Scientific paper

Acetyl Cellulose Film with 18-crown-6 Ether for Colorimetric Phosgene Detection

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Abstract

The use of a cellulose detection film as a carrier for a colorimetric sensor to detect phosgene and allied compounds to be evaluated primarily visually is studied. For the case study, a benzimidazole-rhodamine dye and an acetyl cellulose film were selected. The detection complex was modified using cyclic ether 18-crown-6 to achieve more desirable analytic properties. The chromatic properties of detection film was verified using reflectance colorimetry in the visible light spectrum. The employed detection agent demonstrated high sensibility to phosgene vapours, but acid gases, acyl chlorides, base organic solvents, and in higher concentrations, even some organophosphorus substances interfered. The detection film application was adjusted to the in-situ preparation of simple detection devices (a spray or a marker) as well as to manufacture detection strips with beforehand excluded polymer film.

Keywords: Crown ether, phosgene, polymer film, acetyl cellulose, chromogenic chemosensor

1. Introduction

The highly toxic colourless gas phosgene, mostly in mixtures with other toxic gases, was firstly utilised for military purposes during World War I. From the chemical point of view, it is a derivate of carbonic acid with two allied compounds: diphosgene (trichloromethyl carbonochloridate) and triphosgene (bis(trichloromethyl) carbonate). This highly reactive gas demonstrates distinct toxic properties due to a significant hydrolytic reaction on tissues and is classified as a pulmonary agent. The allied compound diphosgene has risen to military significance. Concerning diphosgene, it is a colourless liquid ensuring easier manipulation.[1] The toxic properties of diphosgene correspond with phosgene, the LC_{50} dose represents 2,000–3,200 mg m^{-3} (500–800 ppm) at 1 min exposure.[1,2] The permissible value of work exposure due to the NIOSH regulations is 0.4 mg m^{-3} (0,1 ppm) at 8 h shift.[1,3] Phosgene is currently utilised when producing agrochemicals, polycarbonates, and pharmaceutical substances; in 2015, the world production amounted to 8.526 million tonnes.[4]

The colorimetric detection of phosgene/diphosgene is currently conducted using the well-known reaction with benzylpyridine derivates, for example 4-(4-Nitrobenzyl) pyridine: distinct red colouring. The method has been predominantly applied in the form of detection tubes or paper strips also known as continuous detectors in the form of cards.[5–10] Furthermore, the reaction of phosgene with Harrison's reagent (4-(dimethylamine) benzaldehyde/diphenylamine) produces a yellow condensation product.[11–13] Newer detection methods use more complex chromogenic agents with organic chemosensor structures, or other heterocyclic compounds, which, after the reaction with an analyte, change colours distinctly. To illustrate the case, the reaction between phosgene and substituted BODIPY oxime forming orange colouring or with phenylenediamine/BODIPY unit as fluorophore can be utilised.[14,15] Out of other detection agents, the compounds with coumarin, benzothiazole, imidazole, benzimidazole-rhodamine, o-phenylenediamine/pyronine, o-hydroxyaniline, carboxyimide, and quinazolinone skeletons were employed for colorimetric and fluorometric detection.[16–30]

The authors, purposefully and on a long-term basis, concentrate on the issues of phosgene and its allied compounds detection. The aim of the work was to propose a different carrier of detection agents in the form of a thin polymer film. It is going to be carry several advantages of the solution, such as the abilities to prepare a detector in the place of detection (in situ), to minimise the usage of chemicals and supporting materials, and to allow the continuous monitoring of the environment to check the presence of toxic substances.

2. Experimental

2. 1. Chemicals and Materials

To prepare polymer films, acetyl cellulose (Carl Roth GmBH, Germany), cyclic ether 18-crown-6 (Sigma-Aldrich, USA), and acetone as a dissolving agent (Merck, Darmstadt, Germany) were employed. Benzimidazole/rhodamine B dye was employed as a detection agent (The University of Chemistry and Technology, Prague, CZE; the spectral data correspond with the literature). To verify the method, trichloromethyl chloroformate (diphosgene), ammonia, benzoyl chloride, diethyl ether, hydrochloric acid, nitromethane, pyridine, carbon disulphide, (all Sigma-Aldrich, USA), isopropyl methylphosphonofluoridate (sarin, The University of Defence, CZE), and petrol (Cepro, CZE) were employed.

To apply polymer films, a refillable marker with a dosing valve and 4 mm tip 211EM (Molotow, Lahr, Germany) was utilised. The objective colorimetric measurements were conducted using the reflectance spectrophotometer Ultrascan XE (HunterLab, Reston, USA) with 9.5 mm entrance slit. The micrographs were taken using a scanning electron microscope (SEM).

