SUPPORTING INFORMATION

4-Aminothiophenol Functionalized Gold Nanoparticles−Based Colorimetric Sensor for the Determination of Nitramine Energetic Materials

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Optimization of Hydrolysis Conditions for Nitramine Detection

The representative nitramine compounds, RDX and HMX, could be both individually and simultaneously detected/quantified using differential hydrolysis, because Heilmann and coworkers reported that alkaline hydrolysis of RDX proceeded 10 times faster than HMX, and possible reaction products included NO_2^- (which may be suitable for indirect nitramine detection) as well as N_2O, NH_3, N_2, and HCOOH.[1-3] Hydrolysis was optimized by varying the base composition/concentration (*i.e.*, NaOH and Na_2CO_3, or their mixtures), temperature (*i.e.*, 25, 50, 60 and 70^oC on a water bath) and time (*i.e.*, ½, 1, 2, 3 h). The possible catalytic effect of activated carbon on hydrolysis was also investigated,[1] but use of C was later abandoned due to the decrease of absorbance of hydrolysis products using the proposed method. Colorimetric analyses were applied without delay to hydrolyzed samples using the Griess method,[4] which basically responded to nitrite among the hydrolysis products. Hydrolyzed samples for a short time of standing gave very low absorbances, whereas hydrolysis products after ½ h standing gave very close absorbances, causing the selection of 30 min as optimal time. Appreciable concentrations of NaOH in the alkaline medium of hydrolysis could not differentiate between RDX and HMX, while Na_2CO_3 alone could not produce enough nitrite

for colorimetric detection, necessitating the use of a mixture of these two bases for hydrolytic efficiency. Along with a constant concentration of 1 M Na_2CO_3, variable NaOH concentrations in the range of 0.01 M-5% (w/v) were tested to yield an optimal combination of (1 M Na_2CO_3 + 0.04 M NaOH). Room temperature (24±1^oC) hydrolysis gave rise to the detection of RDX only, whereas HMX was not hydrolyzed. On the other hand, hydrolysis at 60^oC on a water bath produced sufficient response from both nitramine compounds at environmentally relevant concentrations, enabling usage of the principle of additivity of absorbances for mixture analysis. Therefore, hydrolysis was only performed at room temperature and at 60^oC for 30 min to differentially analyze the two nitramines in synthetic and real mixtures.

Griess colorimetric reaction[4] can be used for the selective spectrophotometric determination of nitramines in nitro explosives−contaminated soil because TNT did not interfere.[5] It was further investigated whether TNT would interfere with the optimized hydrolysis procedure by itself yielding nitrite, and the individual constituents corresponding to the composition of a Comp B sample (*i.e.*, a composite explosive containing 60% RDX, 39% TNT, and 1% wax) upon dilution with 1:1 acetone-water to final concentrations of 120 ppm RDX and 80 ppm TNT gave Griess absorbances of 0.72 and 0.11, respectively. This result indicates that the minor absorbance due to nitrite derived from the more stable TNT could be completely quenched by proper dilution of a Comp B sample, and RDX constituent alone could be determined after applying the recommended hydrolysis. On the other hand, reductive hydrolysis with Zn dust + acetic acid would produce substantial nitrous acid (which may be easily degraded in acidic medium) from both TNT and RDX, making the subsequent colorimetric analysis less selective for nitramines. Pink-coloured azo-dye formation from nitrite in the Griess reaction can be represented by the following scheme:

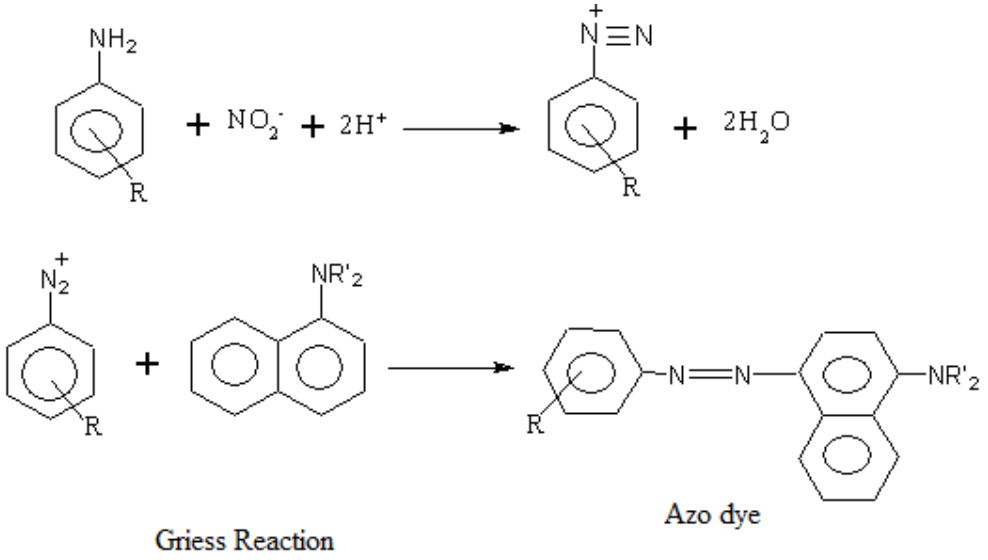

Figure S-1. Schematic diagram of Griess reaction.

Working curve for RDX with the use of (4-ATP+NED) without AuNPs

Room temperature hydrolysis products of RDX were reacted with 4-aminothiophenol (4-ATP) and N-(1-naphthyl)-ethylenediamine dichloride (NED) to see the extent of the involvement of gold nanoparticles (AuNPs) in the recommended procedure of nitramines determination. For this purpose, 10 mM 4-ATP solution was mixed with distilled water (as a substitute, instead of the AuNPs in the recommended procedure) at 1:8 ratio at pH=3, summarized as follows:

Take 2 mL RDX (of variable concentration) + 2 mL alkaline hydrolysis solution (containing 1.0 M Na_2CO_3 and 0.04 M NaOH in final mixture) → (let stand for 30 min at room temperature) → + 0.5 mL 1 M HCl + 0.6 mL (in 0.1-mL portions) 5 M HCl + 1 mL 4-ATP + 1 mL H_3PO_4 + 0.5 mL NED.

By applying the above procedure, Figure S-2 was obtained as the working curve of A_{565} versus RDX concentration.

