Determination of 2,4,6-Trinitrotoluene in Soil Samples Using a Paired Emitter-Detector Diode-Based Photometer

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This paper reports on developing a low-cost but efficient PEDD-based photometer. The photometer consists of a white LED as the emitter diode, an RGB LED as the detector diode (for the first time), and a multimeter for recoding the signal. The developed PEDD-based photometer was utilized for the determination of 2,4,6-trinitrotoluene (TNT) in soil samples. A Meisenheimer complex of TNT with NaOH in acetonitrile was used as a probe to monitor the presence of residual TNT in soil samples. The calibration curve in the soil sample was linear in the concentration range of 0.86 to 110 µg g^{-1}, with a detection limit of 0.27 µg g^{-1} and a quantification limit of 0.81 µg g^{-1}. Analysis of the soil samples collected from the Iran Cinema and Television Town using the developed method showed trace residual of TNT.

INTRODUCTION

The determination of nitroaromatic explosive compounds is crucial, particularly for security and defense applications, environmental monitoring, forensic investigation, and civic and airport security [1]. 2,4,6-Trinitrotoluene (TNT) is the most common nitroaromatic explosive. TNT is commonly employed in industrial and military operations and has caused major pollution of soil and groundwater [2]. Because nitroaromatic explosive compounds are highly hazardous, they may cause health problems in animals and people, such as altered liver function, skin irritation, anemia, and cataract [2]. As a result, developing selective and sensitive methods for identifying and quantifying nitroaromatics is a major analytical task. Many methods, including Raman spectroscopy [3], infrared spectroscopy [4], reflectance spectroscopy [5], chemiluminescence techniques [6], gas and liquid chromatography coupled with mass spectrometry [7, 8], colorimetry [9], and electrochemical techniques [10] have been developed for the determination of nitroaromatic energetic compounds. However, some of the developed

methods are costly, time-consuming, and require well-trained operators. On the other hand, most of the developed methods are not portable and their on-site application is limited. Therefore, the development of portable methods of low cost but still high sensitivity and selectivity is necessary for the determination of nitroaromatics.

Visible light-emitting diodes (LEDs) were developed in 1962 [11] containing p-n junctions emitting a narrow band of light wavelengths [12]. LEDs have found a wide application for the miniaturization of optical sensors due to their low cost, small size, robustness, and high efficiency. They are also used as light detectors since upon light incident; a potential difference is generated across the p-n junction [13]. Therefore, LEDs can be used as both the light source and the detector in paired emitter-detector diodes (PEDD) optical sensors [12,14]. PEDD-based photometers provide low fabrication cost, low power consumption, ease of miniaturization, and a high signal-noise ratio response in a large wavelength range [12]. Furthermore, their output is a direct pulse-duration-modulated signal, eliminating the need for a costly analog-to-digital converter [15]. These advantages have led to the utilization of PEDD-based optical sensors in various miniaturized photometers as well as a

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flow-through optical sensor for chromatography and flow analysis [16-18].

The need for *in-situ* monitoring of the environment, health, and security is growing, necessitating the development of accurate miniaturized sensors. To this end, proper analytical equipment with operational features such as high accuracy, sufficient sensitivity, low power consumption, cost-effective, autonomous operation capability, and interoperability with wireless communications networks are required. One method that has been effectively implemented in chemical sensing is the use of LEDs as light sources. For the detection of TNT, there are only a few reports on the use of LEDs as light sources for the development of light absorbance-based sensors. A droplet-based microfluidic lab-on-a-chip with electrowetting was used for the determination of TNT [19]. An LED-photodiode system was used to detect the colorimetric reaction between nitroaromatics and a strong base, which resulted in a colored Jackson-Meisenheimer complex [20]. The interaction of strong bases such as methoxide ions or hydroxide with nitroaromatic compounds to form red to violet-colored derivatives is well known. Studies with TNT indicate that several possible products may be formed, depending on the ratio of TNT to base and the solvent composition [8]. It has been reported that the application of acetonitrile as the solvent could lower the detection limit of TNT determination compared to water or methanol as the solvents [21]. Another benefit of using acetonitrile is its direct applicability for extraction of TNT in soil samples where most interferences are not dissolved in.