2. 2. Preparation of Polymer Solution with Detection Agent

The base solution supply of the polymer was prepared by dissolving 4 g of acetyl cellulose in 100 ml of anhydrous acetone in a heated ultrasonic bath. 8 mg of rhodamine-benzimidazole dye was dissolved in 5 ml of the base solution to form a pink solution. The transition of the colouring dye to the colourless form was conducted by adding 750 mg of ether 18-crown-6. The solution turned light pink, colourless after the application on the carrier.

2. 3. Phosgene Detection

The concentration of diphosgene in the range from 0.1 to 5 mg/m^3 in a toluene solution was prepared in the test chamber with the volume of 0.712 m^3 using the forced air circulation. The colouring of the detection film depending on the diphosgene vapour concentration and the exposure time ranging from 1 to 10 min were observed. Apart from the intended, primary visual evaluation, the instrumental reflectance measurement was conducted to objectively evaluate the changes in film colouring. After each exposure in the test chamber, the new concentration of the analyte was prepared for the following measurement.

The chemosensors were prepared by excluding the thin detection film from 50 µl detection polymer solution. The film was subsequently distributed on a PE pad with the diameter of 16 mm. After the distribution, the film was left for drying at the laboratory temperature for the period of 3 min. To evaluate the changes in the colouring of the detection film, the method of reflectance colorimetry in the colour space CIELAB 10°/D65 was employed. The records were interpreted as the dependence of the reflectance on the wavelength of the visible spectrum in the interval of λ = 380–750 nm.

3. Results and Discussion

3. 1. Method Characteristics

To detect phosgene and its allied compounds, the benzimidazole-rhodamine dye was selected. Historically, the phosgene detection was based on its reaction with the nitrogen of the benzimidazole unit releasing the pink form of the dye (Figure 1) that can be evaluated in the UV spectrum of electromagnetic radiation.[19]

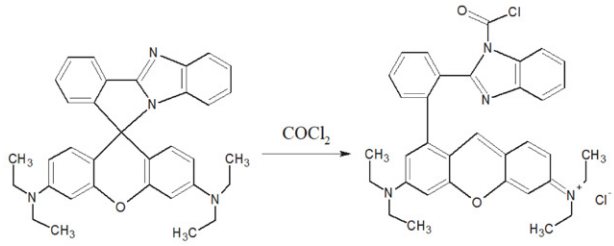

Figure 1: Benzimidazole-rhodamine dye and the end product after the reaction with phosgene are presented.[19]

The previous research already applied the agent into the polymer matrix formed by polyethylene oxide, formed using the technology of electrostatic fibre formation, whose fibrous structure was the functional base for the chemosensor to detect phosgene using colorimetric and fluorescent evaluation.[19] The simple release of the polymer film from the solution by evaporating the dissolving agent was employed. This simple method can be easily utilised for the in-situ preparation of simple detection means to monitor toxic substances in the atmosphere, to simplify the whole testing procedure, and at the same time, to minimise financing costs.

Three ways were utilised to employ the detection film. Firstly, it was utilised in the form of the solution applicated by the refillable marker. Secondly, the preparation of simple detection strips made from supporting materials

(PE strip) and the released detection film on its surface was utilised. Thirdly, the application of the polymer solution using a mechanical spray for larger areas was utilised.

3. 2. Detection Film Characteristics

The naturally released films from acetone were unstable and mostly unable to preserve the transparent

