N-PHENYLBENZYLAMINE AS NOVEL COUPLING REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF NITRITE

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Abstract
This paper introduces a new reagent N-phenylbenzylamine for determination of nitrite in water and aqueous solutions. The reagent in the acidic medium coupled with diazotized dapsone to form the azo dye. The reaction provides a sensitive and reproducible determination of nitrite without special modifications of reaction conditions. The detection limit is 0.07 μg.ml⁻¹, and linear range 0.1-2.0 μg.ml⁻¹ of nitrite. This method significantly enhances application of N-phenylbenzylamine as an important reagent used in the analysis of some chemical warfare agents and industrial pollutants.

Key words
N-phenylbenzylamine, nitrite, dapsone, spectrophotometry.

INTRODUCTION

N-phenylbenzylamine (PBA) belongs among important chemical reagents in the analysis of chemical warfare agents and industrial injurants. It is used especially in the combination with 4-(p-nitrobenzyl)pyridine for colorimetrical detection or spectrophotometric determination of phosgene, diphosgene, triphosgene and similar substances with acylation properties with which it provides colorful König bases [1,2]. In this combination we can find PBA in simple environments such as testing papers, tubes and also as a part of the equipment of mobile and stationary laboratories of the Army of the Czech Republic or sections of the Integrated Rescue System [3].

Regarding the development of new methods and means of the analysis of toxic substances we can see the obvious effort to extend their set at simultaneous lowering of the absolute number of applied chemical reagents. This trend of application „multipurpose“ reagents is justified especially in case of laboratory sets whose capacity is considerably limited due to their construction. The objective of this paper is to highlight the possibility to use PBA as a reagent for spectrophotometric determination of nitrites, as they are a significant indicator of biological and industrial water pollution. It is the modification of a classical method based on diazotization-coupling reaction according to Griess and Saltzman [4]. For these purposes, already earlier, a wide range of diazotizing substances and even higher number of copulation reagents based on aromatic amines, phenols and other compounds have been tested [5-11]. This range of coupling reagents is suitably complemented by newly proposed PBA in combination with dapsone.

EXPERIMENTAL PART

Reagents and Devices

For the experiment we applied, as a standard, sodium nitrite (Sigma-Aldrich). Stock solution (50 mg.ml⁻¹) was prepared by solution of responding amount of dry sodium nitrite in
water and stabilized by a small amount of chloroform. Working solutions were prepared by responding dilution of stock solution. Furthermore we applied 0.2% solution of dapsone (4,4'-diaminodiphenyl sulfone) and 0.5% solution of N-phenylbenzylamine (PBA) in absolute ethanol (all Sigma-Aldrich). To modify the reaction medium we applied from 0.1 to 5.0 mol.l⁻¹ hydrochloric acid (HCl). All chemicals were of analytical grade (Sigma-Aldrich, min. 97%), water was double distilled. For spectrophotometric measurement we used the spectrophotometer Aquamate (Thermo Spectronic, UK) with the cuvette 1.0 cm.

**Basic Working Procedure**

For all spectrophotometric measurements we used a uniform working scheme. Into a volumetric flask 10 ml we pipetted 1 ml solution of nitrite ions of concentration 0.5-50 μg.ml⁻¹, then we added 1 ml of solution of dapsone and 1 ml of hydrochloric acid solution. The solution was diluted by water (about 7 ml) and allowed to diazotization for 2 minutes. Then we added 1 ml of solution PBA and filled with water to the mark. After 10 minutes of standing we measured at room temperature the absorbance of colored solution at wave length 503 nm.

**RESULTS AND DISCUSSION**

The method is based on diazotization-copulation reaction between nitrite, dapsone and PBA to give a rose-colored reaction product with the maximum absorption at 503 nm. The reaction proceeds in two stages. In the first stage the nitrites react with dapsone in acidic environment to give yellow-colored diazonium salt. In the second stage (also in acidic environment) the reactive diazonium salt copulates with PBA to relevant azodye, probably bis(N-phenylbenzylamino)-4,4'-diazodiphenyl sulfone. The reaction is described in the scheme (fig. 1). The course of the absorbance curve of a reaction product is given in fig. 2.

![Scheme of the reaction of nitrites with dapsone and PBA](image-url)
Indispensable condition of the analytical course of the reaction was the optimal pH environment. The test results were achieved with the addition of 0.5 mol.l⁻¹ of hydrochloric acid. As it is obvious from fig. 3, the decrease in concentration of acid was manifested by rapid decolorization of samples due to the decomposition of azodye, higher concentration, on the contrary, considerably extended the time to achieve the reaction balance and maximal level of absorbance. In paralell, with the addition of hydrochloric acid, also the effect of concentration of chemical reagents was studied. We discovered that the optimal concentration of dapsone was 0.02% and PBA 0.05% in a measured sample. Higher concentration of reagents did not affect the value of absorbance at all, on the contrary, lower concentrations manifested the decrease of the coloring intensity.
The validity of Lambert-Beer law was discovered for the extent 0.1-2.0 μg.ml\(^{-1}\) of nitrites, molar absorption coefficient of a color system was 6.0.10\(^4\) l.mol\(^{-1}\).cm\(^{-1}\) and Sandell sensitivity (A=0.001) 0.007 μg.ml\(^{-1}\). The values of central absorbance, standard deviations and relative standard deviations (n=10) for the concentration of nitrites 0.5 μg.ml\(^{-1}\) were 0.357, ±0.016 a 4.48 %. The detection limit and correlation coefficient (r) had the value 0.07 μg.ml\(^{-1}\), or 0.9963.