This paper reports on developing a low-cost but efficient PEDD-based photometer. The photometer consists of a white LED as the emitter diode, an RGB LED as the detector diode for the first time, and a multimeter for recording the signal. The developed PEDD-based photometer was utilized for the determination of 2,4,6-trinitrotoluene (TNT) in soil samples. A Meisenheimer complex of TNT with NaOH in acetonitrile was used as a probe to monitor the presence of residual TNT in soil samples.

EXPERIMENTAL

Reagents and Materials

HPLC-grade ethanol, methanol, and acetonitrile were purchased from Sigma-Aldrich Company (St. Louis,

Missouri, United States). Analytical grade sodium hydroxide, 4-nitroaniline, toluene, and picric acid were purchased from Sigma-Aldrich Company. 2,4,6-Trinitrotoluene (TNT) and 2,4-dinitrotoluene were provided by the Iranian Defense Ministry and recrystallized before usage. The rest of the chemicals were purchased from Merck Company (Darmstadt, Germany). Deionized water (resistivity of ≥18.2 MΩ) was used in the whole study. TNT stock solution was prepared in acetonitrile.

Apparatus

A MEGATEK power supply model MP-3003S (Albania) was used for the illumination of the LED emitter diode. A SOAR digital multimeter model ESC820D-L (Utah, United States) was used for recording the detector LED potential. A WPA UV-Vis Spectrophotometer model Lightwave II was used for the spectrophotometric study of the product of sodium hydroxide solution and TNT. A PERSIAN3D FDM 3D printer model Founder 2X (Iran) was used for the construction of the PEDD-based photometer body.

Paired Emitter-Detector Diode-Based Photometer

A schematic illustration of the developed PEDD-based photometric system for the determination of TNT in soil samples is presented in Fig. 1. A rectangular cube photometer

Fig. 1. A schematic illustration of the developed PEDD-based photometric system for the determination of TNT in soil samples.

body with dimensions of 3×2×3 cm with a cubic hole (1.1×1.1×2.8 cm) in the center for inserting a cuvette was fabricated by an FDM 3D printer using ABS filament. A Bridgelux chip 3W natural white LED was used as the emitter diode. It was powered using a power supply. A 6-pin 3W YD-XGJH RGB SMD LED chip (wavelengths: 620-625 nm for red, 520-525 nm for green, and 460-465 nm for blue LEDs) was used as the detector. Each detector LED was connected to a multimeter for recording the voltage. A 1 cm light path quartz cell was used.

Photometric Method for TNT Determination in Acetonitrile

The photometric determination of TNT was based on the formation of a red-violet colored Meisenheimer complex between TNT in acetonitrile and hydroxide ion in water. For quantitative determination of TNT in acetonitrile, 100 µl NaOH aqueous solution of 25 mM was added to 5.0 ml TNT solution in acetonitrile. The samples were shaken for 20 s for color development. For the PEDD-based photometer, the green LED was utilized as the detector, and the applied voltage to the emitter LED was 2.8 V. The voltages of the detector LED for the addition of 100 µl of deionized water and 100 µl NaOH aqueous solution, V_0 and V, respectively, were recorded and used to calculate the voltage difference (ΔV) according to the following equation:

$$\Delta V = V - V_0 \qquad (1)$$

Soil Samples Analysis

Soil samples were collected from different TNT explosion sites at the Iran Cinema and Television Town located in Tehran, Iran. The samples were dried at 80 °C for 3 h. Then the samples were powdered and sieved through a 2 mm mesh. To 1.0 g of the samples, 5 ml pure acetonitrile was added and the mixture was shaken for 10 min. The mixture was centrifuged at 4000 rpm for 4 min and the supernatant solution was separated. To this solution, 100 µl NaOH aqueous solution of 25 mM was added. The samples were shaken for 20 s for color development. The blank solution was prepared using the same procedure except for the addition of 100 µl of methanol instead of NaOH solution.

