SPECTROPHOTOMETRIC DETERMINATION OF HEXAMETHYLENETRIPEROXIDEDIAMINE (HMTD) WITH A POLYMERIC SENSOR

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Hexamethylenetriperoxidediamine (HMTD) is a cyclic peroxide-type primary explosive that has been partially characterised in recent years. It is a white solid that is exceptionally sensitive to initiation by impact, friction and electrical discharge [1]. In the years to come, special emphasis must be directed towards the development of online methods for HMTD determination. Although it is almost as dangerous as triacetoneperoxideoxide (TATP), no such analytical method has been reported for HMTD as yet, due to its low vapour pressure. Because of their lack of characteristic absorption bands in the UV/Vis range of the electromagnetic spectrum, TATP and HMTD can rarely be detected using classical optical spectroscopy. Therefore, only few direct spectroscopic methods have been described so far [2]. HMTD was secured synthesized in our laboratories (in amounts not exceeding 100 mg). HMTD was taken up with acetone, hydrolyzed with 4 M HCl to hydrogen peroxide, the acidic solution containing the liberated H_2O_2 was neutralized, and determined by the copper(II)neocuproine spectrophotometric method [3]. In this reaction, Cu(II)-neocuproine oxidized H_2O_2 to O_2, and was itself reduced to the Cu(I)-neocuproine chromophore showing maximum absorption at 454 nm. The linear calibration equation and molar absorptivity (ε) of the developed method for HMTD were: A_454 = 2.1 x 10^4 c_{ppm} - 2.42 x 10^{-2} and ε = 4.18 x 10^4 L mol^{-1}cm^{-1}, respectively, with a correlation coefficient of r=0.9998. The common soil ions of Ca^{2+}, K^+, Cl^{-}, SO_4^{2-} ve NO_3^{-}, NH_4^+ were found not to interfere with the determination of HMTD at 100-fold amounts. The widely used military-purpose explosives of TNT, RDX, and PETN, either individually or in admixtures with HMTD, were also found not to interfere with the proposed assay, which constitutes a distinct advantage in criminologic applications. Current studies are directed to the development of a polymeric membrane sensor for HMTD assay. The linear calibration equation and molar absorptivity (ε) of the developed method for HMTD sensor were: A_454 = 1.39 x 10^4 c_{ppm} - 4.84 x 10^{-2}, ε = 2.39 x 10^4 L mol^{-1}cm^{-1}, with a correlation coefficient of r=0.9998. The selectivity of the proposed method was tested by investigating the sensor response to similar nitro-explosives such as TNT, RDX, and PETN in multi-explosive synthetic mixtures. The possible interferences of common cations and anions (Ca^{2+}, K^+, Cl^{-}, SO_4^{2-} and NO_3^{-}, NH_4^+) found in soil and water to the proposed sensing method was explored.

References