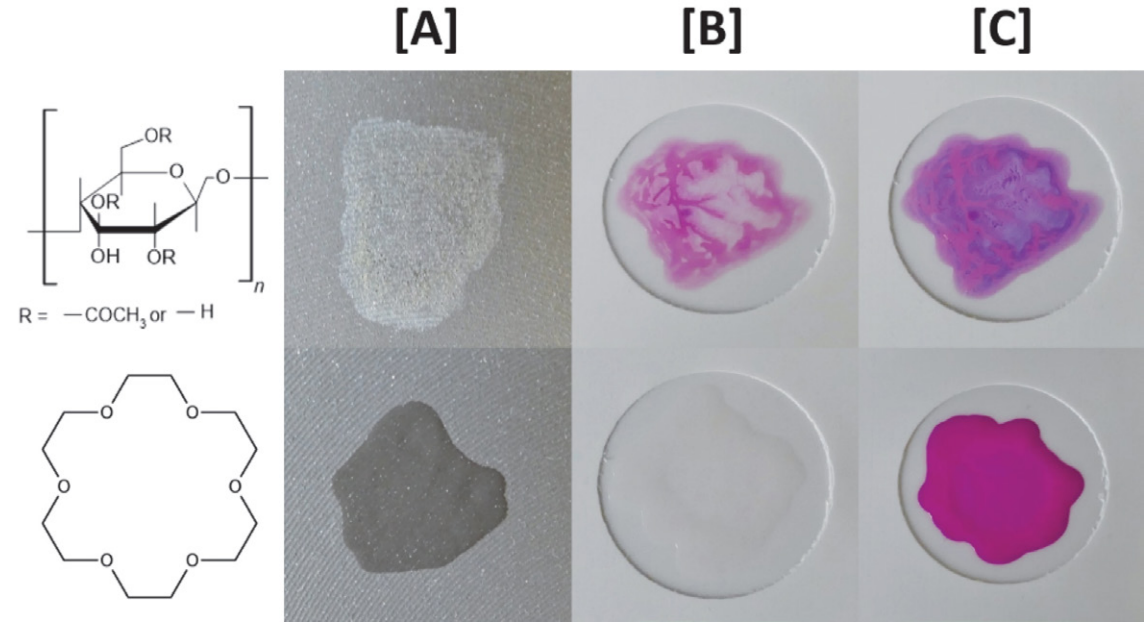

Figure 2: The non-modified (the upper row) and the modified 15% ether 18-crown-6 acetyl cellulose film (the lower row) are compared. The natural appearance of the polymer film after the evaporation of the dissolving agent [A], the excluded polymer film with the benzimidazole-rhodamine agent [B], and after being exposed to diphosgene vapours [C] are presented.

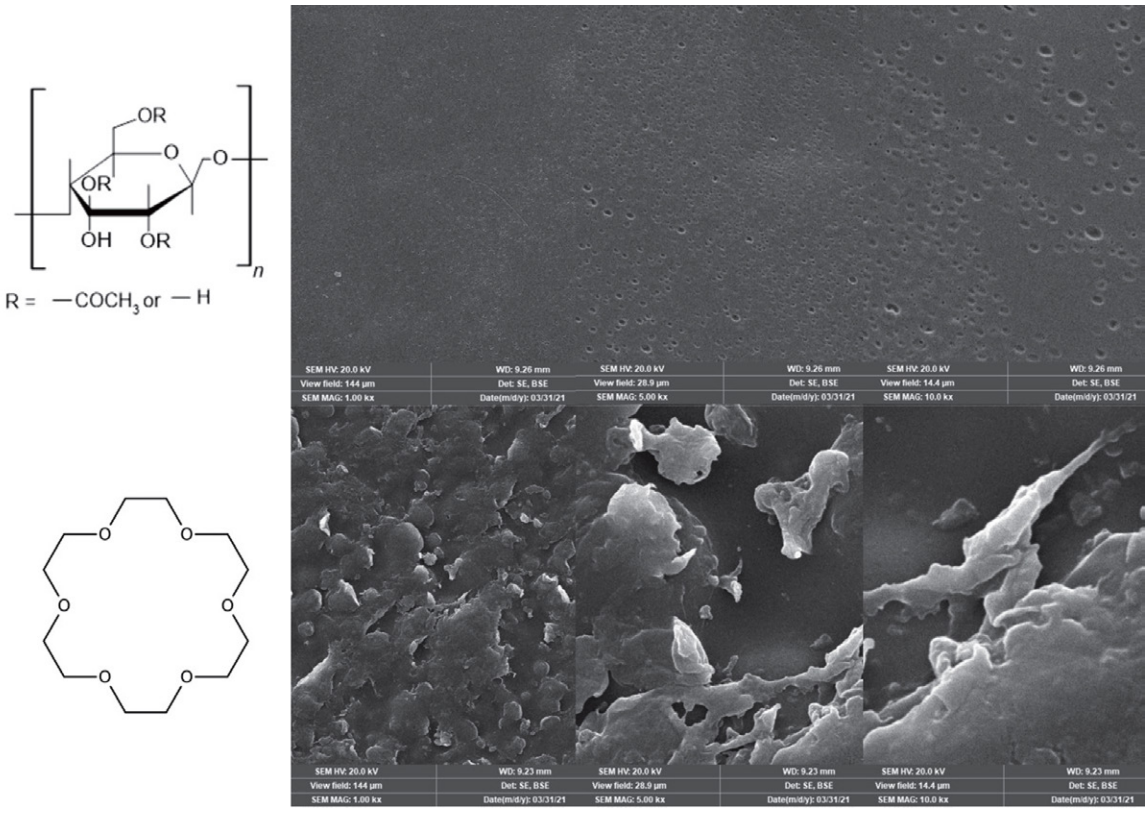

Figure 3: The micrographs of the acetyl cellulose film (the upper row) and the film with the addition of 15% ether 18-crown-6 (the lower row) are compared at various magnifications.

appearance. Besides, the colouring agent was also unable to preserve the transparent appearance and after the evaporation of the dissolving agent, it coloured heavily (Figure 2).