For the PEDD-based photometer, the green LED was utilized as the detector, and the applied voltage to the emitter LED was 2.8 V. The voltages of the detector LED for blank and the sample, V_0 and V, respectively, were recorded and used to calculate the voltage difference (ΔV) according to Eq. (1).

RESULTS AND DISCUSSION

Optimization of The Condition for the Meisenheimer Complex Formation

The formation of red-violet Meisenheimer complex between TNT in acetonitrile and NaOH in methanol has been presented in Fig. 2. To optimize the condition for the formation of the complex, the effect of solvent type, incubation time, and NaOH concentration was studied using a benchtop spectrophotometer.

Solvent type. To study the effect of solvent on TNT, 5 ml of 0.5 mM solutions of TNT were prepared in water, ethanol, methanol, and acetonitrile using the TNT stock solution. To these solutions, 100 µl NaOH in methanol solution portions of 25 mM were added. The solutions were incubated for 2 min and the absorbance spectra were recorded using the benchtop spectrophotometer. As the results show (Fig. 3a), only ethanol and acetonitrile result in a significant colored product formation. Water, ethanol, and methanol are polar-protic (dielectric constant: 78.5, 24.3, 32.6, respectively), while acetonitrile is polar-aprotic (dielectric constant: 36.6). Therefore, it is expected that acetonitrile as a polar-aprotic result in the highest stability constants of the donor-acceptor complex among the studied solvents [22]. Therefore, acetonitrile was selected as the solvent.
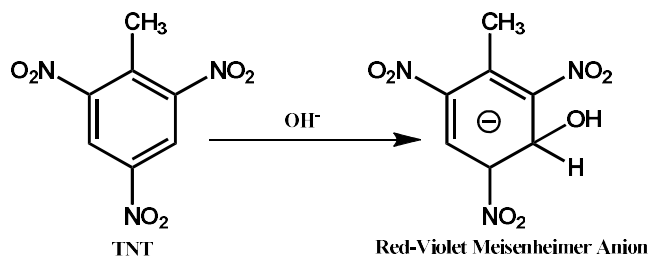

Fig. 2. The reaction between TNT and NaOH for the formation of the red-violet Meisenheimer anion.
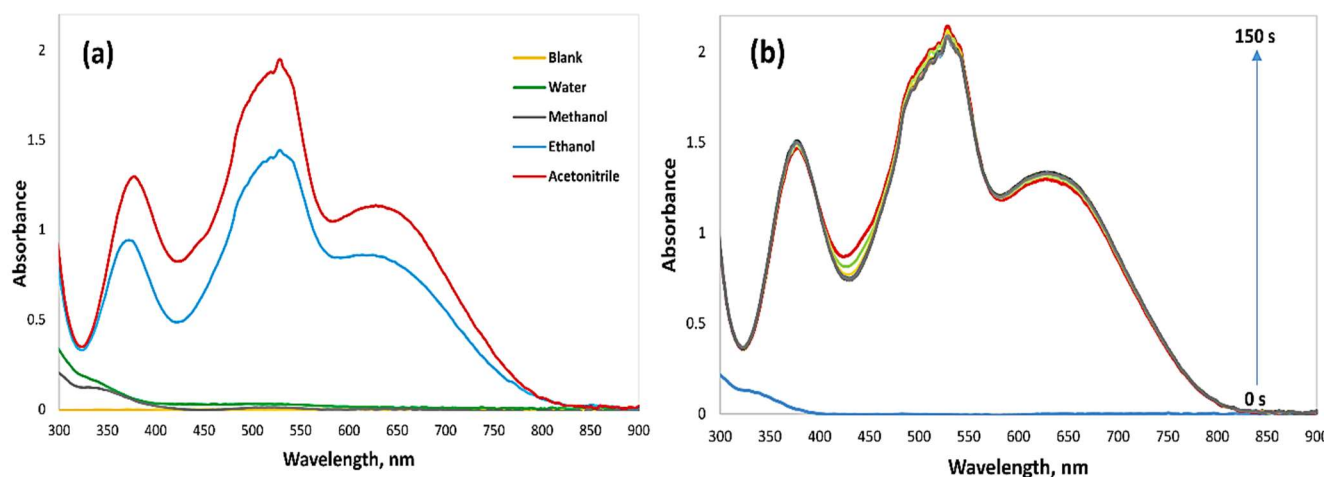
Fig. 3. Effect of (a) solvent (conditions: 100 µl NaOH in methanol solution of 25 mM plus 5 ml of 0.5 mM solutions of TNT in different solvents at room temperature) and (b) time (conditions: 100 µl NaOH in methanol solution of 25 mM plus 5 ml of 0.5 mM solutions of TNT in acetonitrile at room temperature) on the Meisenheimer anion formation.

