

Detection tube with composite carrier for detection of phosgene and diphosgene in air

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Abstract

A new highly sensitive detection tube for measurement of concentration of phosgene and diphosgene in air has been developed. The detection is based on chemical reaction of 4-(*p*-nitrobenzyl)pyridine and *N*-phenylbenzylamine which with phosgene (diphosgene) give a characteristic red methine dye. Spherical granules (pellets) of composite material prepared by granulation of microcrystalline cellulose with MgO serve as a carrier. This new indication filling is stable, resistant to interferences and climatic influences. The detection limit (0.05 mg m⁻³) meets the requirements for conducting hygienic checks of air quality in the workplace environment. In addition, the tube allows a prolonged and continuous monitoring of phosgene and diphosgene in air for at least 240 min.

Keywords: detection tube; diphosgene; 4-(*p*-nitrobenzyl)pyridine; composite material; microcrystalline cellulose; magnesium oxide.

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Phosgene (carbonyl chloride) is an important industrial substance used in large quantities as a highly reactive halogenation and acylation agent in organic syntheses. Diphosgene (trichloromethyl chloroformate), with its similar chemical, but more suitable physical, properties, finds mainly laboratory use. Both of these industrial pollutants belong to traditional chemical warfare agents and currently there is concern about their possible misuse by terrorists [1].

Detection and determination of phosgene and diphosgene is therefore given special attention. Apart from the specific but complicated and often automated analytical procedures, there exist also simple orientational and operational methods. These simple procedures, based usually on color reactions, are used in the form of detection papers, strips, crayons, or detection tubes. Although phosgene and diphosgene are structurally and physically different substances, they can be detected by the same methods and technical means, making use of the fact that diphosgene decomposes into two molecules of phosgene.

At present, simple colorimetric detection devices make use basically of two processes. The first is based on the reaction of phosgene or diphosgene with *p*-dimethylaminobenzaldehyde affording *p*-dimethylaminobenzalchloride which with a number of amines produces diphenylmethane or triphenylmethane dyes [2]. The most frequently used amine is diphenylamine,

which provides yellow coloration, or *N,N*-dimethylaniline and *N,N*-diethylaniline, whose presence gives green to blue coloration [3]. Other reactive amines such as *N*-ethyl-*N*-(2-hydroxyethyl) aniline, *N,N*-dimethyl-2-naphthylamine or *N,N*-dimethyl-3-aminophenol [4] are used to a lesser extent. The second process is based on the color reaction of phosgene or diphosgene with 4-(*p*-nitrobenzyl) pyridine, a group reagent for alkylation and acylation agents [5–7]. The reaction gives yellow to orange-colored urea-type product, which passes into a meso-quinoid form of methine dye. In the presence of *N*-phenylbenzylamine the color becomes deeper and changes to red. Both of these reactions are used for the preparation of detection papers [8], detection crayons [9], detection filters [10], monitoring tapes [11] and also for the preparation of detection tubes [12,13]. Recently, detection papers based on the reaction of diphosgene with pyridine and 1,3-dimethylbarbituric acid and leading to a polymethine dye have also been suggested [14].

The known detection tubes are characterized by different structures, methods of use, sensitivity and lifetime (stability of the filling). Recently, a major trend in the development of tubes for detection of phosgene and diphosgene mainly involves lowering of the detection limit and extension of stability of the indication filling. However, these requirements are usually incompatible. Particularly in the field of defense and security, structural designs are required that would enable a continuous and long-term detection of phosgene (diphosgene) in air while maintaining high sensitivity. Detection tubes used for continuous monitoring thus far are usually not sensitive enough. On the other hand,

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although commercial detection tubes are highly sensitive, they are not acceptable for continuous monitoring.

The present communication describes a new detection tube designed to detect trace concentrations of phosgene and diphosgene in air. This detection tube is based on indication filling which contains a stabilized mixture of 4-(*p*-nitrobenzyl)pyridine and *N*-phenylbenzylamine applied (immobilized) on a composite carrier consisting of a homogenized mixture of microcrystalline cellulose and MgO. The advantage of this new detection tube is its high sensitivity, stability of the indicator filling and ability to use it for a long-term continuous monitoring of phosgene (diphosgene) in air.

