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A New Trace Ferrous Metal Detection Reagent

Since the early 1970s there has been substantial use of the 8-hydroxyquinoline test for determining whether a person has handled a weapon [1]. This test, now generally referred to as the TMDT test [2], involves spraying the hands of a person suspected of handling a weapon with a 0.2% solution of 8-hydroxyquinoline in isopropanol and observing the sprayed area with ultraviolet light. If a person has handled a weapon to the extent that oxidized ferrous ion is transferred to the hands, a dark area is noted in those areas of contact. Often a pattern of the object handled will be apparent. A positive reaction must be recorded by photography, however, and attendant complications exist in the ultraviolet fluorescent photography which must be employed [3].

We wish to report the use of a newly developed iron reagent which serves the same purpose as 8-hydroxyquinoline in the TMDT test. The reagent is 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-*p,p'*-disulfonic acid, disodium salt trihydrate, also known as PDT or ferrozine. The reagent results in a magenta complex with submicrogram levels of iron. The sensitivity of the test is comparable to that of 8-hydroxyquinoline and the results may be recorded by visible light photography with comparative ease.

PDT

The reagent PDT is the newest in a rather extensive series of compounds known as the ferroin type. Blau [4], in the latter part of the 19th century, observed that molecules containing the atomic configuration $\text{-N}=\overset{\text{C}}{\underset{\text{C}}{\text{=}}}\text{N-}$ gave intensely colored complexes with ferrous ion. Such compounds also react with cuprous ion and cobaltous ion, but since the reactivity is much greater with ferrous ion the group of compounds with this structural configuration was given the trivial name of ferroin.

Dozens of the compounds have been synthesized [5] and evaluated for their ability to react with iron and other metals. Although all ferroins react as bidentate ligands, most of the complexes formed with metallic ions are weakly colored, are unstable, or react only over a very narrow pH range. A few of the ferroins, however, form stable, intensely colored complexes with the ferrous ion and have been employed for the colorimetric determination of iron. Among these are 1,10-phenanthroline [6], 2,4,6-tris(2-pyridyl)-1,3,5-triazine [7], 2,6-bis(2-pyridyl)-pyridine [8], 4,7-diphenyl-1,10-phenanthroline [9], 2,2-bipyridine [8], and phenyl 2-pyridyl ketoxime [10].

Many of these reagents are the product of tedious and difficult syntheses, and the resultant high cost of these compounds has prevented their widespread use as iron

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reagents; but PDT is substantially cheaper to produce than other members of the ferroin family. The compound was first synthesized by Case [11] and its use as an iron reagent was described by Stookey [12].

In the presence of divalent iron, PDT reacts to give an intensely colored, water-soluble magenta complex. The reaction is quite rapid and takes place over a wide range of pH values (pH 4 to pH 10). The molar absorptivity of PDT with ferrous iron is 27 900 at 562 nm, making it the second strongest chromogen for iron (II)² presently known. Terrosite, or 2, 6-bis(4-phenyl-2-pyridyl)-4-phenylpyridine, is more reactive, with a molar absorptivity of 30 200 at 583 nm, but it is much more expensive and much less stable than PDT [13].

On the basis of its structure and spectral characteristics, the $\text{Fe}(\text{PDT})_3^{++}$ complex probably reacts in the same manner as other ferroin compounds, that is, with three planar bidentate ligands coordinated to the ferrous ion, each of the ligands having two nitrogen atoms bound to iron to form a five-membered ring, with all six nitrogen atoms in an octahedral arrangement around the central ferrous ion. The intense absorptivity of the $\text{Fe}(\text{PDT})_3^{++}$ suggests that electron delocalization in the chelate is pronounced. In other words, there is a high degree of conjugation, indicative of a planar conformation. The configuration of the complex is depicted in Fig. 1.

Experimental

Reagent

The PDT reagent is made up as a solution of 10 mg of the salt (Aldrich Chemical Co.) in 10 ml of methanol. The reagent may be stored for extended periods in the refrigerator although its reactivity should be tested periodically with ferrous ion at the lower limits of sensitivity.

Procedure

The methanolic solution of PDT is sprayed over the hands of the test subject. If

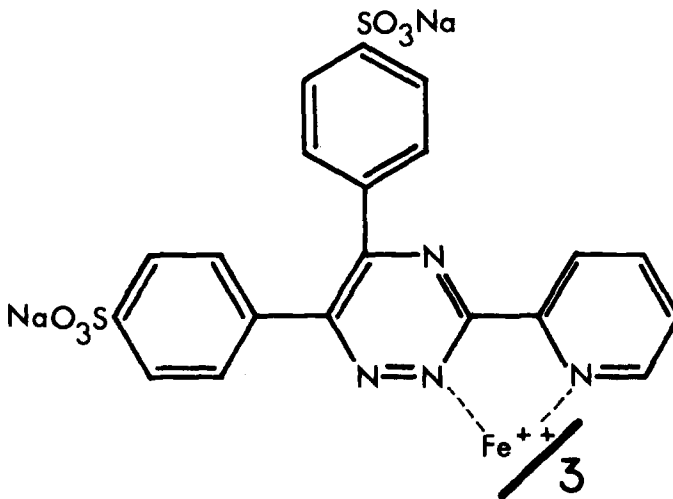


FIG. 1—Structural conformation of the planar $\text{Fe}(\text{PDT})_3^{++}$ complex.

² Iron (II) indicates the iron to be in the +2 oxidation state, distinguishing it from iron (III).

iron (II) is present, a magenta stain will appear within a minute. The color will slowly intensify over a period of 1 to 2 h. Exposure for a brief period to long wavelength ultraviolet light will accelerate the reaction. Once formed, the magenta complex may be removed from the skin by washing. Complete spraying is necessary to completely develop all the iron present. Very weak reactions may not be visible immediately but will develop after a longer time.

Figure 2 illustrates the resultant stain on the hand of a person who held a handgun for a short period of time.

Discussion

The reactivity of PDT with residual ferrous ion on the hands of a person who handled metal of this type is comparable in sensitivity with the TMDT technique. When used as a spectrophotometric test for iron (II), PDT can demonstrate as little as $0.090 \mu\text{g}$ of iron [14]. When PDT is used as a stain, sensitivity data are not particularly meaningful, since the sensitivity is dependent on the surface area involved. When PDT tests were conducted in solution, we observed the visible threshold of detectability to be on the order of 4 to $8 \mu\text{g}$; detectability is substantially more if the solution is exposed to ultraviolet light.

The PDT test has one striking advantage over the TMDT test; the color developed is readily visible and may be easily photographed. As the complex is a deep magenta, orthochromatic film would be well suited for the photography. As with the TMDT test, a positive reaction is dependent to a considerable extent on the amount of perspiration on the hands of the subject.



FIG. 2—Pattern developed on the hand of a person holding an Astra Model 600/43 9-mm automatic pistol for 1 min. The development of the visible stain was according to the procedure outlined in the text.

Most heavy metal ions may compete to some extent to complex with PDT, but the reactivity is so slight that both a lengthy contact period and a lengthy development period would be required for the production of a visible stain. Certain anions may compete effectively with PDT for the iron and may tend to give false negative reactions when low concentrations of iron are involved [13]. The strongest competitor of this type is the cyanide ion CN^- . Oxalate ion C_2O_4^- and nitrite ion NO_2^- are also moderately strong competitors. Fluoride ion F^- and molybdate ion MoO_4^- are relatively weak competitors and should not present a credible source of interference.

Certain considerations apply to any test for the handling of weapons. Complexes, whether of a fluorescent or a visible nature, are formed with ions, not the nascent metal. For any test of this type, the metal must be sufficiently oxidized to provide the ionic species. Certain metals, which may be encountered in the surface finish of some weapons, occupy relatively lower positions in the electromotive series and are relatively less susceptible to oxidation. Consequently, since the ions of these metals are not available, there is a diminished probability of a successful demonstration of the ions by PDT or any other reagent.

Other considerations are essentially common sense. The oxidation of iron in the atmosphere is diminished by a film of oil over the surface, the precise situation often encountered with handguns. It would also be reasonable to expect that a new weapon, with relatively little opportunity to undergo extensive oxidation, would react poorly with iron reagents relative to an older, poorly cared for weapon.

Information available at the present time does not indicate PDT to have a carcinogenic effect. The long-term effects of this chemical have not been fully explored, however, and caution should be taken to avoid prolonged contact or repeated exposure without adequate protection.

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