Reaction time. To study the effect of reaction time, 5 ml of 0.5 mM TNT solutions were prepared in acetonitrile using the TNT stock solution. To these solutions, 100 µl NaOH in methanol solution portions of 25 mM were added. The absorbance spectra were recorded as a function of time using the benchtop spectrophotometer. As the results show (Fig. 3b), the reaction rate is relatively fast and reaches semi-equilibrium conditions in 20 s reaching the maximum absorbance which remains constant for at least 150 s. Therefore, the reaction time of 20 s was chosen as the optimum.

NaOH concentration. To study the effect of NaOH concentration, 5 ml of 96 µM TNT solutions were prepared in acetonitrile using the TNT stock solution. To these solutions, 100 µl NaOH in methanol solution portions of different concentrations in the range of 1 to 25 mM were added. The absorbance spectra were recorded using the benchtop spectrophotometer. The result showed (the results are not shown) that the solution absorbance increases as the concentration of NaOH increases and reaches a steady state at concentrations above 20 mM. Thus, the NaOH concentration of 25 mM was chosen as the optimum.

Calibration Curve in Acetonitrile Using the Benchtop Spectrophotometer

For the construction of calibration curves using the benchtop spectrophotometer, 5 ml TNT solutions of different concentrations were prepared in acetonitrile using the TNT stock solution. To these solutions, 100 µl NaOH in methanol solutions of 25 mM were added. The solutions were incubated for 20 s and then the absorbance spectra were recorded. The calibration curves were obtained using the benchtop spectrophotometer at maximum absorbance wavelengths of 377, 530, and 640 nm. The obtained calibration equations were A (377 nm) = 0.0078 C (µM) + 0.0619 (R^2 = 0.9953), A (530 nm) = 0.0116 C (µM) + 0.0819 (R^2 = 0. 9949), and A (640 nm) = 0.0068 C (µM) + 0.0473 (R^2 = 0.9949) in the linear concentration range of 3.0 to 97 µM TNT. Among studied wavelengths, the 530 nm wavelength provided the highest sensitivity.

Optimization of the PEDD-Based Photometric System

Type of the detector LED. Previous studies on the development of PEDD-based photometers have utilized rationally paired LED systems to improve the selectivity of the system as it comes from its name [13,18,23,24]. This means that the wavelength of the emitter LED should be shorter than the detector LED. This study utilizes an RGB detector LED and a white emitter LED for the first time. This approach led to the development of a multifunctional photometer that can be used for other applications apart from the main aim of this study.

Table 1. A summary of the Calibration Curve Equations Obtained Using the Developed PEDD-based Photometer Using Different Detector LEDs (Conditions: 5 ml TNT Solutions of Different Concentrations and 100 μl NaOH in Methanol Solutions of 25 mM were Mixed and Incubated for 20 s. For the PEDD-based Photometer, the Applied Voltage was 2.8 V and a 1 cm Quartz Cuvette was Used)

Detector LED	Emission wavelength (nm)	Detection wavelength (nm)	Calibration equations	Linear range (μM)	R^2
Green LED	520-525	< 520	$\Delta V\ (V) = 0.0132\ C\ (\mu M) + 0.0091$	0.75-97	0.9939
Red LED	620-625	< 620	$\Delta V\ (V) = 0.0013\ C\ (\mu M) + 0.0007$	1.5-48	0.9948
Blue LED	460-465	< 460	$\Delta V\ (mV) = 0.0125\ C\ (\mu M) + 0.0165$	1.5-24	0.9819

