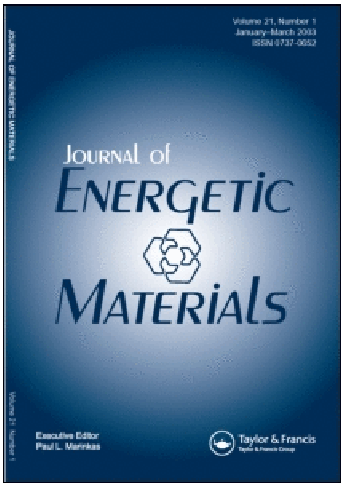

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Improved reagents for firing distance determination

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IMPROVED REAGENTS FOR FIRING DISTANCE DETERMINATION

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ABSTRACT

Modification of reagents used in the Walker test for firing distance determination are described.These modifications increase the color intensity and sharpness of the reacted gunpowder residues,thus improving the sensitivity of the test. In this new method, the diazotization and color coupling reaction is performed by sulfanilamide and N-(1-naphthyl)ethelenediamine in a dilute phosphoric acid solution.It is thus possible to avoid a quite concentrated acetic acid solution used in the traditional method,which is unpleasent to work with.

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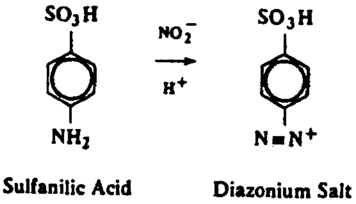
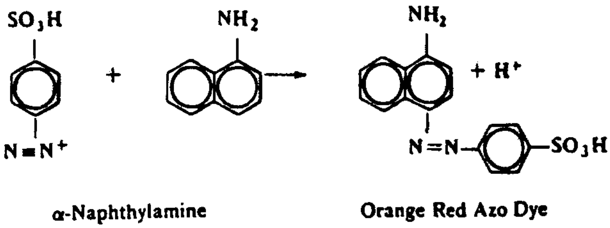
INTRODUCTION

Differentiating among accident, self defense, suicide and criminal homicide in a shooting case may hinge on an expert determination of the distance between the gun muzzle and the first surface of the victim: clothing or skin. At the time of firing, besides the projectile, flame, primer residues, metal particles, lubricants and partially burned and unburned gunpowder are also propelled out for a distance varying with each component's physical properties. The pattern that may be observed on the target may represent the composite of some or all of these components.

One of the most common methods for determining firing distance is the Walker test[1], which uses the Griess reaction to detect inorganic nitrite ion, which is derived from the ester nitrate group rich molecules in gunpowder residues. In this test, Griess reagent consisting of sulfanilic acid and α-naphthylamine in acetic acid solution is used. The detection of nitrites is based on the formation of a diazonium ion which couples with α-naphthylamine, in an acidic media to form an azo dye as follows:



(1)



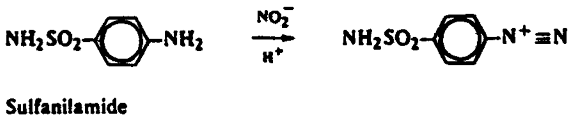
(2)

In this test only inorganic nitrite reacts and all organic residues such as nitocellulose and /or nitroglycerine cannot be detected.

It is well known that nitrate esters, on hydrolysis, partly disproportionate to carbonyl compounds and nitrous acid[2]. Lloyd described the use of alkaline hydrolysis prior to the Griess reaction to characterize small samples of explosive components[3]. Ravreby applied a similar procedure for a firing distance determination reaction[4]. As a result the total nitrite is detected, namely inorganic plus hydrolyzable nitrite ion, thus improving the sensitivity of the method. He also modified the original Walker's physical arrangement for carrying out the diazotization and color coupling reactions, making it simpler and more efficient.

The present study deals with further improvement of the above method using modified reagents for diazotization and coupling. Numerous pairs of reagents were suggested for these reactions[5].

One of the pairs namely : sulfanilamide and N-(1-naphthyl)ethylenediamine dissolved in dilute phosphoric acid whose reaction scheme is as follows:



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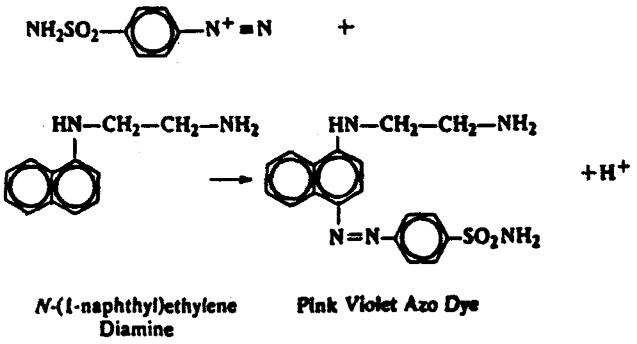

(4)

was used by Twibell for the identification of nitroglycerine from hand swabs[6]. This pair was also used successfully in the development of the Explosive Test Kit (E.T.K) by Almog, Kraus and Glattstein[7]. These same reagents were adopted by us for firing distance determination.

