a 50:50 ethanol–glycerol mixture. The intensity of the formed red coloration of the filter is evaluated visually or by a tristimulus colorimeter (LMG 173, Lange, Germany). The detection limit is 0.01 mg m^{-3}. Acetyl chloride and benzoyl chloride react in 150 and 50 times higher concentrations, respectively. The method is suitable for mobile field analysis.

Keywords: tristimulus colorimetry, diphosgene, air analysis, 4-(*p*-nitrobenzyl)pyridine, *N*-phenylbenzylamine.

INTRODUCTION

Diphosgene (trichloromethyl chloroformate) was developed especially as a choking war agent and a more stable alternative to gaseous phosgene. Liquid diphosgene, as well as solid triphosgene (hexachlorodimethyl carbonate), has found laboratory use as a substitute for phosgene and recently there has also been a growing interest in the industrial utilization of both compounds as highly reactive halogenation and acylation reagents.

In spite of the different physical properties and structures of phosgene, diphosgene and triphosgene,[1] their chemical behavior is genetically similar. Thus, *e.g.*, both diphosgene and triphosgene decompose thermally to give phosgene and therefore the same methods and technical means are often employed for their chemical analysis. Naturally, papers in the literature most often deal with the analysis of the industrially most important phosgene. Prevalent methods of phosgene

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determination are based on its color reactions with some chromogenic reagents. One of the oldest color reactions of phosgene consists in the halogenation of *p*-dimethylaminobenzaldehyde followed by condensation with aromatic amines, which is utilized particularly for the preparation of indicator papers and detection tubes. A classical reagent of this type is a mixture of *p*-dimethylaminobenzaldehyde with diphenylamine which gives a yellow coloration.[2] A similar reaction of phosgene with *p*-dimethylaminobenzaldehyde in the presence of *N,N*-dimethylaniline affords a green to deep blue color due to products of the diphenylmethane or triphenylmethane type,[3,4] an oxidized form of crystal violet. This reaction has been repeatedly modified.[4–10]

A great variety of analytical techniques are based on the reaction of phosgene with 4-(*p*-nitrobenzyl)pyridine, affording a yellow to orange product.[10] This reaction has been improved by the addition of *N*-phenylbenzylamine, which gives an intense red coloration. This modification can also be used for simple detection devices[10,11] and for spectrophotometric determination.[12] The reaction has been employed also for the automatic determination of phosgene in air.[13,14]

This paper relates to a simple and sensitive method for the determination of diphosgene in air using tristimulus colorimetry. This method is currently employed in the industry for controlling the surface quality of a variety of colored materials and has recently also found application in analytical chemistry, *e.g.*, in the determination of iron, cobalt and nickel,[15] mercury,[16] arsenic,[17] alkylbenzenesulfonates,[18] phosphates[19] and residual chlorine.[20] The devised method consists in the reaction of diphosgene with a chromogenic reagent based on 4-(*p*-nitrobenzyl)pyridine and *N*-phenylbenzylamine, with the formation of a red coloration. The reaction occurs on a special filter made of modified cotton fixed in a special adapter. The chromogenic reagent is applied on the filter and air is sucked through it. The intensity of the formed color spot is then evaluated by a tristimulus colorimeter or visually.

EXPERIMENTAL

Chemicals and equipment

Diphosgene of 98 % purity (VOZ Zemianske Kostolany, Slovak Republic) served as a standard. The chromogenic reagent was prepared with 4-(*p*-nitrobenzyl)pyridine, *N*-phenylbenzylamine, glycerol (all Sigma–Aldrich, of at least *p.a.* grade) and absolute ethanol (Riedel de Haen). The chromogenic reagent was prepared by dissolving 2.0 g of 4-(*p*-nitrobenzyl)pyridine, 4.0 g of *N*-phenylbenzylamine and 50 ml of glycerol in ethanol, after which the solution was made up to 100 ml.

The coloration intensity of the spot was evaluated with a portable tristimulus colorimeter (spectrophotometer LMG 173, Lange, Germany). Diphosgene vapors were generated in a thermostated test chamber of 617 dm^3 volume (Lamon, Czech Republic). Samples were taken using a hand-operated suction apparatus Universal-86 (Kavalier Votice, Czech Republic), stroke volume 100±5 cm^3, suction under pressure 23.33±0.66 kPa. The diphosgene concentration in the chamber was controlled using a XDS-10C vacuum pump (BOC Edwards, UK) with an attached flowmeter and a Helios-α UV-VIS spectrophotometer (Thermo Electron, UK).

