Spectrophotometric Determination of Cyclotrimethylenetritramine (RDX) in Explosive Mixtures

A. Üzer Arda, E. Erçag, G. Saroğlu, Ş. Eren and R. Apak
Istanbul University, Faculty of Engineering, Department of Chemistry, Avcilar 34320
Istanbul, Turkey, auzer@istanbul.edu.tr

Cyclotrimethylenetritramine is a heterocyclic nitramine compound commonly referred to as RDX. It is also known as cyclonite or hexogen. RDX is a nitrate compound that has been widely used as a plastic explosive. As RDX and its degradation products can be found in the environment, most of the methods developed are for its detection and determination in water, soil, forensic specimens, and human plasma. The analytical methods used are high performance liquid chromatography combined with UV detection (HPLC-UV), thermal energy analyzer (HPLC-TEA), and mass spectrometry (HPLC-MS). However, the requirements for quick decision making in criminology laboratories or reclaimed military sites (e.g., the area surrounding former ammunition plants or post-blast debris of military land forces firing sites contaminated with RDX residues or its degradation products) often impose the use of rapid, simple, cheap, and selective field techniques such as colorimetry and spectrophotometry.

The existing colorimetric method for cyclotrimethylenetritramine (RDX) based on a Griess reaction suffers from the non-quantitative reduction to nitrite and from the unstable character of HNO₂ in acidic medium. Thus we propose a novel spectrophotometric RDX assay in explosive mixtures and residues, based on (Zn + HCl) reduction of RDX in a microwave oven, followed by neutralization of the reduction products to ammonia and low molecular-weight amines, and Berthelot reaction of these amine-compounds with phenol and hypochlorite in alkaline medium to give an intensely blue indophenol dye absorbing at 631 nm. The linear calibration equation, molar absorptivity and limit of detection (LOD) for RDX were: \( A_{631} = 4.85 \times 10^{-2} C_{ppm} + 1.17 \times 10^{-2} \) (correlation coefficient: \( r=0.9995 \)), \( \varepsilon = (1.08 \pm 0.04) \times 10^6 \) L mol\(^{-1}\) cm\(^{-1}\) and 0.18 mg L\(^{-1}\), respectively. Application of the method to synthetic mixture solutions of RDX and trinitrotoluene (TNT) at varying proportions showed that there was minimal interference from TNT (which could be compensated for by dicyclohexylamine colorimetry), since the Berthelot reaction was essentially non-responsive to \( m \)-substituted anilines derived from TNT upon (Zn + HCl) reduction. The proposed method was successfully applied to military-purpose explosive mixtures of (RDX + inert matter) such as Comp A5, Comp C4, and Hexal P30, and to (RDX + TNT) mixtures such as Comp B. The molar absorptivity of RDX was much higher than that of either ammonium or nitrate; RDX could be effectively separated from ammonium and nitrate in soil mixtures, based on solubility differences. The Berthelot method for RDX was statistically validated using Comp B mixtures against standard HPLC equipped with a Hypersil C-18 column with (40% MeOH–60% H₂O) mobile phase, and against gas chromatography–thermal energy analysis (GC–TEA) system.