The further study of the issue aimed at removing these drawbacks by modifying the film using ether 18-crown-6. The cyclic ether improved the structure of the released film and preserved the detection agent in the transparent form (Figure 2). The homogeneity of the distribution of the detection agent inside the polymer film was significantly improved. The growing percentage of ether 18-crown-6 in the polymer decreases its rigidity; with over 20% percentage of ether 18-crown-6, it formed a gel-like mixture. The 15% value of ether 18-crown-6 mass in the acetone solution of the polymer was selected to reach the compromise between the sufficient film rigidity and the positive impact on the detection.

The stabilisation of the colouring agent can be probably assigned to the ability of the cyclic ether to bind a hydrogen cation inside the cyclic molecule in the form of hydronium cation.[31–33]

After evaluating the impact of the addition of ether 18-crown-6 to the structure of the released acetyl cellulose films, the scanning electron microscopy of the samples without the detection agent was conducted. The micrographs demonstrated much higher heterogeneity of the modified films (Figure 3) in comparison with the naturally released ones and this probably contributed to the better accessibility of the analytic agent on their surfaces.

3. 3. Verifying Methods of Using Detection Films

Detection marker

Filling the cartridge of the refillable marker by the solution of the detection film allows to produce simple detection devices in the place of detection (in situ) (Figure 4). The advantage of the solution is the sufficient capacity of the cartridge that ensures conducting the tens of tests using a single cartridge; this means an extremely low cost per use. The application is possible on all materials with the good potential of the easy evaluation of the colour change, for example white cotton fibre, paper, plastic material, or ceramics. The 5 ml filling of the detection polymer solution suffices for approximately 500 tests.

Strip detector

The PE strips with the 12 × 80 mm dimensions were marked with the glued label with 5 mm circular openings. 10 µl of the solution of the detection film was applied to the openings using a micropipette. After the evaporation of the dissolving agent, the simple detection device with 5 mm active surface that can be packed into the hermetic packaging (Figure 4) was produced.

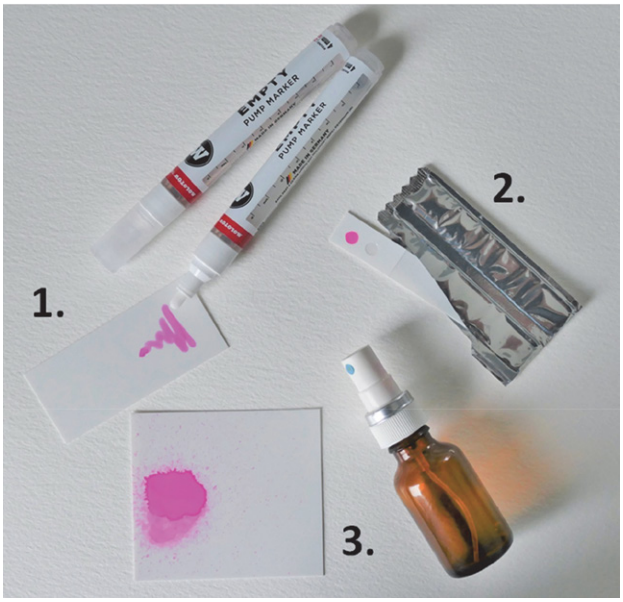

Figure 4: The proposed application utilises either the polymer solution for the in-situ release of the detection films (1 – the detection marker, 3 – the detection spray) or the beforehand released film on the suitable carrier (2 – the test strip). The pink colouring was reached by the exposure of the detection devices to diphosgene vapours.

Detection spray

The simple hand spray was the last laboratory-verified application of the detection film. The volatile dissolving agent helps to the quick drying of the film on the base which lasted only a few tens of seconds. The commercially easily accessible hand spray suitable for the application on larger surfaces was utilised (Figure 4).

3. 4. Sensibility, Stability, and Interference

Measuring the dependence of diphosgene concentration on the colouring intensity of the detection film is depicted in the Figure 5. The absorption maximum of the detection film is in 570 nm wavelength range. The detection limit when visually evaluated is in the case of 10 min exposure on the border of 0.125 mg/m^3. LOD was determined on the set of 5 samples tested at the given concentration and the exposure time which produced colour perception in an observer. The sensibility of the solution when exposed to phosgene satisfies the requirements of workplace hygiene according to NIOSH.

The work verified the stability of the detection films during long-term diphosgene measurement in the atmosphere. The long-term measurements manifested themselves in the measurable decrease of the film colouring; nevertheless, the effect was infinitesimal when evaluated visually (Figure 6). The solution is feasible when considering the visual evaluation and/or continuous atmosphere monitoring.