Filter preparation

The filter consisted of a fabric made of cotton threads of 0.31–0.33 mm thickness. The fabric was impregnated with a solution containing 0.3 g of $Na_2B_4O_7\cdot10\ H_2O$, 0.45 g of H_3BO_3, 0.1g of NaCl, 2.5 g of silica gel (particle size less than 5 μm) and 3.0 g of dextran in 100 ml of water. The impregnated fabric was first dried in air and finally in a desiccator over solid sodium hydroxide. After drying, it was cut into circles of 45 mm diameter.

Sample preparation and checking diphosgene concentration

Various concentrations of diphosgene were prepared in the test chamber by evaporation of its toluene solution. The actual diphosgene vapor concentration was determined spectrophotometrically. The diphosgene vapors were pumped for 30 minutes by vacuum pump at a rate 1 $dm^3\ min^{-1}$ and were absorbed in a bubbler containing 10 ml of 0.1 % 4-(*p*-nitrobenzyl)pyridine in toluene. The absorbency of the solution was measured spectrophotometrically at 422 nm. The air temperature in the test chamber was held at 24±2 °C and the relative humidity at 50±10 %.

Determination by the devised method

Diphosgene concentration was determined using the apparatus depicted in Fig. 1. The filter was fixed in the adapter connected by a tube with a hand-operated suction device. The chromogenic reagent (50 μl) was applied on the center of the filter and then contaminated air was sucked through it (20 strokes, *i.e.*, 2000±100 cm^3). After the sampling, the intensity of the color spot of about 20 mm diameter was evaluated visually, as well as by tristimulus colorimeter (Fig. 2).

Fig. 1. Filter with adapter.

Fig. 2. Measurement of filter coloration by tristimulus colorimeter.

Tristimulus colorimetry

Tristimulus colorimetry is a type of reflectance colorimetry (spectrophotometry) based on the CIE–$L^*a^*b^*$ color system.[21] In this system, L^* represents the neutral axis of lightness, a^* denotes the chromatic green-red axis ($+a^*$ red, $-a^*$ green) and b^* the chromatic blue-yellow axis ($+b^*$ yellow, $-b^*$ blue). In practice, also the color difference, ΔE, is used, which is defined by the Equation:

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

where ΔL^*, Δa^* and Δb^* are the differences between the individual values L^*, a^* and b^* for the standard and for the color in question. All these parameters can be used as analytical signals, which enable the quantification of the course of a color reaction.

RESULTS AND DISCUSSION

Stability of coloration

Passage of diphosgene-contaminated air through the filter practically instanttaneously induced a red coloration, which could be characterized by a reflection curve (Fig. 3). After the sampling, this coloration was relatively stable for a longer period of time. The development of the red component of the coloration (parameter a^*) in the course of 10 minutes is depicted in Fig. 4. During this time the value of parameter a^* increased by 9.7 %.

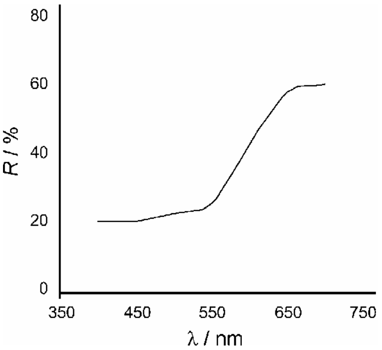

Fig. 3. Reflection curve. Dependence of light reflection (reflection factor R) on wavelength (λ).

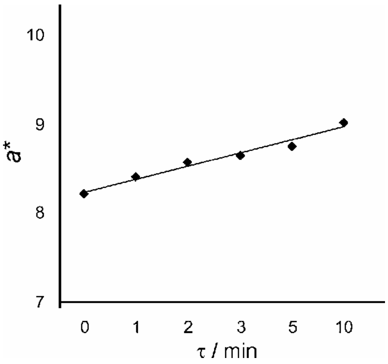

Fig. 4. Time dependence of coloration.

The coloration intensity of the spot on the filter increased with the volume of the analyzed sample. Increasing the sample volume resulted in a darkening of the filter and an increasing value of the yellow (b^*), and particularly of the red (a^*), color component. The individual color differences ΔL^*, Δa^*, Δb^* and the total color differences ΔE are given in Table I.

TABLE I. Dependence of coloration on sample volume (diphosgene concentration 0.4 mg m^{-3})

Parameter	Sample volume, dm^3			
	1	2	3	5
ΔL^*	0.49	–4.20	–5.78	–9.79
Δa^*	2.39	11.72	14.80	21.92
Δb^*	9.88	13.16	13.46	14.57
ΔE	10.18	18.12	20.82	28.08

Calibration graph

The calibration graph for the determination of diphosgene is given in Fig. 5. The limit of detection of diphosgene by the tristimulus colorimeter was 0.01 mg m^{-3}. A reproducibility test showed that, at this concentration, the relative standard deviation of the response (Δa^*) amounted to 15 %. For visual evaluation, it is advisable to compare the intensity of the color spot with a reference standard representing a color scale 0–1.0 mg m^{-3} with a 0.1 mg m^{-3} resolution. For the visual method, the detection limit of diphosgene was 0.05 mg m^{-3}.

