SPECTROSCOPIC AND ELECTROCHEMICAL TECHNIQUES FOR THE SENSING/QUANTIFICATION OF EXPLOSIVE RESIDUES

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Most explosive residues have extremely low vapour pressures, and are therefore detected from the liquid (rather than vapour) phase on solid substrate sensors (paper, resin, polymer membrane, nanoparticles, etc.). Such rapid colorimetric sensing applications have effectively replaced the more sophisticated, but high-cost and high-expertise LC/GC-MS/MS techniques in the field (especially in screening analysis of post-blast debris), and can be used for both qualitative and quantitative purposes. This presentation is aimed to summarize (with examples) the development of the colorimetric and electrochemical methods for explosive residue detection in the analytical chemistry laboratories of Istanbul University. One of the developed methods is based on organic solvent extraction of the Meisenheimer anion of TNT in the presence of a cationic surfactant. Solid phase extraction (SPE) of the Meisenheimer anion of TNT formed in alkaline solution onto a strongly basic anion exchange resin Dowex 1X8 (OH-form) enabled the stabilization of the orange-red colour formed both in the solid resin and aqueous solution phases, suitable for colorimetric measurement. The charge-transfer reagent, dicyclohexylamine, was entrapped in a polyvinylchloride polymer matrix plasticised with dioctylphthalate, and moulded into a transparent sensor membrane sliced into test strips capable of specifically sensing TNT, showing an absorption maximum at 530 nm. The sensor, giving perfectly linear response over a wide concentration range and having a limit of detection 3 mg L\(^{-1}\) for TNT, was only affected by tetryl, but not by RDX, PETN, DNT, and picric acid; sensing was also not interfered by water, pH changes, common soil ions and humates. Hydrolyzed peroxide explosives (TATP and HMTD) were acid-hydrolyzed into H\(_2\)O\(_2\), which then reduced the cupric-neocuproine reagent electrostatically attached onto a Nafion cation-exchange membrane, producing a cuprous-neocuproine chelate on the membrane surface suitable for colorimetric measurement at 450 nm. Identities of unknown explosives found in the field could be determined with specially designed colorimetric kits by observing their colour change after spraying appropriate reagents onto a chromatographic paper containing explosive residues following vaporization of acetone used as solvent for SPE. Different spray reagents were used for detecting explosive traces of nitro-aromatics, nitramines/nitrate esters, and inorganic nitrates, and the proposed qualitative analysis could also be made quantitative by replacing substrate paper with PVC tablets. One of our recent studies includes the analysis of real or synthetic samples of energetic materials individually or in admixtures with voltammetric methods. Also recently, a sensitive colorimetric method for the determination of RDX and HMX individually and in admixtures was proposed based on differential kinetics in the hydrolysis of the two compounds followed by their colorimetric determination using thiol-modified gold nanoparticles and a coupling agent for diazo-dye formation.

REFERENCES: