analytical chemistry

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Technical Note

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Anal. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.analchem.5b01775 • Publication Date (Web): 10 Sep 2015

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Determination of Triacetone Triperoxide (TATP) with a N,N-dimethyl-*p*-phenylene diamine (DMPD) Sensor on Nafion using Fe3O4 Magnetic Nanoparticles

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ABSTRACT: The explosive triacetone triperoxide (TATP) can be easily manufactured from readily accessible reagents, and is extremely difficult to detect, owing to the lack of UV absorbance, fluorescence, or facile ionization. The developed method is based on the acidic hydrolysis of TATP into H_2O_2, pH adjustment to 3.6, and the addition of magnetite nanoparticles (Fe_3O_4 MNPs) to the medium to produce hydroxyl radicals from H_2O_2, owing to the peroxidase-like activity of MNPs. The formed radicals converted the N,N-dimethyl-*p*-phenylene diamine (DMPD) probe to the colored $DMPD^+$ radical cation, the optical absorbance of which was measured at a wavelength of 554 nm. The molar absorptivity (ε) of the method for TATP was 21.06 x 10^3 L mol^{-1} cm^{-1}. The colored $DMPD^+$ product in solution could be completely retained on a cation-exchanger Nafion membrane, constituting a colorimetric sensor for TATP and increasing the analytical sensitivity. The proposed method did not respond to a number of hand luggage items like detergent, sweetener, sugar, acetylsalicylic acid (aspirin) and paracetamol-caffeine based analgesic drugs. On the other hand, TATP could be almost quantitatively recovered from a household detergent and sweetener that can be used as camouflage for the analyte. Neither common soil and groundwater ions (*e.g*., Ca^{2+}, Mg^{2+}, K^+, Cl^-, SO_4^{2-}, and NO_3^-) at 100-fold ratios nor nitro-explosives of TNT, RDX, and PETN at 10-fold amounts interfered with the proposed assay. The method was statistically validated against the standard GC-MS reference method.

Introduction

Triacetone triperoxide (TATP) was first discovered and synthesized in the 19th century by Wolffenstein[1]. TATP can be easily manufactured from hydrogen peroxide and acetone using hydrochloric or sulfuric acid as catalyst[2]. TATP is estimated to be 88% of trinitrotoluene (TNT) blast strength and classified as a primary explosive[3]. However, TATP is both sublimable and unstable, and therefore unsuitable for military and engineering uses[4]. Because of its high blast power and simple synthesis, this homemade explosive is frequently used in terrorist actions[5].