EXPERIMENTAL

Chemicals and equipment

The indication filling was prepared using the following chemicals: Avicel PH101-NF microcrystalline cellulose (FMC BioPolymer, Ireland), magnesium oxide, 4-(*p*-nitrobenzyl)pyridine 98%, *N*-phenylbenzylamine 99% (all Sigma-Aldrich) and anhydrous ethanol (Riedel de Haen). The composite carrier was prepared using the Stephan UMC 5 homogenizer (Stephan, Germany) and a single-screw axial extruder and spheronizer Pharmex 33 T (Wyss-Probst, Germany). As a body of the detection tubes served glass tubes of 5 mm inner diameter with polyethylene sealing and distributing elements (Tejas, Czech Republic).

The tubes were tested using a standard solution of diphosgene (95% purity, VOZ Zemianské Kostolany, Slovakia) in spectrophotometrically pure toluene (Sigma-Aldrich). Purity of diphosgene was determined by titration with silver nitrate with ISE potentiometric indication [15]. A Universal 86 hand suction pump (Kavalier, Czech Republic) (stroke volume $100 \pm 5 \text{ cm}^3$) was used in the tests. For the determination of diphosgene concentration in the test chamber, it was extracted by a Lavat oil pump (Fisher Scientific). Prolonged suction was performed with a CHP-5 chemical detector equipped with an electric pump (Oritest, Czech Republic) allowing simultaneous air sampling through five detection tubes. Objective measurements of color changes in the solutions were performed with a Helios- α spectrophotometer (Unicam, Great Britain).

Preparation and characterization of the carrier

A powdered mixture of MgO and microcrystalline cellulose was homogenized in a high-speed mixer at 1000 rpm for 5 min. In the same device, the mixture was moistened with water. The moistened material was fed into an extruder with a 1.00 mm thick barrier with holes of 1.25 mm diameter. The extrusion continued for 10 min at 110 rpm. The extruded material was collected in a bowl and transferred on a running spher-

onization plate (hatched pattern – grid size 1.0 mm, 2.0 mm apart). The spheronization was carried out at 1,000 rpm for 5 min. The resulting pellets were dried at 80 °C for 20 h.

Physical parameters of the carrier (sieve analysis, pycnometer density, mechanical strength and other factors) were determined by standard procedures [16]. The shape of particles in the carrier was observed by an Olympus SZX 12 microscope with a digital camera and monitor (Japan).

Preparation of indication filling and tubes

The impregnating solution was prepared by dissolving 1.0 g of 4-(*p*-nitrobenzyl)pyridine and 3.0 g of *N*-phenylbenzylamine in 100 ml of anhydrous ethanol. To impregnate 100 g of the carrier, 50 ml of impregnation solution was used. In order to moisten the carrier evenly, the impregnating solution was added in portions. The mixture was thoroughly mixed and air-dried in a hood until the ethanol was completely removed. The thus-prepared perfectly powdery white-to-grayish filling was stored in ground stoppered brown glass bottles.

The indication filling was placed into a glass tube in a 50 mm long layer. To prevent any movement, the layer was secured by standard distribution and sealing components. At the end, the tubes were hermetically sealed (length of the sealed tube $100 \pm 5 \text{ mm}$).

Testing of detection tubes

Function, sensitivity and concentration measurement range of the detection tubes were tested in a 0.712 m^3 test chamber equipped with a fan and thermostated heating. Various concentrations of diphosgene in the chamber were obtained by evaporating an exactly calculated and measured quantity of standard solution. The actual content of diphosgene in the chamber was monitored spectrophotometrically: diphosgene was sucked from the chamber for 10 min at flow rate $1 \text{ dm}^3 \text{ min}^{-1}$ and was absorbed in 5 ml of 0.1% solution of 4-(*p*-nitrobenzyl)pyridine in toluene. Then the absorption solution was made up to 5 ml with toluene (to replace the losses) and its absorbance was measured at 422 nm with toluene as a blank. The calibration curve was constructed analogously.

In tests of the detection tubes, the contaminated air in the chamber was sucked by a hand pump and the coloration of the indicator filling was evaluated visually (comparison with a blank). The results obtained with diphosgene are also given for phosgene.