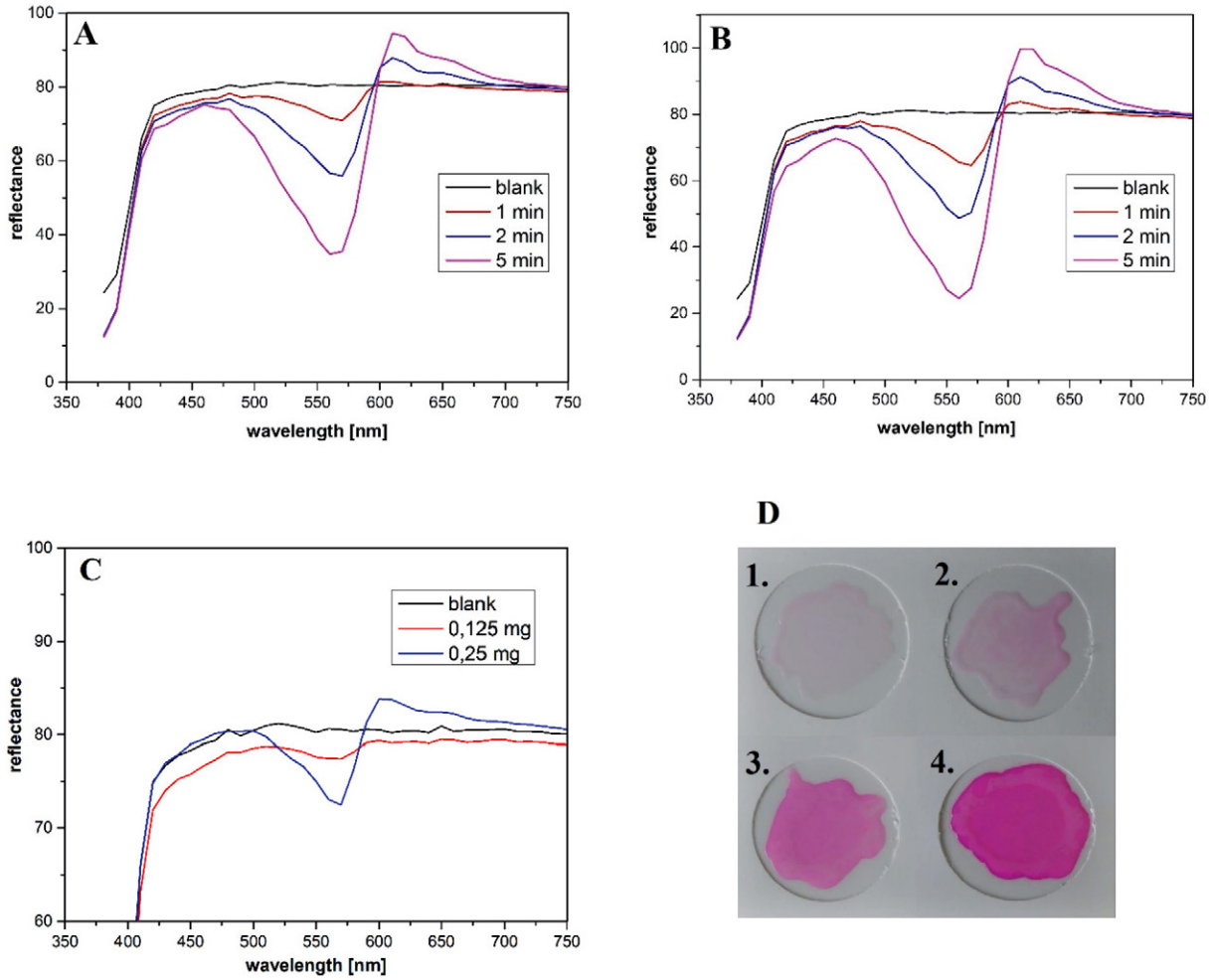

Figure 5: The colouring of the detection film at the diphosgene concentration of 2.2 mg/m^3 (A) and 4.4 mg/m^3 (B) depending on the exposure time is measured. The low concentrations (C) were measured at 10 min exposure time. The colouring examples of the detection film (D) (diphosgene concentration/exposure time) were given at 1) 0.25 mg/m^3/5 min; 2) 0.5 mg/m^3/5 min; 3) 2.2 mg/m^3/2 min; 4) 4.4 mg/m^3/2 min.

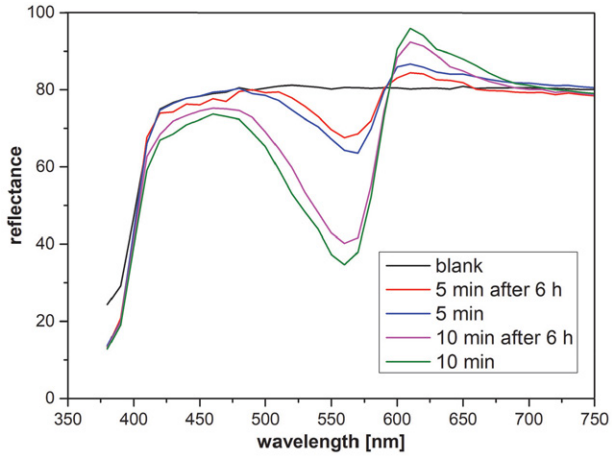

Figure 6: The colouring of the detection film after the diphosgene vapour exposure at the concentration of 1 mg/m^3 and 5, 10 min exposure is presented. The sample set was placed in uncontaminated environment for 6 h and subsequently exposed to the corresponding analyte concentration.

