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A new simple method for monitoring permeation through clothing materials of dibutyl sulphide, a chemical warfare agent simulant

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Abstract

A new simple method is proposed for monitoring permeation of dibutyl sulphide through protective clothing materials. The method is based upon the reaction of sodium nitroprusside with sulphide ions in alkaline medium. It is carried out as a spot test on the filter paper previously impregnated with sodium nitroprusside as indicator compound or directly on clothing material. The violet colour that indicates the presence of sulphide ions is detectable with a magnifying glass and even with the naked eye. The method was applied for the determination of breakthrough times of some intermediates in the fabrication of protective clothing materials, based on polyester fibres technologically treated among other chemicals, with 4,4′-dithiomorpholine, 2-mercaptobenzothiazole disulphide and dipentamethylenethiuram tetrasulphide. The widely recommended fluorescence quenching technique was in this case shown to be inapplicable because of severe interferences caused by technological pretreatment of clothing materials, resulting in diminished fluorescence signals of indicator compounds by mere contact with clothing materials. The new analytical method is sensitive enough, shows no interferences and is a simple, fast, and low cost test for permeation monitoring of dibutyl sulphide. © 1997 Elsevier Science B.V.

Keywords: Dibutyl sulphide; Warfare agent simulant; Sodium nitroprusside; Spot test method

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1. Introduction

There is constant concern regarding skin exposure to chemical warfare agents for personnel involved in their handling as well as for civilians who may, by accident, come into contact with them. Although the use of chemical weapons and bulk stocks of hazardous chemical agents is prohibited by the Chemical Weapon Convention [1], the newest events, even in Croatia, show the need for caution.

In the accessible literature there are data on the efficacy of some protective clothing materials against chemical warfare agents. Recently, new methods for examining the permeability of various materials against chemical agents and their simulants have been published [2–6]. One of the methods, reported as a simple and efficacious one, involves monitoring of the fluorescence quenching of phenanthrene as the indicator compound built into the crude carrier, in reaction with chemical agents and their simulants [2,3]. The other method uses spot disc test and FTIR-ATR determination for examining the permeability of various materials [5,6].

Concerning the great risk of exposure and the complexity of detection procedures for minute amounts of chemical warfare agents, there is a vivid need for the development of new simple and reliable methods for their detection. The present paper deals with the determination of breakthrough times of various materials, tested for permeability against dibutyl sulphide (DBS), a generally accepted simulant for sulphur mustard, the chemical warfare agent. Two methods of determination were applied—the well known fluorescence quenching technique, and the presently modified method for the sulphide spot test analysis with sodium nitroprusside. They were applied for the determination of breakthrough times of some intermediates in fabrication of protective clothing materials, based on polyester fibres technologically treated, among other chemicals, with 4,4′-dithiomorpholine, 2-mercaptobenzothiazole disulphide and dipentamethylenethiuram tetrasulphide. Considerable fluorescence quenching was observed, resulting from the mere contact of clothing materials with the filter paper previously impregnated with phenanthrene as the indicator compound (blanks). This fact led to the conclusion that the fluorescence quenching technique using phenanthrene as the indicator compound, was inadequate as the analytical method for monitoring dibutyl sulphide permeation in materials previously technologically treated with the chemicals that could cause quenching themselves. Literature data [2–4] do not describe any influence of blanks upon the results of dibutyl sulphide permeation based on fluorescence quenching measurements of phenanthrene as indicator compound, although according to our knowledge serious interferences are likely to occur, because of different technological pretreatment of protective clothing materials. Therefore, a new method has been developed for monitoring dibutyl sulphide permeation, based upon the reaction with sodium nitroprusside in alkaline medium. It is carried out as a spot test on the filter paper previously impregnated with sodium nitroprusside as indicator compound, or directly on clothing material. This method does not suffer from interferences due to the technological process in the manufacturing of protective clothing materials, and is sensitive enough to enable reliable dibutyl sulphide permeation monitoring. Further advantages with respect to the former method are enhanced speed of performance, lower costs of monitoring, transportability of equipment, and therefore applicability in field monitoring.