EXPERIMENTAL

Test shots were fired on white cotton cloth using a Beretta semiautomatic pistol with 7.65 mm Israel Military Industries ammunition at a range of 25 cm.

The modified reagent solution consists of 0.5% N-(1-naphthyl)ethylenediamine and 1% sulfanilamide dissolved in 3% phosphoric acid. It is thus possible to avoid the concentrated acetic acid solution, used in the traditional method, which is unpleasent to work with, especially while applying heat.

The procedure which is similar to that used by Ravreby[4] is as follows: The exhibit, containing a bullet entrance hole, is sprayed with 8% alcoholic KOH and placed in a drying oven at 110-120°C for fifteen minutes. Photographic paper which has been stripped of its silver salts using fixer is sensitized with the modified reagent for about one minute. The exhibit is placed on a clean white cloth with the bullet entrance hole facing up. The moist sensitized photographic paper is placed with the emulsion side down onto the exhibit. A clean white cloth is placed above the photographic paper and this "sandwich" arrangement is ironed at moderate heat for about one minute. The photographic paper is then removed and pink-violet color spots develop where nitrite ions were present.

For comparison the diazotization and coupling reactions were carried out using the original Griess reagent and also the reagent pair :0.25% p-aminoacetophenone and 0.25% N-phenyl 1-naphthylamine in 50% acetic acid reagent.

The latter pair was used for some time in our laboratory to replace the original Griess reagent, because it was reported that α-naphthylamine is a carcinogenic reagent[8] .

The reflectance spectra of the developed color spots were recorded using the Docuspec TM/I microspectrophotometer, (Nanometrics, Inc.).

RESULTS AND DISCUSSION

It was found that sufficient sensitization of the fixed photographic paper, needed to obtain intense color development, with the modified reagent, occurs after about one minute. This time is not enough to obtain any color development with the traditional Griess reagent, while very faint color develops with the reagent pair : p-aminoacetophenone and N-phenyl 1-naphthylamine. Comparison of the results of the latter reagent with the modified one is shown in Figure 1.

Even after fifteen minutes sensitization using the original Griess reagent or using the reagent pair : p-aminoacetophenone and N-phenyl 1-naphthylamine, the maximum optical density obtained is less than one third of the maximum optical density obtained after one minute sensitization using the modified reagent (Figure 2). It should be noted that there was not a considerable difference in color intensity developed, between a one minute sensitization and fifteen minute sensitization when using the modified reagent.

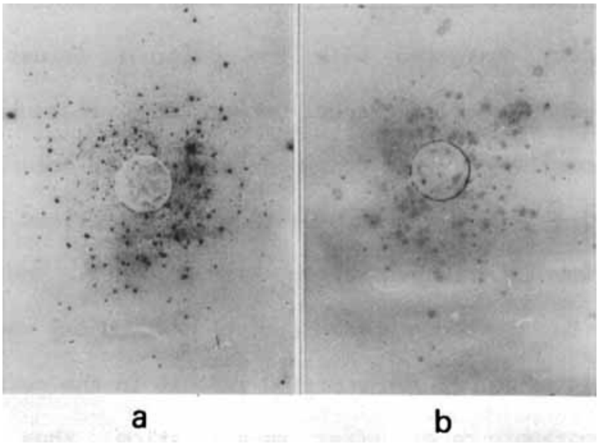

FIGURE 1

Nitrite determination in test shots: (a) One minute sensitization using the modified Griess reagent. (b) One minute sensitization using the reagent pair: p-amino acetophenone and N-phenyl 1-naphtylamine.

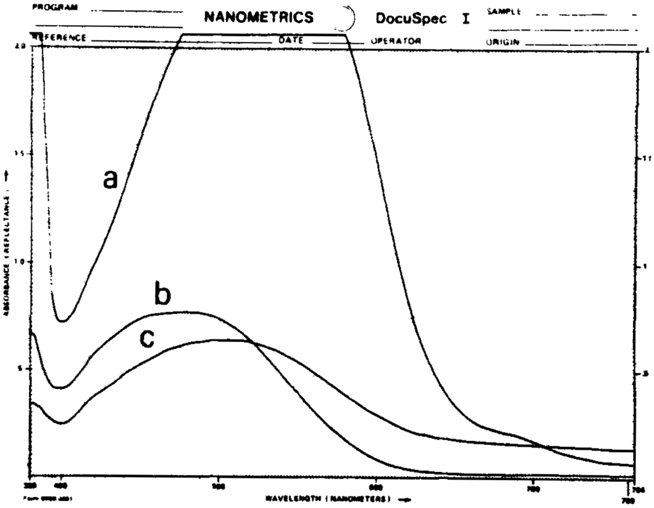

FIGURE 2

Maximum optical density obtained in nitrite determination: (a) One minute sensitization using the modified Griess reagent. (b) Fifteen minute sensitization using the original Griess regent. (c) Fifteen minute sensitization using the reagent pair: p-amino acetophenone and N-phenyl 1-naphtylamine.