3.4 Interference Substance Influence on Detection Film

The detection agent is sensitive to acidic gases, or the substances which produce acidic products when in the presence of atmospheric humidity; the acidic products protonate the imidazole nitrogen in the molecule.[34] The reaction of colouring films on the selected most significant interfering substances was instrumentally measured (Figure 7). Based on the measured data, it is evident that the most significant interfering substance is hydrogen chloride which leads to the highly sensitive reaction with the detection film, as in the case of diphosgene. Benzoyl chloride is a less significant interferent; in the concentration of 2.8 mg/m^3 and 2 min exposure time, it does not produce any colour change of the film.

Due to the possible need of toxic substance analysis in the military, the nerve agent sarin (GB) was tested as an analyte; however, at the selected 0.5 mg/m^3 sarin concentration and 10 min exposure time, no colouring of the detection film was observed. The colour reaction was ob-

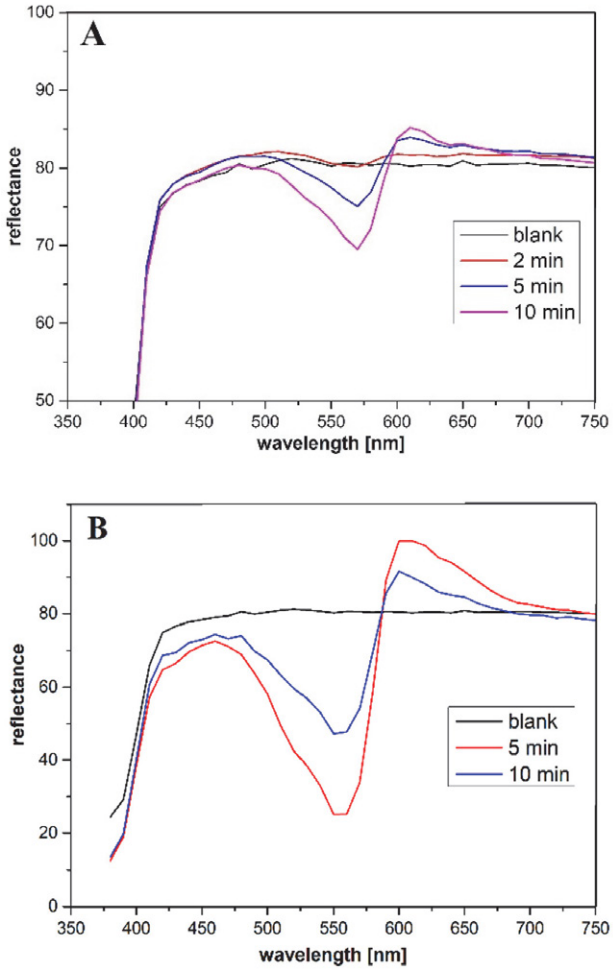

Figure 7: The colour reaction of the detection film depending on the exposure time concerning the most significant interfering substances, for example (A) benzoyl chloride at the concentration of 2.8 mg/m^3 and (B) hydrogen chloride at the concentration of 5.8 mg/m^3, were measured.

servable at the high concentrations of sarin, over 10 mg/m^3. Contrarily, the colour reaction of the detection system was not observed in aliphatic and aromatic hydrocarbons, chlorinated dissolving agents, base substances, and other dissolving agents (the Table 1). The colour reaction of the diphosgene after the exposure to common dissolving agents and chemicals was examined. The detection film demonstrated high affinity to pyridine when its vapours significantly inhibited the colour reaction even after longer period after the interrupting the exposure. Nitromethane achieved the same, even though a bit weaker result. Ammonia, on the other hand, inhibited the reaction only slightly as it was quickly released from the film.

4. Conclusions

The tested solution provides a cheap and simple carrier of the detection chemicals which represents a possible alternative to the currently commonly used carriers (paper or silica gel) The proposed cellulose carrier, modified with ether 18-crown-6, represents the possibility to prepare simple detection devices in the place of detection (in situ) owing to the thin polymer film with evenly distributed detection chemicals on its surface. To verify the abilities of the carrier, the rhodamine-imidazole dye integrated into the polymer matrix was utilised. This simple detection device in the form of a PE card with the applied detection film was exposed to diphosgene vapours. The ascertained LOD when evaluated visually and 10 min exposure time amounted to 0.125 mg/m^3 (0.03 ppm). All the considered detection solutions (a marker, a strip sensor, and/or a spray) were functional.