2. Experimental

2.1. Materials and Instrumentation

Phenanthrene (Aldrich) was used as 1×10^{-2} M solution in ethanol, prepared by weighing the appropriate mass and dissolving the compound in the exact volume.

Sodium nitroprusside (Merck) was used as a 20% solution in ethanol, freshly prepared for each experimental series. The concentration of sodium hydroxide aqueous solution was approximately 7 M.

Dibutyl sulphide (Aldrich, 96%), a warfare agent simulant, was used undiluted and without further purification.

Whatman No. 42 filter paper and Schleicher–Schuell Blue Band filter paper were used as crude carriers for indicator compounds.

The fluorescence measurements were made by means of a Perkin–Elmer spectrofluorometer Model LS 50.

The protective clothing materials tested were intermediate products of Croatian textile and rubber industries.

2.2. Procedures

The contact between dibutyl sulphide, various materials and indicator compounds built into the filter paper as sorbent material was achieved in the same manner [2–4] regardless of the analytical method used for sulphide detection. Rectangular pieces (approx. 2.5×3.5 cm) of the clothing material were placed over the oval-shaped open end of glass vials (open end approximately 1.5×0.7 cm; total volume of a single vial about 2 ml) containing 1 ml of dibutyl sulphide. Filter paper treated with the indicator compound was positioned over the clothing material, and another piece of filter paper was applied to hold the indicator filter paper in contact with the material and to protect it from external contamination. The whole setup was mounted in an especially designed metal clamp [2–4] to provide a seal between the clothing material and the vial. To start permeation the vials were inverted at the same time, so that dibutyl sulphide could come into contact with the outside surface of the clothing material. After a chosen time interval individual vials were returned to the upright position, the indicator and the clothing materials were removed and dibutyl sulphide was detected by fluorescence quenching of phenanthrene or by spot test analysis with sodium nitroprusside.

The procedure for monitoring the permeation of chemical agent simulants through various protective clothing materials by means of the fluorescence quenching technique was described earlier [2–4]. Relative fluorescence intensities were measured at 409 nm, and the degree of quenching was calculated as the ratio of the decrease in relative intensity to the phenanthrene original relative fluorescence intensity.

The spot test analysis for sulphide ions was carried out on the filter paper previously treated with sodium nitroprusside solution (1.6 ml; filter paper $\Phi = 9$ cm), by adding a few drops of sodium hydroxide solution. Spot tests were performed both on the indicator papers and the clothing material on the opposite side of the contact with dibutyl sulphide. The red–violet colour indicated the presence of sulphide ions. It was detected visually by means of a magnifying glass and even with the naked eye.

3. Results and discussion

The fluorescence quenching technique [2–4] was applied for the determination of dibutyl sulphide (DBS) permeation and for measurement of breakthrough times of various clothing materials. The filter paper was the crude carrier for phenanthrene as the indicator compound, having the excitation maximum at 349 nm and the emission maximum at 409 nm. Relative fluorescence intensities were measured at 409 nm, and the degree of quenching was calculated as the ratio of the decrease in relative intensity to the phenanthrene original relative fluorescence intensity. Results obtained for one of the intermediate products in the process of fabrication of protective clothing materials are shown in Fig. 1. Blanks were prepared in the same manner as samples, only dibutyl sulphide was omitted. It is obvious that the mere contact of clothing material with phenanthrene incorporated into crude carriers results in fluorescence quenching of the indicator compound. Therefore, in blank samples various materials (cell tissue, filter paper, cigarette paper, cellophane, plastic sheet, aluminium foil, weft of the investigated clothing material) were placed between the clothing material and the filter paper as the protective layer. Only the aluminium foil did not allow fluorescence quenching of the indicator compound. All the other protective layers induced by themselves a certain degree of fluorescence quenching. However, the aluminium foil prevented quenching by DBS too, probably because of its general impenetrability. This fact led to the conclusion that the materials which contained a chemical component capable of reacting with phenanthrene, causing diminished fluorescence, could not be analysed by means of the described method. Indeed, during the technological process the tested polyester clothing material was treated, among other chemicals which could give rise to fluorescence interferences, with 4,4′-dithiomorpholine, 2-mercaptobenzothiazole disulphide and dipentamethylenethiuram tetrasulphide, the source of sulphide ions which very likely

