Screen-Printed Electrode based Electrochemical Detector Coupled with in situ
Ionic Liquid Assisted Dispersive Liquid-Liquid Microextraction for determination
of 2,4,6-trinitrotoluene

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ABSTRACT

A novel methodology is reported, whereby screen-printed electrodes (SPELs) are combined with dispersive liquid-liquid microextraction. *In situ* ionic liquid (IL) formation has been employed as an extractant phase in the microextraction technique, proving to be a simple, fast and inexpensive analytical method. This approach uses miniaturized systems both in sample preparation and detection stage, helping to develop environmentally friendly analytical methods and portable devices to allow rapid and onsite measurements. The microextraction methodology is based on a simple metathesis reaction in which a water-immiscible IL (1-hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide, [Hmim][NTf₂]) is formed

from a water-miscible IL (1-hexyl-3-methylimidazolium chloride, [Hmim][Cl]) and an ion-exchange reagent (lithium bis[(trifluoromethyl)sulfonyl]imide, LiNTf₂) into sample solutions. The explosive 2,4,6-trinitrotoluene (TNT) has been used as model analyte to develop the method. The electrochemical behaviour of TNT in [Hmim][NTf₂] has been studied in SPELs. The extraction methodology was initially optimized with a two-step multivariate optimization strategy, using Plackett-Burman and central composite designs. Under the optimum conditions the method was evaluated and a good level of linearity was obtained with a correlation coefficient of 0.9990. Limits of detection and quantification were found to be 7 µg L⁻¹ and 9 µg L⁻¹, respectively. The repeatability of the proposed method was evaluated at two different spiking levels (20 and 50 µg L⁻¹) and coefficients of variation of 7% and 5% (n=5) were obtained. Tap water and industrial wastewater were selected as real-world water samples in order to assess the applicability of the method.

Keywords: Liquid-phase microextraction; dispersive liquid-liquid microextraction; ionic liquid; screen-printed electrodes; 2,4,6-trinitrotoluene; water samples.

INTRODUCTION

Miniaturization of both analytical methodologies and instrumentation has become very popular in recent years, and many efforts have focused on carrying out chemical analysis at a reduced scale. Miniaturization of sample preparation methodologies has significantly increased with the development of a great number of solid-phase and liquid-phase microextraction techniques

[1,2]. Liquid-phase microextraction (LPME) offers simplicity, ease of handling, minimal sample and solvent consumptions, and an important reduction in residues generated, in contrast with traditional liquid-liquid extraction techniques. Since its appearance in the nineties, several LPME techniques have been developed being single drop microextraction, hollow-fiber liquid-phase microextraction and dispersive liquid-liquid microextraction [3] (DLLME) the most commonly used. Although organic solvents have traditionally been used as extractants in LPME techniques, the use of ionic liquids (ILs) has recently attracted interest as a promising alternative [4]. ILs are melted salts at room temperature that possess unique properties among which we can highlight their being highly thermal and chemically stable, with negligible vapor pressure, tunable viscosity, electrolytic conductivity, a wide electrochemical window and good extractability of organic compounds and metal ions [5]. The utilization of ILs has helped to overcome problems associated with LPME techniques using organic solvents [4] and enabled the development of new methodologies such as temperature-controlled IL dispersive liquid-liquid microextraction [6] and *in situ* IL formation dispersive liquid-liquid microextraction (*in situ* IL-DLLME) [7,8]. During *in situ* IL-DLLME the extractant phase is formed into sample solution via a metathesis reaction between a water-miscible IL and an ion exchange reagent to form a water-immiscible IL. Homogeneously dispersed fine drops of the extractant phase are generated and high enrichment factors are obtained with low extraction times due to the high contact surface between phases. Dispersion of the IL takes place via metathesis reaction, and a disperser agent is not needed, thus avoiding competition with the IL and decreasing extraction efficiency. Moreover,

77 additional devices are avoided such as vortex or ultrasound bath, which have
78 also been used to assist IL-DLLME [9,10].

79 In most cases, LPME procedures are followed by chromatographic
80 separations, in either liquid or gas modalities, coupled with different detection
81 systems (UV-Vis, inductively coupled plasma optical emission spectrometry or
82 mass spectrometry, among others). Most of these detection systems are slow,
83 expensive and bulky, so analytical instrumentation employed for detection has
84 not achieved the same degree of miniaturization as miniaturized sample
85 preparation methodologies, which are more widely used. Furthermore, ILs
86 present some disadvantages when chromatographic techniques are used. For
87 example, special devices are needed when ILs are injected in gas
88 chromatography due to their high boiling points [11,12], or shorter column life
89 and resolution problems appear in liquid chromatography. Accordingly,
90 electrochemical sensors are presented as an attractive option for use in
91 detection methodologies. Recent advances in microfabrication and screen-
92 printing technologies enable the development of miniaturized and easy-to-use
93 electrochemical systems for rapid and de-centralized onsite measurements.
94 Screen-printed electrodes [13] (SPEs) are inexpensive, mass-produced,
95 disposable devices, which are ideal for low volume sample analysis. Moreover,
96 the versatility and ease of modifying these electrodes make them advantageous
97 when improving their performance and adapting them to specific analytes.