TATP detection by conventional explosive identification devices or real-time use of canines at hot spots of public safety control (such as airline terminals) is a challenging task, because the chemical structure of TATP is devoid of nitro- and other easily reacting functional groups[6]. TATP neither has a significant UV-Vis absorption nor fluorescence emission, and additionally its (sugar-like) appearance is quite unsuspicious[7]. In the recent decade, three reviews dealing with the detection of peroxide-based explosives have been published[6,8,9]. Several tandem instrumental techniques involving spectroscopy have been used to detect peroxide-based explosives. Methods based on MS are very sensitive and can detect trace amounts of explosives, but instruments are expensive and often not suitable for on-site testing. Ion mobility spectrometry (IMS), Fourier transform infrared spectroscopy (FTIR), and Raman spectroscopy are some of the instrumental analytical methods that have been used on-site for explosive residues detection, but their field use has certain limitations, because they are costly, bulky, require an easily consumable battery pack as power source, and depend on volatile or aerosol type analytes. As a result, they may not be available in many on-site investigations[10]. The results from IMS are affected by factors such as temperature and moisture, whereas fluorescence suffers from light scattering from luminophore impurities[5]. For both military and improvised explosives, more appropriate devices and colorimetric methods of on-site analysis measuring liquid[11] and air samples[12,13] have recently been developed in laboratory scale, but are basically unavailable commercially. Molecularly imprinted polymer-based electrochemical sensors[14], electrogenerated chemiluminescence (CL)[5] and other CL techniques[15] also utilizing nanoparticles[16] have been used for the determination of TATP. Our research group has colorimetrically determined TATP with the aid of a molecular spectroscopic sensor based on the reaction of H_2O_2 with cupric-neocuproine reagent[17]. In addition to these, microfluidic paper-based analytical devices (μ-PADs) for colorimetric TATP determination in the field have been recently developed, using ammonium titanyl oxalate and acidic KI reagents[10,18]. For optical (colorimetric or fluorometric) sensing of the hydrogen peroxide obtained from peroxide explosives, some researchers have focused on peroxidase-based methods, which are known to be prone to various interferences and poisoning of enzymes by false substrates added to biocatalysts[19]. Thus, a combination of nanomaterial-based degradation and optical sensing of peroxide explosives is believed to enable field-applicable development of simple, low cost and sensitive methods of determination. Firstly, Goa *et al*. reported that Fe_3O_4 nanoparticles have an intrinsic peroxidase-like activity widely used in oxidative conversions of environmental treatment or analytical detection[20]. After this report, several colorimetric[19,21,22] and fluorometric[23] methods were developed for hydrogen peroxide determination and Fe_3O_4 MNPs were used for removing organic pollutants[24,25]. Peroxidase-like activity of Fe_3O_4 MNPs stems from its structural similarity to the Fenton's reagent (Fe^{2+}/Fe^{3+} ions in solution)[20]. In this regard, it was aimed to perform acid hydrolysis on TATP, degrade the liberated hydrogen peroxide with the use of Fe_3O_4 MNPs as catalysts, and finally produce the colored *p*-quinone-imine oxidation products ($DMPD^+$ radical) with a *p*-phenylenediamine-based (DMPD) reagent, thereby enabling their spectrophotometric determination, and to develop a related molecular spectroscopic sensor for the rapid, selective, and sensitive assay of TATP on-site. Also, a colorimetric sensor designed in our laboratories for antioxidant and prooxidant compounds has been simultaneously developed for hydrogen peroxide sensing[26]. The devised method was favorably applied to complex samples containing nitro-energetic materials (such as TNT, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and pentaerythritol tetranitrate (PETN)), detergents bearing percarbonate- and perborate-based bleaching agents, analgesic drugs having acetylsalicylate, paracetamol and caffeine ingredients, and finally sugar and synthetic sweeteners. Common ions present in soil extracts were also shown not to interfere, as demonstrated by using loamy clay soil as analyte matrix.

Experimental

Safety Note

TATP is an extremely dangerous material, which may lead to explosions under impact, friction, and temperature changes. Its synthesis may only be carried out by highly qualified personnel, and at small quantities not exceeding 100 mg (as higher amounts may cause spontaneous explosions)[27].

Instrumentation and Chemicals

All reagents were of analytical reagent grade unless otherwise stated. DMPD (suitable for peroxidase test) and Nafion 115 perfluorinated membrane were purchased from Sigma-Aldrich and all other reagents from Merck and Sigma-Aldrich. The TATP-spiked standard loamy clay soil (51.9% sand, 28.2 clay, and 19.9% soil dust) for recovery studies was kindly provided by the Forestry Faculty of Istanbul University. As percarbonate is known to release hydrogen peroxide and sodium carbonate upon hydrolysis, a household detergent containing sodium percarbonate was studied for interference testing. In addition, the hand-luggage items of aspartame-based sweetener (CANDEREL), acetylsalicylic acid, paracetamol-caffeine based analgesic drugs and sugars having similar color and appearance to that of TATP were studied as possible interferents. TNT, RDX and PETN were kindly provided by the Mechanical and Chemical Industry Corporation (MKEK) of Turkey.

The spectra and absorption measurements were recorded in matched Hellma quartz cuvettes using a Varian CARY Bio 100 UV-vis spectrophotometer. The optical thickness of the cuvettes was 1 cm for solution phase, and 1 mm for Nafion membrane measurements. The proposed method for TATP assay was validated against GC-MS utilizing a Thermo Scientific Trace gas chromatograph coupled with a DSQII mass spectrometer containing electron impact ionization and quadrupole analyzer. SEM images of Fe_3O_4 MNPs were recorded with the aid of FEI Model Quanta 450 FEG scanning electron microscope.