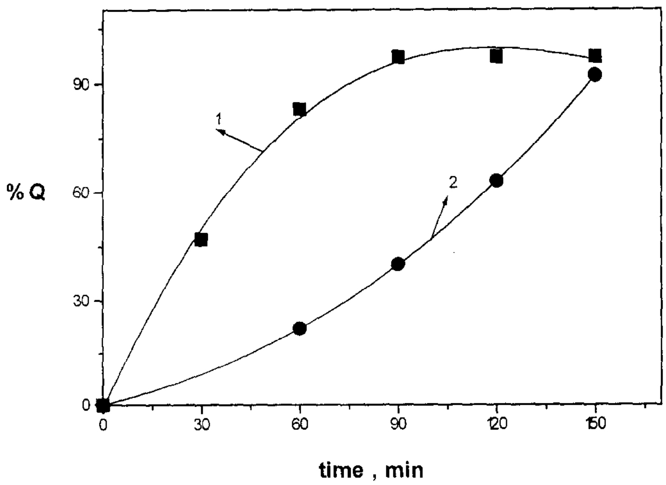

Fig. 1. Fluorescence quenching (% Q) of phenanthrene as a function of contacting time between the protective clothing material and DBS; 1 ⇒ clothing material tested for DBS permeation; 2 ⇒ blanks (DBS omitted).

caused quenching in blank samples. The fluorescence quenching method was therefore considered to be inadequate for determining permeation of DBS through the materials previously treated with sulphur containing chemicals.

Therefore a new method for monitoring DBS permeation through various clothing materials pretreated with sulphur containing chemicals has been developed. The well known spot test for sulphide ion detection with sodium nitroprusside, $Na_2[Fe(CN)_5NO]$, is already described in the literature [7]. In the alkaline solution sodium nitroprusside gives an intense red–violet colour in reaction with soluble sulphide ions. The coloured reaction product has the empirical formula $Na_4[Fe(CN)_5NOS]$, which might be the addition compound formed from the components or the compound having the complex anion $[Fe^{II}(CN)_5N^{III}OS]^{4-}$ as a result of the reduction of iron [7]. The method was modified for monitoring the permeation of sulphide ions from DBS through clothing materials. The experimental technique of preparing samples for measurement was the same as in the spectrofluorometric analysis, with a difference that sodium nitroprusside was used as the indicator compound. Filter papers were previously treated with sodium nitroprusside solution and dried at room temperature. Spot tests were performed on the filter paper by addition of sodium hydroxide. Intense violet coloured points were the indication of sulphide ions passing through the clothing materials. Even better results were achieved by performing the spot test analysis directly on the clothing material on the opposite side of the contact with DBS, at the same time as on the filter papers. The reaction on the clothing material was performed either by addition of only a drop of sodium hydroxide, when it was evident that some sodium nitroprusside was taken up by the material, or a drop of indicator compound was added as well. The spot test results were observed by means of a magnifying glass, but the intense coloured points could be seen even with the naked eye. Blanks did not show any interference, regardless of the technological pretreatment of protective clothing materials. The analysis was carried out for different time intervals of contact between the clothing materials and DBS.

The sensitivity of the method was established as the detection limit for the series of various concentrations of Na_2S and DBS solutions, respectively, on the filter papers treated with sodium nitroprusside and NaOH. Positive reaction, as the red–violet spot indicating detection limits for sulphur, was gained for 1 μg Na_2S (the value is in accordance with the literature data [7]) and for 10 μg DBS. Both values are comparable as the sulphur detection limits. Thus, the sensitivity of the method related to Na_2S is 0,41 μg S, and to DBS is 2,19 μg S.