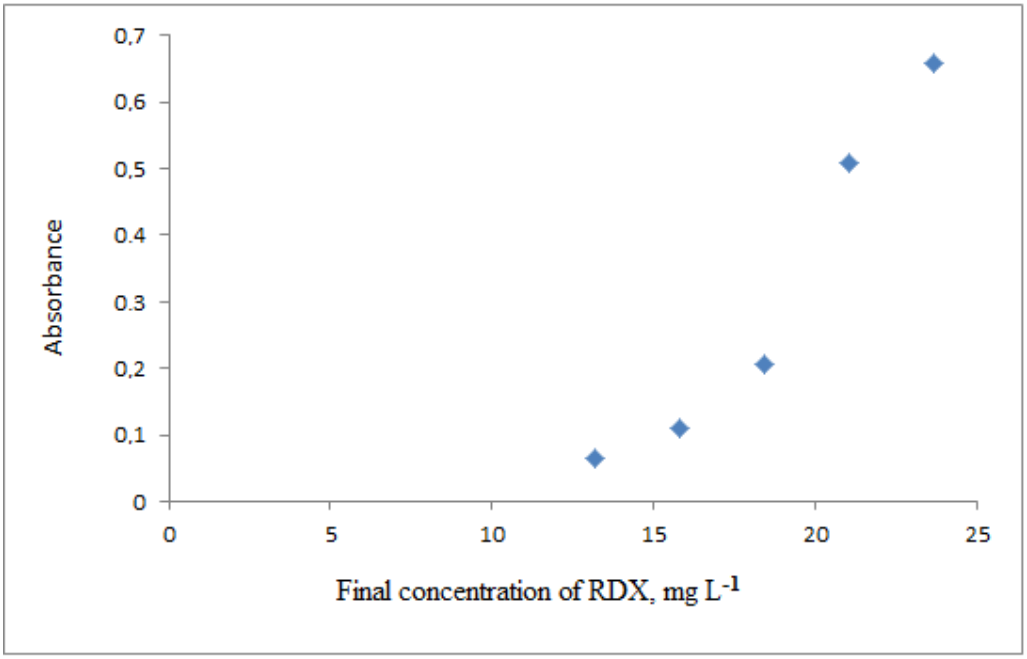

Figure S-2. The working curve of A_{565} versus concentration in the range of 13.16-23.68 mg L^{-1} RDX using the (4-ATP+NED) procedure without involvement of AuNPs.

Figure S-2 indicates a non-linear increase of A_{565} with nitramine concentration, and the sensitivity is distinctively lower than that involving AuNPs. On the other hand, the proposed (AuNP−4-ATP+ NED) procedure gave a linear response over a wider RDX concentration range of 2.63−13.16 mg L^{-1}, and the sensitivity was higher because of the extra charge-transfer interactions of the produced azo-dye with the surface plasmon resonance of AuNPs. Thus, the proposed (AuNP−4-ATP+ NED) method was shown to be superior to the application of (4-ATP+NED) binary combination without involvement of AuNPs, due to its much improved sensitivity and linearity with respect to nitramine concentration.

Another important advantage of the developed AuNPs-based optical sensing method of nitramines over solution-phase colorimetric methods like Griess nitrite assay is the adaptation potential of the developed method to chemical sensors constituting ‘miniaturized analytical devices which can deliver real-time, on-line information on the presence of specific analyte compounds’.[6] On the other hand, it is rather difficult (if not impossible) to automate the two-

step Griess reaction because of the requirement to change acidity from diazotization to azo-coupling and to maintain strict reaction conditions, oxidizability of reagent components, and insufficient stability of azo compound solutions during storage.[7]

Recovery from artificially contaminated clay soil

The standard loamy clay soil (51.9% sand, 28.2% clay, and 19.9% soil dust) was kindly provided by the Forestry Faculty of Istanbul University, Sariyer Campus (Istanbul), and artificially contaminated with RDX and HMX. For extracting RDX from this soil, the usual practice for extracting nitramines[5] was followed. Two grams of loamy clay soil-containing flasks were artificially contaminated with 2.5 mL aliquots of 200 mg L^{-1} RDX, 200 mg L^{-1} HMX and {RDX+HMX} mixture (200+ 200 mg L^{-1}) solution in acetone. The suspension was homogenized, and allowed to dry under ambient temperature. Ten millilitres of acetone was added to each spiked sample, the flask was stoppered, kept in an ultrasonic bath for 15 min, the contents transferred to a centrifuge tube, and centrifuged for 5 min at 5000 rpm. Extraction was repeated with a successive 10-mL aliquot of acetone. The flask was washed with acetone, centrifuged, and all centrifugates and washings were combined in a 25 mL-flask with dilution to the mark. Assuming negligible loss of analyte during recovery studies, the initial solutions were thus 10-fold diluted. All solutions (acetone extract) were diluted with distilled water (in 1:1 (v/v) ratio) before application of the proposed and HPLC methods of determination. The recovery of RDX component with the proposed method was 97±5 %, and of HMX component 92±4 %, whereas the same percentages with HPLC were 96±4 % for RDX and 93±3 % for HMX, showing that both nitramines could be recovered with acetone extraction from contaminated soil with reasonable efficiency, and determined simultaneously by the proposed method.

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