The proposed polymer carrier is suitable also for the integration of analytical agents sensitive to other toxic va-

Table 1: The overview of the interferences of the proposed detection film, the substances were tested in the form of concentrated gases.

Chemicals	The reaction of the film to chemicals	The reaction of the film to diphosgene after the exposure to chemicals
ammonia	No reaction	Slight decrease in sensibility
benzoyl chloride	Pink-purple colouring, weaker than gaseous hydrogen chloride	–
diethyl ether	No reaction	Detection potential preserved
hydrogen chloride	Pink-purple colouring, significant interference	–
car petrol	No reaction	Detection potential preserved
nitromethane	No reaction	Decrease in sensibility
pyridine	No reaction	Significant decrease in sensibility
sarin (GB)	0.5 mg/m^3, 10-min exposure – no reaction, the reaction noticed over concentrated vapours	Detection potential preserved
carbon disulphide	No reaction	Detection potential preserved

pours and gases which will be the topic of the subsequent development of the research.

5. References

1. E. Halámek, Z. Kobliha, V. Pitschmann, Analysis of Chemical Warfare Agents; University of Defence: Brno, Czech republic, **2009**. ISBN: 978-80-7231-658-8.
2. J. Borak J, W. F. Diller**,** *J. Occup. Environ. Med.* **2001**, *43* (2), 110–119. **DOI:**10.1097/00043764-200102000-00008
3. Centers for desease control and prevention, The National Institute for Occupational Safety and Health (online), NIOSH Pocket Guide to Chemical Hazards – Phosgene, https://www.cdc.gov/niosh/npg/npgd0504.html (10.3.2021).
4. Gen Consulting Company, Global Phosgene Outlook 2016-2021**, 2016**.
5. A. M. Agree, R. L. *Talanta* **1966**, *13 (8)*, 1151-1160. **DOI:**10.1016/0039-9140(66)80163-7
6. B. Witten, A. Prostak, *Anal. Chem.* **1957**, *29*, 885–887. **DOI:**10.1021/ac60126a008
7. Morphix Technologies (online), SafeAir® Chemical Detection Badges, Phosgene, Virginia, USA, https://www.morphtec.com/safeair/ (10.3.2021).
8. V. Pitschmann, Z. Kobliha, E. Halámek, I. Tušarová, *J. Serb. Chem. Soc.*, **2007**, *72(10)*, 1031-1037. **DOI:**10.2298/JSC0710031P
9. V. Pitschmann, Z. Kobliha, E. Halámek, I. Tušarová, *Chem. Anal.*, **2008**, *53(2)*, 47–57.
10. V. Pitschmann, I. Tušarová, Z. Kobliha, D. Vetchý, *Hem. Ind.*, **2012**, *66(1)*, 79–84. **DOI:**10.2298/HEMIND110530057P
11. A. P. Vargas, F. Gámez, J. Roales, T. Lopes-Costa, J. M. Pedrosa, *ACS Sensors* **2018**, *3*, 1627–1631. **DOI:**10.1021/acssensors.8b00507
12. A. L. Linch, S. S. Lord, K. A. Kubitz, M. R. De Brunner, *Am. Ind. Hyg. Assoc. J.* **1965**, *26 (5)*, 465–474. **DOI:**10.1080/00028896509342759
13. A. P. Vargas, T. Lopes-Costa, M. G. Guillén, M. B. S. Jiménez, J. M. Pedrosa, Detection of phosgene by using TiO_2/indicator nanocrystalline thin films, 10th International Conference on Composite Science and Technology, Lisboa, Portugal, **2015**.
14. T. I. Kim, B. Hwang, J. Bouffard, Y. Kim, *Anal. Chem.*, **2017**, *89*, 12837–12842. **DOI:**10.1021/acs.analchem.7b03316
15. X. Hong-Cheng, X. Xiang-Hong, S. Qin-Hua, *Anal. Chem.*, **2017**, *89 (7)*, 4192–4197. **DOI:**10.1021/acs.analchem.7b00203
16. F. Weiyong, G. Shengyi, Z. Enbo, Y. Xinyu, F. Guoqiang, *Anal. Chim. Acta*. **2018**, *1029*, 97–103.
17. X. Hong-Cheng, X. Xiang-Hong, S. Qin-Hua, *ACS Sensors*, **2017**, *2 (1)*, 178–182.