Table 1 shows the results gained by means of the new spot test method for the intermediate in the fabrication of polyester clothing materials earlier tested by the fluorescence quenching technique (see Fig. 1). The first appearance of the violet colour, clearly indicated the breakthrough time of DBS through the tested material. Different breakthrough times were obtained as a result of the reaction on the filter paper previously treated with sodium nitroprusside, and the reaction on the clothing material. The positive reaction for sulphide detection on the clothing material appeared earlier, compared to the one on the filter paper. Therefore, different technologically treated intermediates in the fabrication of the same polyester clothing material were tested for their breakthrough times (Fig. 2), and the results were compared. Clearly, the breakthrough times measured directly on clothing materials were detected much earlier than

Table 1
Spot test monitoring of DBS permeation through the clothing material using sodium nitroprusside as indicator compound

Time (min)	Spot test reaction	
	Filter paper	Clothing material
30	−	−
45	−	−
60	−	+
75	−	+
90	−	+
120	+	+
150	+	+
180	+	+

on the filter paper containing the indicator compound. Breakthrough times depended on the number of layers of impregnating chemicals and their vulcanization conditions, showing a trend towards a decrease in permeability, as a result of changes in the technological procedure.

The results presented in Fig. 2 were obtained by repeated analysis of the clothing materials yielding the same breakthrough times. The reproducibility of analysis and the acceptable sensitivity make the present modified method recommendable as a simple and sensitive method for permeation monitoring of dibutyl sulphide through various materials which contain a sulphide component as a technological constituent. The main

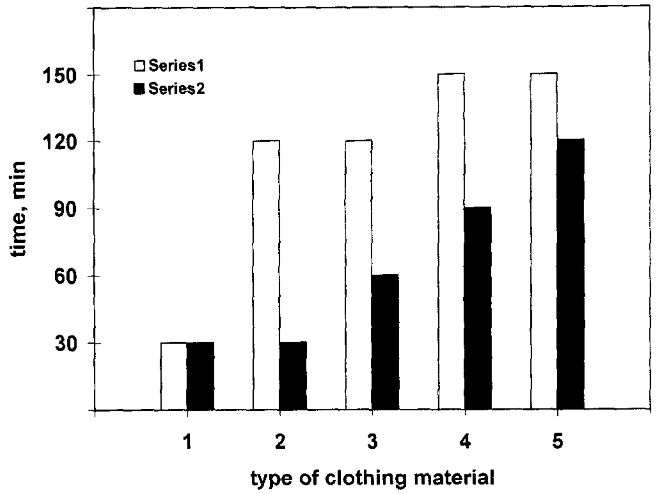

Fig. 2. Determination of DBS breakthrough times for various protective clothing materials by the presently modified spot test method; Series 1 ⇒ spot test on filter paper after DBS permeation; Series 2 ⇒ spot test on clothing materials (opposite side) after DBS permeation; clothing materials 1–5 ⇒ types of clothing materials with increased impregnation and vulcanization.

advantages of the proposed method are low cost, no need of sophisticated instruments, and simplicity of analysis. The required technical equipment (vials, clamps) is simple and transportable, and the reaction is readily detectable even with the naked eye—an ordinary lens can be used for detection. Therefore the method can be proposed as the analytical method of choice for dibutyl sulphide permeation monitoring. Moreover, since DBS is an accepted simulant for the chemical warfare agent sulphur mustard [3], the presented method, with minor adaptations, could be proposed for routine analysis of sulphur mustard permeation through protective clothing materials in field monitoring.

4. Conclusion

The spectrofluorometric detection of permeation of dibutyl sulphide through clothing materials as reported in literature proved to be inadequate for analysis of clothing materials technologically pretreated with chemicals containing sulphur, such as 4,4′-dithiomorpholine, 2-mercaptobenzothiazole disulphide and dipentamethylenethiuram tetrasulphide, because of highly possible interferences. Therefore, it is necessary to test protective clothing materials alone (blanks) for quenching of phenanthrene fluorescence, in order to gain reliable results. The presently modified spot test analysis with sodium nitroprusside in alkaline medium, turned out to be more adequate for monitoring dibutyl sulphide permeation through protective clothing materials. Its sensitivity is satisfactory, detection limit being 10 μg DBS (2.19 μg S), and there are no interferences due to the technological process. It is recommended that the spot test be carried out directly on the clothing material to enhance the sensitivity of the technique. Further advantages with respect to the former method are enhanced speed of performance, lower costs of monitoring and, with minor adaptation, applicability in field work.

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