98 To our knowledge, this is the first report of an analytical method in which
99 SPEs are used as electrochemical detector for LPME. ILs possess intrinsic
100 conductivity, a wide electrochemical window and thermal stability, therefore they
101 have been recognised as ideal alternative electrolytes in electrochemical

102 devices [14]. Taking into account the electrochemical properties of ILs and the
103 low volume of the IL-phase formed during *in situ* IL-DLLME (10-20 μL), SPELs
104 seem to be ideal and perfectly compatible candidates for analyzing IL drop after
105 microextraction without any further modification. The explosive 2,4,6-
106 trinitrotoluene (TNT) has been used as a model analyte to develop the
107 proposed methodology since its electrochemical behaviour has been widely
108 characterized. Additionally, nitroaromatic explosives, such as TNT, have
109 received increasing interest in recent years. Concerns about terrorist activity
110 have led to intensification of security measures in airports and public buildings,
111 demanding highly sensitive analytical methods to detect these compounds at
112 trace levels. Furthermore, their presence in surrounding soils, waterways and
113 reservoirs must be monitored in areas where they are produced, stored or
114 detonated. The mutagenic and toxic properties of nitroaromatic explosives
115 make their presence in the environment dangerous [15]. A great number of
116 analytical methods using gas [16], liquid [17] and micellar electrokinetic [18]
117 chromatography and immunoassay techniques [19] have been developed to
118 determine TNT and other related explosives in environmental samples.
119 However, the inherent redox activity of TNT makes electrochemical sensors a
120 very suitable alternative. Electrochemistry offers simplicity, a rapid response,
121 low-cost instrumentation with portable options, as well as analytical
122 requirements of sensitivity and reproducibility.

123 Screen-printed electrodes have previously been used in electrochemical
124 devices for TNT analysis. Hydrogel-coated SPELs have been used to detect
125 thermally desorbed TNT from an integrated preconcentration system for both
126 solid and liquid samples [20]. An electrochemically pre-anodized Nafion-coated

screen-printed carbon electrode (SPCE) has been used in a disposable sensor developed to determine different nitroaromatic compounds [21]. With this system, TNT can be detected in spiked lake water at a concentration of 30 μM ($6.8 \mu\text{g mL}^{-1}$). A wearable textile-based screen-printed electrochemical sensor, which is highly suitable for monitoring the surroundings of the wearer, has been tested to detect nitroaromatic explosives both in gas and liquid phase, obtaining a limit of detection (LOD) of around 1 $\mu\text{g mL}^{-1}$ for TNT in water [22]. Recently, a very simple and low-cost sensor based on unmodified SPCEs has been described to determine TNT and 2,4-dinitrotoluene in aqueous solutions, obtaining LODs as low as 0.4 μM ($90 \mu\text{g L}^{-1}$) and 0.7 μM ($73 \mu\text{g L}^{-1}$), respectively [23].

The research presented here combines the advantages of LPME techniques with the benefits that SPEs offer as electrochemical sensors. The resulting novel methodology includes miniaturized systems in both sample preparation and in detection stage. In addition, the use of an IL as extractant phase not only provides the advantage of good extractability of organic compounds, but also provides the electrolyte behaviour needed for detection. The proposed method has been optimized using a multivariate optimization strategy and has been evaluated in order to demonstrate its applicability to determine TNT in real-world water samples.

EXPERIMENTAL SECTION

Reagents and real-world water samples. A TNT standard of 1000 mg L^{-1} in acetonitrile was obtained from LGC Standards (Warsaw, Poland). Stock solution of TNT (10 mg L^{-1}) was prepared in acetonitrile HPLC grade from

Sigma-Aldrich (Seelze, Germany) and stored in the dark at 4°C. Working solutions were prepared daily by proper dilution of this stock solution in ultrapure water from a water purification system (Mili-Q Biocel A10) supplied by Milipore (Billerica, MA, USA). ILs 1-hexyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([Hmim][NTf₂]) (98%) and 1-hexyl-3-methylimidazolium chloride ([Hmim][Cl]) (98%) were purchased from Iolitec (Heilbronn, Germany). The lithium bis[(trifluoromethyl)sulfonyl]imide (LiNTf₂) salt was supplied by Sigma-Aldrich (St. Louis, MO, USA) and NaCl reactive grade was from ACS Scharlau (Barcelona, Spain).

Tap water from a drinking water treatment plant in Seville (Spain) and industrial wastewater from Ourense (Spain) were utilized as real-world water samples. The industrial wastewater contained a chemical oxygen demand of 1004 mg O₂ L⁻¹, a biochemical oxygen demand of 278 mg O₂ L⁻¹ and 429 mg L⁻¹ of suspended solids. Samples were collected in amber glass containers and stored in the dark at 4°C. Tap water was used without any further pretreatment whereas the wastewater was filtered with a 0.22 µm pore-size nylon filter before use. The real-world water samples were previously analyzed and the target analyte was not detected.