During the course of the development of the method for the determination of nitrites in water with the application PBA we studied also the effect of various substances (ions) usually present in water. We found out that for example the nitrates, cyanides, thiocyanates, perchlorates, phosphates, sulfates or mercuric salt do not disturb the determination of nitrites (0,5 μg.ml\(^{-1}\)) even in the thousandfold excess. On the contrary, the presence of aliphatic and aromatic amines or strong oxidants (chlorine, hydrogen peroxide) is undesirable. We also verified the effect of some chemical warfare agents and their hydrolytic products (table 1).

**Table 1**

The effect of some chemical warfare agents (CWAs) and their hydrolytic products for the determination of nitrites (0.5 μg.ml\(^{-1}\)). The tolerance share is the share of the concentration of CWAs and nitrites

<table>
<thead>
<tr>
<th>CWAs</th>
<th>Tolerance share</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur mustard</td>
<td>&gt;2400</td>
</tr>
<tr>
<td>Thiodiglycol</td>
<td>&gt;2800</td>
</tr>
<tr>
<td>2-(diisopropylamino)ethanethiol</td>
<td>10</td>
</tr>
<tr>
<td>Agent CS</td>
<td>&gt;100</td>
</tr>
</tbody>
</table>

The proposed method was applied for the determination of nitrites in water and in the soil samples (brown earth, Prague – Smichov). The water samples were taken from various sources and before the analysis they were filtrated. As long as they did not contain the nitrites, the samples were prepared by adding the known amount of nitrites and analyzed as during the basic analytical procedure (with double distilled water). The same procedure was followed with the analysis of soil samples. The results achieved during the determination of nitrites in water and soil samples were linear an identical to the calibration graphs constructed for distilled water. The results were compared to the known dapsone/diphenylamine method [5]. Statistic analysis of results proved the equivalence of both methods, detected differences in the content of found nitrites in the sample did not exceed ± 5 %.

**Table 2**

Comparison of the proposed method with other spectrophotometric methods based on diazotation-copulation reactions with dapsone

<table>
<thead>
<tr>
<th>Reagent</th>
<th>(\lambda_{\text{max}}, \text{nm})</th>
<th>Extent (Lambert-Beer), μg.ml(^{-1})</th>
<th>Molar absorption coefficient, l.mol(^{-1}).cm(^{-1})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dapsone, diphenylamine</td>
<td>450</td>
<td>0,1-2.5</td>
<td>1,5.10(^4)</td>
<td>5</td>
</tr>
<tr>
<td>Dapsone, iminodibenzyl</td>
<td>570</td>
<td>0,02-0,5</td>
<td>7,5.10(^4)</td>
<td>6</td>
</tr>
<tr>
<td>Dapsone, NEDD</td>
<td>540</td>
<td>0,002-0,6</td>
<td>7,2.10(^4)</td>
<td>7</td>
</tr>
<tr>
<td>Dapsone, phloroglucinol</td>
<td>425</td>
<td>0,008-1,0</td>
<td>4,2.10(^4)</td>
<td>8</td>
</tr>
<tr>
<td>Proposed</td>
<td>503</td>
<td>0,1-2,0</td>
<td>6,0.10(^4)</td>
<td></td>
</tr>
</tbody>
</table>
CONCLUSION

PBA as a novel copulation reagent for the determination of nitrites in the combination with dapsone is fully comparable to known and structurally close to diphenylamine (table 2). The method is suitable for simple and reliable determination of nitrites in water and soil samples as well. The simplicity, good reproducibility and resistance to interference mean that the method is versatile and convenient. The reagent is relatively non-toxic, cheap and easily available. The detection limit of nitrite ions is 0.07 μg.ml⁻¹, the calibration graph is linear within the range 0.1-2.0 μg.ml⁻¹. The authors of this essay believe that by a suitable adjustment of the methodic, the reagent can be used also for the determination of dangerous nitrogen dioxide in the air [4] or in cases where the determination of toxic substances presupposes their conversion to nitrites /chloropicrin) or reactive substances such as diazonium salts (substance CR).

Résumé

Nitrites are important indicators of biological and industrial pollution. This paper describes a spectrophotometric method for the determination of nitrite, which is based on a modified diazotization coupling reaction. N-phenylbenzylamine in combination with dapsone is introduced as a new coupling agent. The method was applied for the determination of natural waters and soil samples. The results achieved were compared with other spectrophotometric methods. The method can also be used in the field of population protection.

References


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