RESULTS AND DISCUSSION

Carrier and its characteristics

In our preliminary studies we tried several composite materials containing microcrystalline cellulose

mixed with MgO, TiO₂ or silica gel powder in different proportions. The best results were achieved with MgO/microcrystalline cellulose mixtures, which were further subjected to a more detailed study. Table 1 shows the selected physical properties of this material. We have found that the pycnometer density of the material increases with increasing proportion of MgO, but at the same time its mechanical resistance (strength) decreases. Other parameters vary. The best Hausner ratio, characterizing the compressibility of loose materials (the ratio of tapped density to bulk density), has been obtained with materials containing 70% of MgO. Irregular shape and size comparison of individual carrier particles, captured by a microscope, are shown in Figure 1.

Table 1. Physical properties of the microcrystalline cellulose/MgO composite material

MgO content, %	20	30	50	70	80
Microcrystalline cellulose content Avicel PH 101-NF, %	80	70	50	30	20
Fraction 0,8–1,25 mm, %	74.83	86.56	66.73	72.72	64.10
Density, g.cm ⁻³	1.45653	1.75048	1.92839	2.09114	2.18024
Strength, N (average)	16.46	13.26	8.40	5.67	5.14
Abrasion, %	0.086	0.105	0.08	0.079	0.124
Hausner ratio	1.106	1.094	1.047	1.042	1.074
Color	Yellowish	Yellowish	Yellowish	Grayish	Grayish

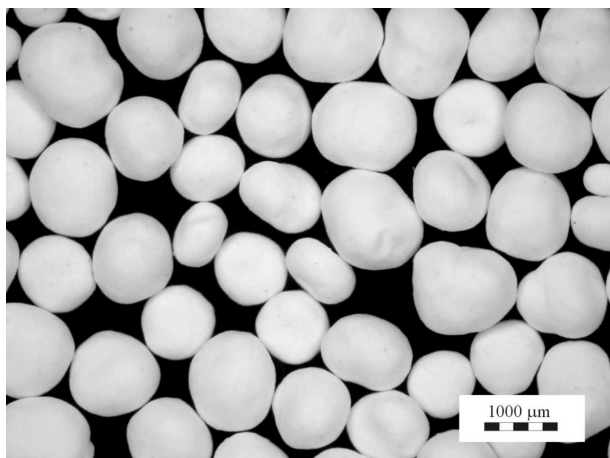


Figure 1. Photo of the composite carrier particles (microcrystalline cellulose/MgO, 30/70 wt.%).

Color characteristics

The detection is based on the formation of a substituted urea type product that passes into a mesoquinoid form of methine dye (Figure 2). The presence of phosgene and diphosgene in air, as measured with our new detection tube, creates a continuous zone of pale red color that contrasts well with the background of the indicator filling. The evaluation is also simplified by the sharp and easy to read borderline. The length of the colored zone is beneficially influenced by higher

proportion of MgO in the composite material. Thus, e.g. with 20% MgO content the colored zone length is 7 mm whereas with 70% MgO it is already 12 mm (sample volume 2 dm³, concentration 0.8 mg m⁻³).

Sensitivity and detection limit

The sensitivity and detection limit of the new detection tube was determined from dependence of the colored zone length on concentration of diphosgene in air (Figure 3). The average resolution ability of the tube, R_s , given by the equation $R_s = \Delta c/L$, where Δc is the difference of the measured concentrations (mg m⁻³) and L (mm) is the length of the color zone, is under these conditions about 0.1 mg m⁻³ mm⁻¹. The formation of the red ring is well discernible even at a con-

centration 0.05 mg m⁻³ (detection limit). Thus, the new detection tube can prove the presence of phosgene in concentrations lower than required by workplace hygiene standards (0.08 vs. 0.4 mg m⁻³). The same results as with the hand pump were obtained with an oil pump or electric pump – chemical detector. The sensitivity of the detection tube (extension of the color zone) can be improved by increasing the sample volume. However, with volumes higher than 3 dm³ the dynamics of the extension decreases (the dependence of the coloration length on sample volume is not linear). The sensitivity of the detection tube can also be increased by lowering the concentration of reagents in the carrier, but at the expense of the color brilliance, filling stability and resistance to interfering influences.