Interference

A higher concentration of acidic vapors and gases which lower the intensity of the formed coloration interfere with the determination of diphosgene in air.

The presence of oxidizing and reducing substances may induce undesirable color changes. No interference was observed with 10 mg m^{-3} HCl, 15 mg m^{-3} Cl_2, 250 mg m^{-3} NO_2, 150 mg m^{-3} SO_2 or 50 mg m^{-3} NH_3.

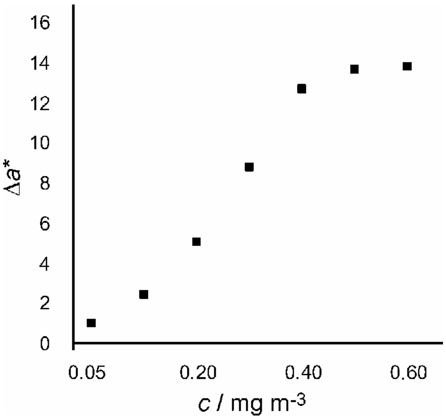

Fig. 5. Calibration graph.

Concerning organic compounds, no interference was observed *e.g.*, with benzyl chloride, trichloroethylene and chloroform at a concentration of 100 mg m^{-3}. Coloration similar to that of diphosgene (phosgene, triphosgene) was also produced by other compounds with an analogous propensity to acylation, however, it appears only at higher concentrations. Table II contains data on the interference by acetyl chloride and benzoyl chloride.

TABLE II. Interference of benzoyl chloride and acetyl chloride (the interference factor β is the ratio of the detection limit of the interfering compound to the detection limit of diphosgene)[22]

Compound	Detection limit, mg m^{-3}	Interference factor β	Concentration, mg m^{-3}, at $\Delta a^* = 5$
Diphosgene	0.01	–	0.2
Benzoyl chloride	0.5	50	2.5
Acetyl chloride	1.5	150	5

Application to field analysis

The devised visual and tristimulus colorimetric method of diphosgene determination can be applied to many types of field analysis. If stored in hermetically sealed containers, the filter is usable for several years. Solutions of the chromogenic reagents are usable for at least 12 months.

The method is comparable with existing colorimetric methods for the determination of phosgene (Table III). Using the tristimulus method, it is possible to evidence trace amounts of diphosgene in air. The method can be applied also at night or at reduced visibility and the obtained data can be stored. Moreover, the devised method is universal, *i.e.*, it enables use of other liquid chromogenic reagents for the determination of a number of various toxic substances in air.

TABLE III. Comparison of the devised method with some active-sampling colorimetric methods of phosgene determination in air

Method	Detection limit, mg m^{-3}	Sampling conditions
Paper (Dixon, Hands)	1	0.12 dm^3 of air, 40 s
Detection tube Dräger	0.08	2 dm^3 of air, 240 s
Tape analyzer (Nakano)	0.02	0.4 dm^3 min^{-1}, 60 s
Devised method	0.01	2 dm^3 of air, 30 s

ИЗВОД

ЈЕДНОСТАВНА *IN SITU* ВИЗУЕЛНА И ТРИСТИМУЛУС КОЛОРИМЕНТРИЈСКА МЕТОДА ЗА ОДРЕЂИВАЊЕ ДИФОЗГЕНА У ВАЗДУХУ

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Развијена је једноставна визуелна и тристимулус метода (тродимензионални систем CIE–*L*a*b**) за одређивање дифозгена у ваздуху у траговима. Метода се заснива на усисавању паре дифозгена кроз прилагођени филтер од памучне тканине који је фиксиран у специјалном адаптеру. Пре анализе, филтер је засићен хромогеним реагенсом базираном на 4-(*p*-нитробензил)пиридину. Оптимални састав реагенса је 2 g 4-(*p*-нитробензил)пиридина и 4 g *N*-фенилбензиламина у 100 ml 50:50 смеше етанол–глицерол. Интезитет насталог црвеног обојења филтера одређиван је визуелно или помоћу тристимулус колориметра (LMG 173, Lange, Немачка). Граница детекције износи 0,01 mg m^{-3}. Ацетил хлорид и бензоил хлорид реагују у 150 и 50 пута већој концентрацији, респективно. Метода је погодна за анализе на терену.

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