To choose the best detector LED that provides both selective and sensitive determination of the Meisenheimer complex, calibration curves in the concentration range of 0.75 to 97 μM using each detector LED were constructed individually under the same conditions. The results are shown in Table 1. The results showed that the green detector provides the highest sensitivity and widest linear range. The results are in good agreement with those obtained in acetonitrile using the benchtop spectrophotometer. The green diode detector is sensitive to wavelengths lower than 520 nm corresponding to the absorbance of the solution at 377 and 530 nm. Therefore, it makes sense that the green detector results in the highest sensitivity. For the red diode, a saturation of the detector can occur due to a wider range of wavelengths that the detector is sensitive to, which leads to lower sensitivity and selectivity. Using the green LED detector, the linear range, the limit of detection (LOD), and the limit of quantification (LOQ) were 0.75-97 μM (170-22032 μg l^{-1}), 0.22 μM (50 μg l^{-1}), and 0.73 μM (167 μg l^{-1}), respectively.

The power supply voltage. The applied voltage to the detector LED is an important parameter. It acts as a double edge sword. As the applied voltage increases, the saturation of the detector gets more significant. On the other hand, as it decreases, the sensitivity decreases. To study the effect of applied voltage, 5 ml TNT solutions of different concentrations and 100 μl NaOH in methanol solutions of 25 mM were mixed and incubated for 20 s. For the PEDD-based photometer, the applied voltages were in the range of 2.65 to 2.80 V, the green detector was utilized, and a 1 cm quartz cuvette was used. The obtained results (Fig. 4) showed

that increasing the applied voltage from 2.70 to 2.75 V improved the detector response for all studied concentrations. However, further increasing the applied voltage to 2.80 V led to decreasing the detector response for low concentrations but increases the detector response for high concentrations.
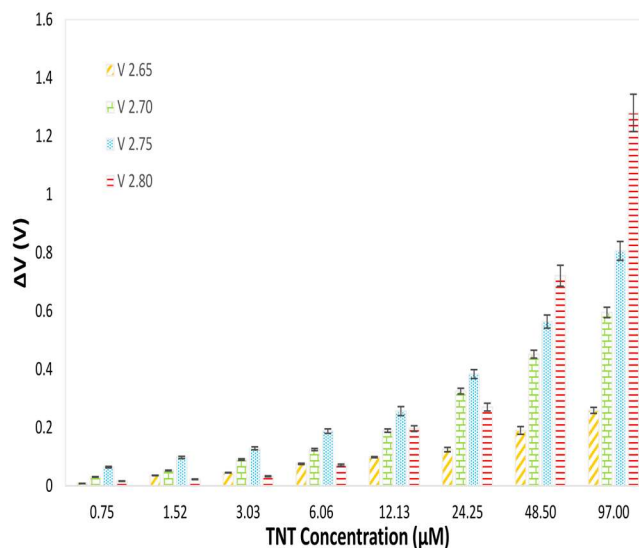

Fig. 4. Effect of applied voltage on the recorded green detector LED response for different concentrations of TNT in acetonitrile using the developed PEDD-based photometer (conditions: 5 ml TNT solutions of different concentrations and 100 μl NaOH in methanol solutions of 25 mM were mixed and incubated for 20 s. For the PEDD-based photometer, the applied voltages were in the range of 2.65 to 2.80 V, the green detector was utilized, and a 1 cm quartz cuvette was used, n = 3).

Therefore, higher applied voltages were not studied and the applied voltage of 2.80 V was chosen as the optimum value.