Preparation of Solutions

The working solutions of TATP at 10-100 mg L^{-1} were prepared from corresponding stock solutions of 500 mg L^{-1} concentration in acetone. HCl solution (4 M), NaOH solutions (2 M and 4 M), pH 3.6 acetic acid buffer (containing a total CH_3COOH/CH_3COONa concentration of 2 M), Fe_3O_4 MNPs (100 mg L^{-1}), and DMPD (5 x 10^{-3} M) were prepared in water and stored at room temperature before use.

Synthesis

For synthesis of TATP and Fe_3O_4 MNPs, literature methods were applied directly[2,19] (for details of synthesis, see Supporting Information).

Recommended Procedure for TATP Determination

TATP assay consisted of three parts, namely, acidic hydrolysis of TATP into hydrogen peroxide, oxidative degradation of the H_2O_2 product with the aid of Fe_3O_4 MNPs, and spectrophotometric determination of the oxidized $DMPD^+$ cation.

Acidic hydrolysis of TATP: A volume of 2 mL of 4 M HCl was added to 1 mL of TATP solution at 10-100 mg L^{-1} concentration, and allowed to stand for 5 min for H_2O_2 formation. The sample was neutralized with 2 mL of 4 M NaOH, and adjusted to pH 3.6 with 2 mL of acetic acid buffer solution.

Degradation of H_2O_2 and Oxidation of DMPD to the Colored Cationic Product: After adjustment of pH, 2 mL of 100 mg L^{-1} Fe_3O_4 MNPs were added to the solution for degradation of the liberated H_2O_2 to reactive oxygen species (ROS, essentially comprised of hydroxyl and perhydroxyl radicals). Finally 1 mL of $5x10^{-3}$ M DMPD was added, where DMPD was oxidized to the colored $DMPD^+$ cationic radical. After 30 min, the tubes were centrifuged at 5000 rpm for 5 min and the absorbance of the final solution at 554 nm was read against a reagent blank. For measurement on a Nafion membrane, the membrane was sliced into 4.5 x 0.5 cm pieces, and was immersed in a sample tube after adding DMPD to the sample solution. The tube was placed in a rotator and agitated for 30 min so as to enable color development on the membrane surface. After 30 min, the colored membrane was placed in a 1 mm optical cuvette containing H_2O (to prevent sticking of membrane to the walls of the cuvette), and its absorbance at 550 nm was read against a blank membrane prepared under identical conditions.

The scheme for the method is summarized as: Add 1 mL of TATP solution + 2 mL of 4 M HCl (allow to stand for 5 min for hydrolysis into H_2O_2) + 2 mL of 4 M NaOH + 2 mL of pH 3.6 buffer + 2 mL 100 mg L^{-1} Fe_3O_4 MNPs + 1 mL of $5x10^{-3}$ M DMPD in this order. In the application of the solution and membrane sensing methods, measure A_{554} and A_{550}, respectively, against a reagent blank after 30 min of DMPD addition (Studies concerning method optimization are given in the Supporting Information. For optimization of pH, DMPD concentration, Fe_3O_4 MNPs concentration and reaction time, see Figures S-1, S-2, S-3 and S-4, respectively.)

Determination of TATP in Complex Materials

For interference tests, the recovery of TATP was studied in mixtures of nitro-explosives (RDX, TNT and PETN), in synthetic solutions containing common soil ions, in spiked household detergent and sweetener, and in artificially contaminated clay soil (for details of methods, see Supporting Information).