Selectivity and interferences

We have also studied the detection tube selectivity. A number of organic compounds with acylating properties, such as acetyl chloride, benzoyl chloride or methyl chloroformate, react similarly as phosgene and diphosgene. The sensitivity of detection is reduced by acidic vapors and gases, whereas alkaline substances in concentrations allowed in the workplace environment have no effect. Benzyl chloride, thionyl chloride, carbon dioxide, formaldehyde or bis(2-chloroethyl)sulfide (sulfur mustard) also have no effect. When detecting diphosgene in the presence of chloroacetophenone,

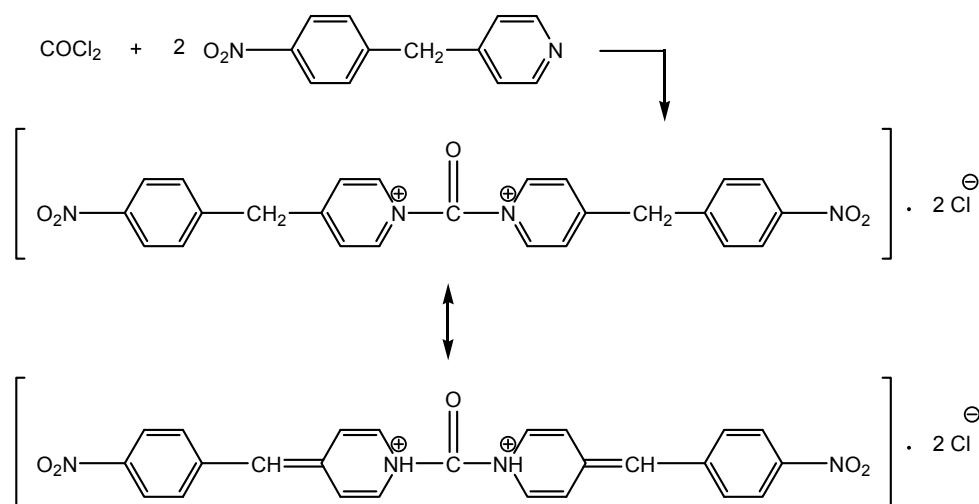


Figure 2. Mechanism of phosgene reaction with 4-(*p*-nitrobenzyl)pyridine.

the original red color changes to blue-violet. An overview of some interfering substances and tolerance limits are shown in Table 2.

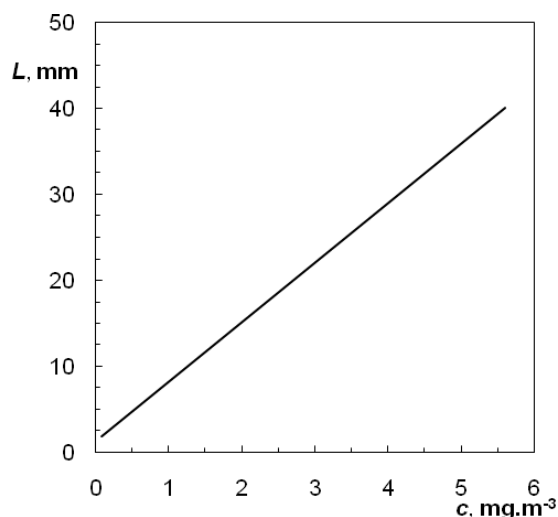


Figure 3. The characteristic length depending on the course of the color zone detection tubes for concentration of diphosgene. Sample volume 2 dm³ (20 strokes by hand suction device).

Stability and effect of temperature

The indication fillings of known detection tubes based on 4-(*p*-nitrobenzyl)pyridine, designed to detect very low phosgene concentrations, show generally low stability and therefore should be stored at temperatures 0–10 °C. In contrast, the stability of our filling design is good: when stored in hermetically sealed containers at temperatures below 25 °C it retains its original functionality for at least 12 months.

We also studied the effect of temperature on the function of our detection tube. Samples of the tubes were placed in a refrigerating box at 4, –18 and –48 °C, and in a heated chamber at 60 °C. After 2 h, the tubes were removed and were immediately exposed to diphosgene in the test chamber at concentration of 0.8 mg m⁻³. In all cases, the results of detection (length of the color zone and color intensity) were comparable with those obtained with tubes stored at room temperature.