Interferences Study

The effect of possible interferences was studied by obtaining the recoveries for a known concentration of TNT (48 μM) in the presence of Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}, Cl^-, Br^-, NO_3^-, CO_3^{2-}, SO_4^{2-}, SiO_2, Fe_2O_3, Fe_3O_4, 4-nitroaniline, toluene, picric acid, 2,4-dinitrotoluene, and p-phenylenediamine. The results (results are not shown) showed that none of the studied potential interferences contribute to the Meisenheimer complex formation. The studied ions at 50-fold concentration did not interfere with TNT determination (no found concentration change more than ±5%). However, the presence of higher concentrations of cations that form insoluble hydroxides (*i.e.*, Mg^{2+} and Ca^{2+}) can cause serious problems. Although the formed precipitate can be separated from the solution before analysis, still the reagent (NaOH) is consumed. Therefore, an additional reagent should be added to the solution after the separation of insoluble hydroxides. The presence of SiO_2 can cause a problem due to its dissolvent in a highly basic medium. However, since SiO_2 solubility in acetonitrile is not considerable, it does not cause a serious problem. The presence of iron oxides can cause high background absorbance. However, the paramagnetic iron oxides can be separated using a magnet. 4-Nitroaniline, picric acid, and 2,4-dinitrotoluene do not contribute to the colored complex formation but picric acid forms a pale yellow colored solution in acetonitrile only at high concentrations.

Method Validation for Soil Samples

The developed method was validated in terms of sensitivity, accuracy, and precision for the determination of TNT in soil samples. To 1.0 g of the TNT-free soil samples spiked with different amounts of solid TNT, 5 ml pure acetonitrile was added and the mixture was shaken for 10 min. The mixture was centrifuged at 4000 rpm for 4 min and the supernatant solution was separated. To this solution, 100 μl NaOH in a methanol solution of 25 mM was added. The samples were shaken for 20 s for color development. The blank solution was prepared using the same procedure except for the addition of 100 μl of deionized water instead of NaOH

solution. For the PEDD-based photometer, the green LED was utilized as the detector, and the applied voltage to the emitter LED was 2.8 V. The calibration curve was constructed under the above-mentioned conditions with three replicates for each concentration. The calibration curve equation was ΔV (V) = 0.0076 C (μg_{TNT} g^{-1}_{soil}) + 0.041 (R^2 = 0.9953) for the concentration range of 0.86 to 110 μg g^{-1}. The LOD and LOQ were calculated as $3S_b/m$ and $10S_b/m$, respectively, where S_b is the blank signal and m is the slope of the calibration curve. The LOD and LOQ were 0.27 and 0.81 μg g^{-1}, respectively. Considering the US-EPA limit for TNT in soil (*i.e.*, 50 mg g^{-1}) [25], the developed method is sensitive enough for the quantification of TNT in soil samples. The spiked/recovery experiments at three concentration levels of 5.0, 25.0, and 70.0 μg g^{-1} were performed to evaluate the accuracy of the developed method. The recoveries of 93.01 (CV = 7.34%), 101.27 (CV = 5.94%), and 100.31% (CV = 4.21%) were obtained, respectively, indicating the high accuracy and precision of the method.

Real Samples Analysis

To evaluate the applicability of the developed method, three soil samples collected from different TNT explosion sites at the Iran Cinema and Television Town located in Tehran, Iran were analyzed using the developed method. To evaluate the accuracy of obtained results, the samples were spiked with TNT at three levels (*i.e.*, 13.77, 27.28, and 55.08 μg g^{-1}). Each data was repeated three times and the mean values were calculated. Table 2 shows the obtained results. TNT was found in one of the studied samples. However, its level is much below the US-EPA limit for TNT in soil. No TNT was detectable in other studied samples. This can be related to the leaching of TNT into the surface and underground water as well as the fact that new explosive materials are used that contain no trace amount of TNT. The spiked/recovery experiments showed that TNT can be determined in soil samples with acceptable recoveries ranging from 97.39% to 112.17% and high repeatabilities ranging from 1.74% to 7.62%. these results indicate that the developed method can be utilized for the determination of TNT in soil samples with acceptable accuracy and precision.