Statistical Analysis

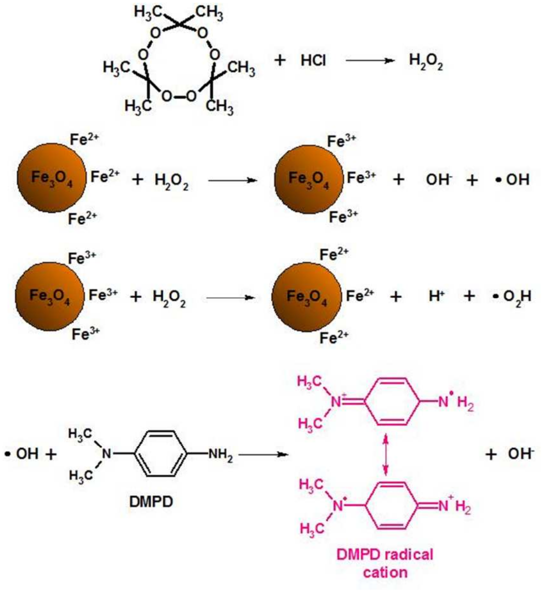
Descriptive statistical analyses were carried out by Microsoft Office 2013, covering the calculation of the population means together with their corresponding standard errors using Excel software. Results were expressed with acceptable precision as {mean ± standard deviation (SD)}. As a measure of accuracy and precision, Student (t-) and F-tests, respectively, were used for validating the proposed method against GC/MS determination of TATP.

Results and Discussion

Analyte, catalyst and method

Mass spectrum of synthesized TATP was checked with the aid of GC-MS, and the characteristic ions generated by the analyte (m/z values of 43, 58, 75, 101 and 117) were observed. For synthesized TATP, compatible results were achieved from both GC-MS library and literature[28].

On the other hand, the size and shape of Fe_3O_4 MNPs were determined by SEM. It was demonstrated that the particles appear spherical with diameter range between 20-30 nm (see Figure S-5). Since Fe_3O_4 MNPs with smaller sizes are reported to show higher catalytic activity, this property is indicative of good catalytic ability[20]. In order to determine the magnetic properties of nanoparticles that can potentially be used for magnetic field guided targeting, Fe_3O_4 MNPs were dispersed in water. After that, a magnet was applied near the tube to separate the nanoparticles by collecting them on one side of the tube wall. The developed method is based on the acidic hydrolysis of TATP into H_2O_2, followed by pH adjustment to 3.6, and addition of Fe_3O_4 MNPs (having peroxidase-like activity) to this medium to produce ROS (*i.e.* hydroxyl and perhydroxyl radicals) from H_2O_2[25]. Finally the produced ROS oxidize DMPD to the colored $DMPD^+$ radical cation, enabling spectrophotometric measurement of this colored product either in solution or on a Nafion membrane, the latter with higher sensitivity (Scheme 1).



Scheme 1. Schematic presentation of H_2O_2 formation upon TATP hydrolysis, catalytic ROS generation, and $DMPD^+$ radical cation formation as the basis of indirect spectrophotometric determination of TATP.

Analytical Figures of Merit

The proposed assay was applied to the determination of pure H_2O_2 without any acidic hydrolysis and neutralization prior to measurement (*i.e.* 4 mL of water was added instead of the solutions used in the recommended procedure), yielding the calibration line equation:

$$A_{554\ nm} = 5426\ C_{H2O2} + 0.0334\ (r = 0.9990) \quad \ldots\ (Eq.\ 1)$$

where C_{H2O2} is the H_2O_2 concentration (in mol L^{-1}) in final solution and the molar absorptivity is: $\varepsilon = 5.43 \times 10^3$ L mol^{-1} cm^{-1}.

TATP solutions at final concentrations ranging between 1 and 10 mg L^{-1} gave a linear calibration curve:

$$A_{554\ nm} = (9.48\pm0.48)x10^{-2}C_{TATP} + (7.40\pm2.93)x10^{-2}$$

$$(r = 0.9993) \quad \ldots\ (Eq.\ 2)$$

where the molar absorptivity for TATP was $\varepsilon = (21.06\pm1.07) \times 10^3$ L mol^{-1} cm^{-1} (the optical thickness of the cuvettes was 1 cm for the solution phase measurements), with a limit of detection (LOD) = 0.47 mg L^{-1} and limit of quantification (LOQ) = 1.57 mg L^{-1} (LOD = $3\sigma_{bl}/m$ and LOQ = $10\sigma_{bl}/m$, where σ_{bl} denotes the standard deviation of a blank and m is the slope of calibration curve). The visible spectra of $DMPD^+$ cation (obtained from oxidation of DMPD with ROS catalytically generated from hydrolyzed TATP solutions) are shown in Fig. 1.