Applications – continuous monitoring

Like the known tubes from reputable manufacturers, our new detection tube can be used for a quick

Table 2. Interfering compounds (diphosgene concentration: 0.8 mg m⁻³, sample volume: 1 dm³)

Contaminant	Interfering compound concentration, mg m ⁻³	Found diphosgene concentration, mg m ⁻³
Acetyl chloride	20	0.9
Benzoyl chloride	2.0	1.0
Thionyl chloride	60	0.7
Benzyl chloride	60	0.7
Acetic acid	30	0.6
Ammonia	120	0.9
Nitrogen dioxide	40	0.8
Formaldehyde	30	0.7
Chloroacetophenone	50	0.8
Bis(2-chloroethyl)sulfide	10	0.8

Table 3. Comparison of some parameters of the new indication tube with those of commercially available phosgene indication tubes from some leading manufacturers (the tubes use sampling systems of different technical parameters (flow rate, flow resistance))

Tube	Evaluation method	Sample volume dm ³	Range of measurement mg m ⁻³	Continuous measurement min
Dräger (81 01521) ^a	Zone length	2 or 4	0.08–4	No
Dräger (CH 19401) ^b	Color intensity	0.1 to 3.3	0.2–6	No
MSA (803949) ^b	Zone length	0.5 or 2	0.4–80	No
Kitagawa (146S) ^a	Zone length	0.1 or 0.5	0.4–80	No
Gastec (16) ^c	Zone length	0.1 or 1	0.2–80	No
Oritest (145) ^a	Color intensity	1	0.1–50	120
New tube ^a	Zone length	1	0.08–5	240

^a4-(*p*-Nitrobenzyl)pyridine, *N*-phenylbenzylamine; ^b*p*-dimethylaminobenzaldehyde, *N,N*-dimethylaniline; ^c*p*-dimethylaminobenzaldehyde, diphenylamine

determination of phosgene (diphosgene) in limit concentrations in air (Table 3). Unlike the known tubes, it can also be used for a long-term continuous monitoring of these pollutants in air. During the test we have employed the following procedure: initially, uncontaminated air (in a laboratory) was collected using an electric pump (chemical detector) for 30 to 240 min (rate 1 dm³ min⁻¹). The tube was then exposed to diphosgene in the test chamber (concentration 0.3 mg m⁻³; 10 strokes by hand suction pump). The results were then compared with measurements using a fresh tube. These experiments show that our new tube can be used for continuous monitoring for at least 240 min without reduction of its sensitivity. The length of the colored zone and color intensity in tubes used for a prolonged sucking were the same as those in the freshly used tubes.

CONCLUSIONS

A new detection tube for detection of phosgene (diphosgene) in air has been developed. Its indication filling consists of a composite carrier made of MgO and microcrystalline cellulose in optimum weight ratio 30% : 70%, impregnated with 4-(*p*-nitrobenzyl)-pyridine and *N*-phenylbenzylamine reagents in the respective concentrations of 0.5 and 1.5 g per 100 g of the carrier. This composition of the filling affords better analytical results than the previously described materials. The sensitivity of this detection tube (detection limit 0.05 mg m⁻³) is better than that of the current devices; this may be utilized for monitoring workplace environment. Other acylating and alkylating agents interfere only in higher concentrations. Owing to the new composite carrier, the detection tube also enables long-term continuous monitoring of phosgene (diphosgene) in air to be performed for at least 240 minutes. This is about twice as long compared with the known devices. Prolonged continuous measurement is advantageous not only in monitoring the workplace environment, but also in cases of a chemical attack or industrial accident.

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IZVOD

DETEKCIJNA CEV ZA MERENJE KONCENTACIJE FOZGENA I DIFOZGENA U VAZDUHU

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(Stručni rad)

Razvijena je nova visoko osjetljiva detekciona cev za merenje koncentracije fozgena i difozgena u vazduhu. Detekcija se zasniva na hemijskoj reakciji 4-(*p*-nitrobenzil)piridina i *N*-fenilbenzilamina koji sa fozgenom (difozgenom) daju karakterističnu crvenu metilensku boju. Kao nosač korišćene su sferične granule (palete) kompozitnog materijala pripremljenog granulacijom mikrokristalne celuloze i MgO. Ovo novo indikatorsko punjenje je stabilno i otporno na smetnje i klimatske uticaje. Granica detekcije (0,05 mg m⁻³) zadovoljava higijenske zahteve za kvalitetom vazduha u radnoj sredini. Pored toga, detekciona cev omogućava dugo-trajno i neprekidno praćenje fozgena i difozgena u vazduhu najmanje 240 min.

Ključne reči: Detekciona cev • Difozgen • 4-(*p*-Nitrobenzil)piridin • Kompozitni materijal • Mikrokristalna celuloza • Magnezijum-oksid