Table 2. Determination of TNT in Soil Samples Using the Developed Method

Sample	Spiked ($\mu g \, g^{-1}$)	Found ($\mu g \, g^{-1}$)	Recovery (%)	CV (%)[a]
Soil sample 1				
	-	ND[b]	-	-
	13.77	13.93	101.16	2.70
	27.28	26.76	98.09	2.40
	55.08	53.64	97.39	1.99
Soil sample 2				
	-	1.37	-	7.62
	13.77	15.13	99.93	5.33
	27.28	28.28	98.64	4.36
	55.08	57.04	101.07	3.11
Soil sample 3				
	-	ND	-	-
	13.77	13.55	98.40	6.54
	27.28	30.60	112.17	5.05
	55.08	55.03	99.91	1.74

[a]Coefficient of variation. [b]Not detected.

CONCLUSIONS

Toward the "analytical chemistry beyond laboratory walls" concept, this paper reports on the development of a low-cost but efficient PEDD-based photometer. Nowadays, photometers are rarely found in ordinary people's homes since the devices are both expensive and difficult to use. However, the developed photometer is potentially portable and its simple and cost-effective technology could be extended to regular customers' homes. Nevertheless, the photometer should be accompanied by an integrated potentiometer and a mobile phone app to improve the device's user-friendly properties. Still, the device should be calibrated by the analytical chemist. Many commercialized TNT determination methods use special chemicals, and the color intensity and stability are depending on the composition of the organic solution comprised of methanol or acetone except for the CRREL method. However, the developed photometric method is based on the extraction of TNT with acetonitrile and the Meisenheimer anion formation from the reaction of TNT and NaOH in a methanol solution. A comparison of the developed method with some previously reported methods for the determination of TNT in soil samples (Table 3) showed that the developed method provides comparable analytical figures of merits while keeping the portability advantage. GC-MS/MS provides the best sensitivity. However, this method is expensive, needs trained operators, and is not portable. Some previously developed methods are relatively less expensive but their portability is not high (such as fluorescence spectrophotometry and voltammetry). Some of the methods require special sample treatment which needs to be done at an analytical chemistry laboratory (such as optoelectrochemistry and surface-enhanced Raman spectroscopy). However, the developed method could be easily portable keeping its low-cost feature. The sample preparation using the developed method requires centrifugation that could be replaced by filtration to improve the on-site application of the developed method.

ACKNOWLEDGMENTS

Table 3. A Comparison of the Developed Method with some Previously Reported Methods for TNT Determination

Procedure	Detection	Sample	Linear range ($\mu g\ l^{-1}$)	LOD ($\mu g\ l^{-1}$)	LOQ ($\mu g\ l^{-1}$)	Ref.
Extraction and determination by test strip modified with dicyclohexylamine charge transfer reagent	Colorimetry	30% aqueous acetone	5000-50000	3000	10000	[22]
Extraction and gas chromatography separation	GC-MS/MS	Water Sediment Mussels	-	0.09×10^{-3} 0.09×10^{-3} 0.09×10^{-3}	0.30×10^{-3} 0.15×10^{-3} 0.68×10^{-3}	[7]
Meisenheimer complex formation with cysteamine and spontaneous self-assembly onto gold nanoparticles	Surface-enhanced raman spectroscopy	Water	0.0227-22.71	0.0227	-	[3]
TNT-amine quenching fluorescence emission of Rhodamine 110	Fluorescence spectrophotometry	Water soil	3000-60000	710	2380	[26]
Electrochemical reduction of Meisenheimer complex in a deep eutectic solvent modified with n-butylamine	Optoelectrochemistry	Water	143.09-411.11	1.82	-	[10]
Gold nanoparticles functionalized with thiram fungicide aggregation in the presence of TNT	Colorimetry	Water soil	20-100	5	15	[9]
Differential pulse voltammetric determination using glassy carbon/multi-walled carbon nanotube/polyethylen eimine/gold nanoparticles	Voltammetry	Water	50-8000	15	-	[1]
Meisenheimer anion formation using NaOH	PEDD-based photometry	Soil acetonitrile	0.86-110 $\mu g\ g^{-1}$ 170-22032	0.27 $\mu g\ g^{-1}$ 50	0.81 $\mu g\ g^{-1}$ 167	This work

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