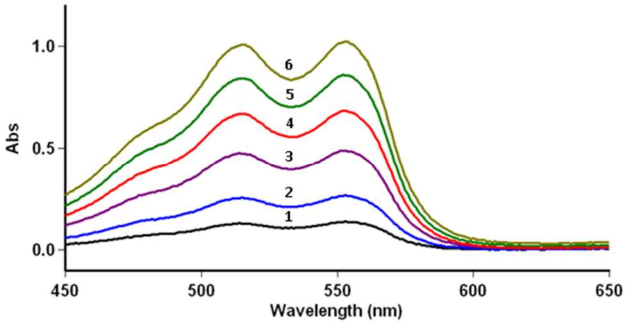


Figure 1. The visible spectra of $DMPD^+$ cation (obtained from oxidation of DMPD with ROS catalytically generated from hydrolyzed TATP solutions) at (1) 1 mg L^{-1} (2) 2 mg L^{-1} (3) 4 mg L^{-1} (4) 6 mg L^{-1} (5) 8 mg L^{-1} (6) 10 mg L^{-1} final concentrations.

Fig. 2 compares the absorption spectra of the DMPD-TATP-Fe_3O_4 MNPs system and DMPD-TATP system (for 40 mg L^{-1} TATP). It was observed that the H_2O_2 intrinsically derived from TATP could oxidize DMPD to a certain extent (spectrum 1 in Fig 2) which would be expected to be advantageous for direct detection of TATP residues in sites of criminologic investigation, but this oxidation could be significantly enhanced in the presence of Fe_3O_4 MNPs (spectrum 2 in Fig 2), due to the peroxidase-like activity of these nanoparticles. The two spectra shown in Fig. 2 have similar characteristics, confirming that the identity of the chromophore in both cases was the $DMPD^+$ cation, but nanoparticles caused a strongly increased signal. Although the colored $DMPD^+$ radical exhibited two absorption maxima at the wavelengths of 554 nm and 515 nm, the higher wavelength maximum at 554 nm was used for all subsequent measurements because of its strength[21], distinctive character and possibly less interference from natural substances found in soil (such as plant pigments and humic acids) which may absorb light at close wavelengths.

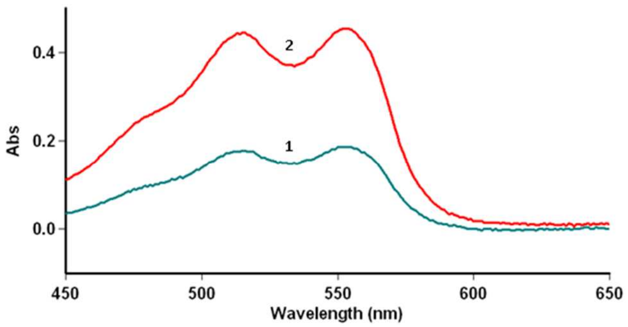


Figure 2. Visible absorption spectra of the solutions from the (1) DMPD-TATP, (2) DMPD-TATP-Fe_3O_4 MNPs systems.

For each concentration, three replicate readings were made, and the relative standard deviation (RSD) of a given set of readings varied in the range of 2.53-6.67%, depending on TATP concentration. On the other hand, the same TATP solutions gave the calibration curve (Eq. 3) when the measurements were carried out on a Nafion membrane:

$A_{550\ nm} = (6.82\pm0.42)\mathrm{x}10^{-2}\ C_{TATP} + (1.08\pm2.56)\mathrm{x}10^{-2}$