It is difficult to reconcile the large difference between the color intensity developed with the modified reagent and the color intensity developed with the original Griess reagent, considering the small difference between the respective molar extinction coefficient (ε) at λ max measured in solution.

The reported ε value at λ max for the original Griess reagent is 33000, and for the modified reagent is 40000[5] . The possible explanation for the above apparent contradiction may be a much higher concentration of the modified reagent in the gelatin layer of the photographic paper after sensitization, thus providing more reagent for reaction with nitrite ions.The latter is probably in a local excess to diazotization and coupling reagents. Therefore the amount of produced azo dye will depend on the concentration of the diazotization and coupling reagents. Confirmation of this assumption is shown in Figure 3 . Spectrum (a) represents the maximum color intensity developed in one of the nitrite spots, using fifteen minute sensitization with the original Griess reagent. Following that the same spot was developed using only one minute sensitization with the modified reagent. The maximum color intensity obtained is represented by the spectrum (b).

It was found that the color spots that were developed from the nitrites with the modified reagent have no single spectral characteristics. The color obtained may vary between pink-violet to orange.

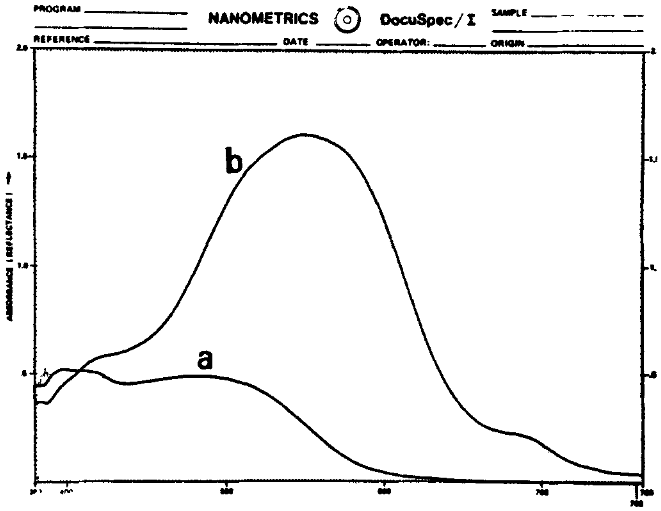

FIGURE 3
Detection of the same nitrite spot using two reagent pairs: (a) Fifteen minute sensitization using the original Griess reagent followed by: (b) One minute sensitization using the modified Griess reagent.

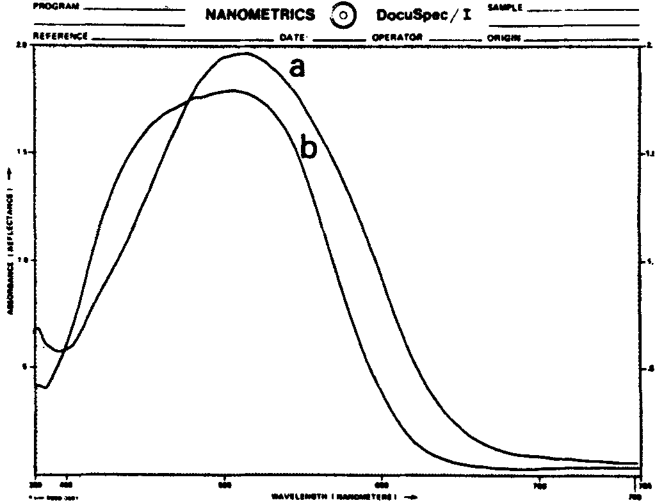

FIGURE 4
Reflectance spectra of two different colors that may be obtained using modified Griess reagent: (a) Pink violet (b) Orange.

Figure 4 shows an example of the spectra of two different colors that may be obtained. At this phase of the study we do not have a plausible explanation for this variability in color.

CONCLUSION

It was shown that using a modified Griess reagent it is possible to obtain high intensity color development of nitrites while using a short time for sensitization. Also using this modified reagent makes it possible to avoid the use of quite concentrated acetic acid solution, which is unpleasant to work with.

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