18. B. Luoyi, F. Weiyong, F. Guoqiang, *Dyes and Pigments*, **2019**, *163*, 483–488. **DOI:**10.1016/j.dyepig.2018.12.013
19. H. Ying, Z. Xin, J. Hyeseung, N. Sang-Jip, H. K. Myung, Y. Juyoung, *Anal. Chem.* **2018**, *90 (5)*, 3382–3386. **DOI:**10.1021/acs.analchem.7b05011
20. W. Cuiyan, X. Hai, L. Yaqian, X. Ruihua, L. Peijuan, P. Xiao, Z. Zile, G. Biao, L. Haitao, Z. Youyu, *Talanta* **2019**, *200*, 78–83. **DOI:**10.1016/j.talanta.2019.03.003
21. X. Zhou, Y. Zeng, C. Lilyan, X. Wu, J. Yoon, *Angew. Chem. Int. Ed.* **2016**, *55*, 4729–4733. **DOI:**10.1002/anie.201601346
22. V. Pitschmann, L. Matějovský, J. Zeman, D. Vetchý, M. Dymák, M. Lobotka, S. Pavloková, Z. Moravec, *Chemosensors*, **2020**, *8(4)*, 107 (8040107). **DOI:**10.3390/chemosensors8040107
23. Q. Hu, T. Gong, Y. Mao, Y. Yin, Y. Wang, H. Wang, *Acta A Mol. Biomol. Spectrosc.* **2021**, *253*, 119589. **DOI:**10.1016/j.saa.2021.119589
24. Z. J. Li, W. J. Zhang, W. Z. Bi, Q. J. Ma, S. X. Feng, X. L. Chen, L. B. Qu, *RSC Advances*, **2021**, *11*, 10836. **DOI:**10.1039/D1RA00811K
25. L. Yang, F. Wang, J. Zhao, X. Kong, K. Lu, M. Yang, J. Zhang, Z. Sun, J. You, *Talanta*, **2021**, *221*, 121477. **DOI:**10.1016/j.talanta.2020.121477
26. Z. Lintao, Z. Hongyan, W. Shuangfei, W. Shan, H. Ji-Ting, Y. Juyoung, *Commun. Chem.*, **2019**, *55*, 13753–13756. **DOI:**10.1039/C9CC07437F
27. H. Qiao, D. Chong, W. Juanjuan, S. Dongdong, Z. Lintao, S. Ruilong, *Anal. Chem.*, **2018**, *90*, *14*, 8686–8691. **DOI:**10.1021/acs.analchem.8b02119
28. Z. Lintao, Z. Hongyan, J. Lirong, W. Shan, H. Ji-Ting, Y. Juyoung, *Anal. Chem.*, **2019**, *91*, *18*, 12070–12076. **DOI:**10.1021/acs.analchem.9b03230
29. Ch. Tianhong, J. Lirong, H. Ji-Ting, W. Wei, Z. Lintao, B. Guang-Ming, *J. Mater. Chem.*, **2020**, *8*, 24695–24702. **DOI:**10.1039/D0TA08333J
30. F. Zeng, G. Bao, B. Zhou, Y. Han, *New J. Chem.* **2021**, 45(*12),* 5631–5636. **DOI:**10.1039/D1NJ00037C
31. J. W. *Steed, J. L. Atwood, Supramolecular Chemistry (2nd ed.), Wiley,* **2009**. ISBN: 978-0-470-51234-0.
32. J. L. Atwood, S. G. Bott, A. W. Coleman, K. D. Robinson, S. B. Whetstone, C. M. Means, J. *Am. Chem. Soc.* **1987***, 109 (26), 8100–8101.* **DOI:**10.1021/ja00260a033
33. J. L. Atwood, S. G. Bott, C. M. Means, A. W. Coleman, H. Zhang, M. T. *May, Inorganic Chemistry,* **1990***, 29 (3), 467–470.* **DOI:**10.1021/ic00328a025
34. X. Zhongwei, Ch. Mingliang, Ch. Jianming, H. Jiahuai, H. Shoufa, *RSC Advances*, **2014**, *4*, 374–378.

Povzetek

Proučevali smo uporabo celuloznega detekcijskega filma kot nosilca za kolorimetrični senzor za detekcijo fosgena in sorodnih spojin na podlagi vizualne evalvacije. Za demonstracijo koncepta smo izbrali benzimidazol-rodaminsko barvilo in acetilcelulozni film. Detekcijski kompleks smo modificirali z uporabo cikličnega etra 18-krona-6, da smo dosegli bolj ugodne analitične lastnosti. Kromatske lastnosti detekcijskega filma smo preverili z odbojno kolorimetrijo v spektru vidne svetlobe. Uporabljen detekcijski agent je pokazal visoko občutljivost na hlape fosgena, vendar pa so interferirali plini kislin, acil kloridi, bazična organska topila in v višjih koncentracijah celo nekatere organofosforne snovi. Aplikacija detekcijskega filma je bila prilagojena in situ pripravi enostavnih detekcijskih naprav (razpršilo ali marker) ter izdelavi detekcijskih trakov s predhodno izločeno polimerno folijo.