(C_{TATP} : mg L^{-1} concn.; r=0.9990) ...(Eq. 3)

where the molar absorptivity for TATP on Nafion membrane surface was ε = (15.15±0.09)x10^4 L mol^{-1} cm^{-1} (the optical thickness of the cuvettes was 0.1 cm for Nafion membrane measurements), with a limit of detection (LOD) = 0.1 mg L^{-1} and limit of quantification (LOQ) = 0.33 mg L^{-1}, RSD varying between 2.61-8.39%, depending on the concentration. The improvement in sensitivity of the sensor-based method (as reflected in lower detection and quantification limits compared to the solution-based method) most probably arose from the lower intercept value of Eq. 3 than of Eq. 2, because all the colored product formed in solution was homogenously collected on the Nafion membrane (Fig. 3). This also increased the apparent molar absorptivity approximately by an order of magnitude.

The coefficients of variation (CVs) of intra-assay measurements for TATP in the solution– and membrane–based determinations were 1.75% and 5.07%, whereas those of inter-assay measurements were 2.31% and 5.84%, respectively (N=5), showing that sensor measurements enabled higher precision.

The physical appearance of Nafion membranes (before and after treatment of TATP samples at different concentrations following hydrolysis to H_2O_2) can be seen in Fig. 3, where the original membrane turned pink-orange colored when loaded with DMPD, and membrane color varied from light pink-red to dark pink-red in the presence of H_2O_2 formed from different concentrations of TATP.

Recovery and interferences

The percentage recoveries of TATP from a nitro-explosive mixture are shown in Table S-1. The recoveries were sufficient for the tested measurement media, both in solution (94-105%) and on the Nafion membrane (96-101%). The results showed the non-interference of nitro-explosives, *i.e.* TNT, RDX and PETN, to the proposed method.

Common ions abundantly found in soil and groundwater (K^+, Mg^{2+}, Ca^{2+}, Cl^-, $NO_3^{-,}$ SO_4^{2-}) at 100-fold concentration of TATP did not affect the recoveries in both solution (96-104%) and Nafion membrane applications (97-108%).

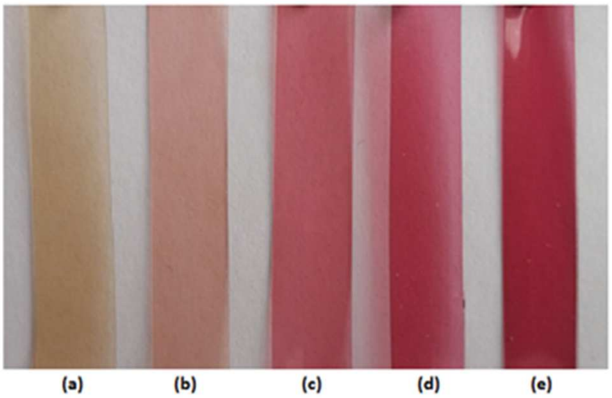


Figure 3. (a) Original Nafion membrane slice, (b) Reference membrane (including all reagents, without TATP), (c) Nafion membrane – as in (b) – in the presence of TATP at 20 mg L^{-1} concentration after hydrolysis to H_2O_2, (d) Nafion membrane – as in (b) – in the presence of TATP at 60 mg L^{-1} concentration after hydrolysis to H_2O_2, and (e) Nafion membrane – as in (b) – in the presence of TATP at 100 mg L^{-1} concentration after hydrolysis to H_2O_2.

Household detergent and sweetener can be used as camouflage material for TATP because of the color and appearance similarities to TATP. For this reason, they were studied as possible sources of interference. When the detergent was dissolved in water, it yielded a mixture of hydrogen peroxide (which eventually decomposed to water and oxygen) and sodium carbonate[29]. The resulting hydrogen peroxide was a potential interference for the proposed assay. For eliminating this effect, we used solubility differences between the analyte and detergent. After selective acetone extraction of TATP from detergent or sweetener mixture, the proposed assay was applied. TATP recoveries from detergent-added sample using the solution– and membrane–based methods were 93 and 109%, and from sweetener-added sample 90 and 97%, respectively. Additionally, the proposed method was directly applied to detergent, sweetener, sugar, acetylsalicylic acid and paracetamol-caffeine. The bar diagram (Fig. 4) shows that these camouflage materials carried by passengers as personal belongings in hand-held luggages had no significant responses.

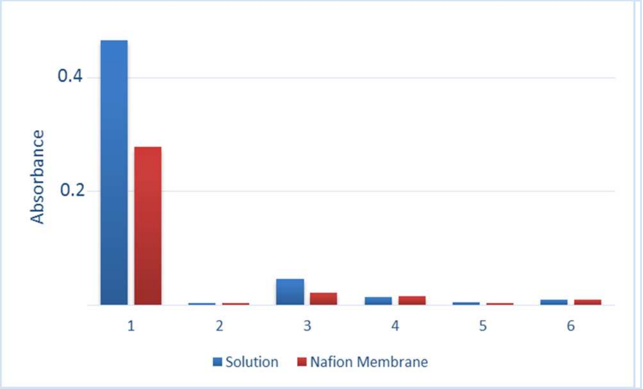


Figure 4. Responses of (1) 40 mg L^{-1} TATP, (2) Acetylsalicylic acid, (3) Paracetamol-Caffeine, (4) Household Detergent, (5) Sweetener, (6) Sugar.

Reusability of membranes

TATP determinations were repeated five times with the use of the same membrane to examine the reusability of Nafion.

After each experiment, the Nafion membrane was immersed in 1 M HNO_3 solution for 2 min, then washed thoroughly with deionized water before next use. The relative standard deviation of measurements was 7.07%.

Method validation against GC-MS Determination of TATP

TATP working solutions in acetone at 1-10 mg L^{-1} concentrations were analyzed with GC-MS, and the mean value of three repetitive injections was used for each calculation. The calibration equation between peak area (A) and concentration was:

$A = 4.17x10^4 C_{TATP}-1.10x10^4$ (r = 0.9998)

The results of measurements carried out in solution and on Nafion membrane were validated against the reference GC-MS procedure[28] using TATP-contaminated soil samples. For the recovery of TATP from 5 mg L^{-1} solutions on N=5 repetitive determinations, the proposed and reference methods essentially showed no significant differences between the precision and accuracy of results (see Supporting Information, Table S-2). The t- (Student) and F-tests were used for comparing the population means and variances, respectively[30]. The confidence level used in validation of solution phase findings was 95% for both t- and F- tests, whereas the corresponding levels in Nafion membrane measurements were 95% and 99%, respectively, for t- and F-tests (Table S-2).

Conclusions

There are a great many complex techniques for TATP analysis in the literature, but methods for field analysis are limited. Some of these methods are patented and some require high-cost and easily inhibited peroxidase enzymes. Alternatively, a novel colorimetric method using Fe_3O_4 MNPs has been developed and converted into a sensor on a Nafion membrane. The method has high selectivity over possible interferents existing in nitro-explosive residues, household detergents, reducing sugars, acetylsalicylic acid, paracetamol-caffeine and soil extracts. Both the Nafion membrane and Fe_3O_4 MNPs are reusable; additionally, unlike peroxidase, MNPs can be magnetically separated from the medium to stop the reaction at any desired point. Because of these advantages, the developed method has a low cost per analysis, enabling the screening of large numbers of samples in the field. In addition, the achieved LOD values for the proposed method are very suitable for field use and results validated against GC-MS. The combined use of magnetite NPs and DMPD membrane sensor enables the development of a precise, sensitive and selective method for TATP assay, which is suitable for both automated and on-site analysis. This membrane sensor increased sensitivity and precision with respect to solution-based measurements, and is believed to find potential use in anti-terror activities for public security.

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ACKNOWLEDGMENT

The authors wish to express their gratitude to the Ministry of National Defence, Office of Technical Services, and to the Mechanical & Chemical Industry Corporation (MKEK) for the donation of nitro- and composite explosive samples. Additionally, the authors thank TUBITAK (Turkish Scientific and Technical Research Council) for the research project 114Z131.

SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This information is available free of charge via the Internet at http://pubs.acs.org/.

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