***In situ* IL-DLLME procedure.** Under optimum conditions, 32 mg of [Hmim][Cl] were placed in a conical-bottom glass tube and dissolved in 11 mL of aqueous standards or sample solutions. An equimolar quantity of LiNTf₂ (45.3 mg) relative to [Hmim][Cl] was added and a cloudy solution was immediately formed. The mixture was manually shaken for 0.5 minutes. In order to accelerate phases separation, the tube was then introduced in an ice bath for 3 minutes. Next, the phases were separated by centrifugation for 5 minutes at

4000 rpm. The aqueous phase was removed with a glass pipette, and 15 μL of the formed IL-phase (*i.e.*, [Hmim][NTf₂]) was withdrawn with a syringe. Finally, this 15 μL was deposited on the screen-printed graphite electrode (SPGE) surface for electrochemical detection. The procedure is described in Figure 1.

Electrochemical analysis. A μ -Autolab III potentiostat/galvanostat from Eco Chemie (Utrecht, The Netherlands) controlled by Autolab GPEs software version 4.9 for Windows XP was used for electrochemical experiments. All measurements were carried out using three electrode configuration SPGEs from Kanichi Research Services Ltd. (Manchester, UK). SPGEs were manufactured as previously described [24]. The working electrode, 3.1 mm diameter, and the counter electrode were made of a graphite ink. A pseudo Ag/AgCl was the reference electrode. Connectors for the electrochemical connection of the SPGEs were also obtained from Kanichi Research Services Ltd. SPGEs were used without any pretreatment or modification of the working electrode surface and a new SPGE was used for each experiment.

Differential pulse voltammetry (DPV) was selected as the electroanalytical technique. Various DPV parameters were optimized with a once-at-a-time strategy, selecting the following optimum conditions: 100 mV modulation amplitude; 10 mV step potential; 0.05 s modulation time and 0.5 s interval time. Pure N₂ from Air Liquide (Madrid, Spain) was flowed for 20 minutes before DPV experiments and maintained during measurements. The signal corresponding to oxygen embedded in the IL [25] appears at the same reduction potential as the analyte, therefore, purging with N₂ was necessary to ensure a deoxygenated atmosphere in which the analyte could be detected at low concentrations. All electrochemical measurements were carried out at room temperature.

Data processing. The current peak of the first cathodic wave of TNT at - 0.80 V vs pseudo Ag/AgCl was used to identify and quantify the analyte in order to evaluate the developed method. A multivariate optimization strategy was carried out to determine the optimum conditions of the microextraction methodology. Statgraphics Statistical Computer Package "Statgraphics Plus 5.1." (Warrenton, VA, USA) was used to construct the experimental design matrices and evaluate the results.

RESULTS AND DISCUSSION

Multivariate optimization

Screening step. Plackett-Burman design is a two-level fractional factorial design for studying $k=N-1$ variables in N runs, where N is a multiple of 4 [26]. Fractional factorial designs are very useful in the first steps of a project when many variables are initially considered but only a few show important effects. The Plackett-Burman design ignores interaction between variables so the main effects can be calculated with a reduced number of experiments, thereby leading to more economical experimentation. A saturated Plackett-Burman design was used to construct the matrix of experiments, including 11 variables: eight real variables and three dummy variables. The effects of dummy variables were used to evaluate the experimental error [27,28].

Based on the literature and previous experience of the research group [7,29], the eight real experimental variables selected at two levels were: amount of [Hmim][Cl], sample volume, molar ratio between [Hmim][Cl] and the salt LiNTf_2 , ionic strength, extraction time, centrifugation speed, centrifugation time and purge time with N_2 before electrochemical measurements. Table 1 shows

the experimental variables and levels considered in the Plackett-Burman design. A total of twelve experiments were carried out using aqueous standards of 100 $\mu\text{g L}^{-1}$.

The data obtained were evaluated using an ANOVA test and the results were visualized with the Pareto chart shown in Figure S1(a) (see Electronic Supplementary Material). The length of each bar was proportional to the influence of the corresponding variable and the effects that exceed the reference vertical line can be considered significant with a 95% probability.

According to Figure S1(a), only the amount of [Hmim][Cl] was a statistically significant variable, with 95% probability, having a negative effect. This negative effect is in agreement with the fact that if a lower amount of [Hmim][Cl] is used, a smaller volume of IL-phase is formed in the microextraction procedure, thus a higher concentration of the analyte is obtained in the extraction phase.

Sample volume is the second most important variable having a non-significant positive effect but being much larger than purge time. According to our previous experience, sample volume is an important variable to consider in microextraction techniques. In general, greater sample volume involves a greater amount of analyte and therefore increases the response. For this reason, both the amount of [Hmim][Cl] and sample volume were selected as the main variables affecting the response of the system, and were investigated in the optimization of the significant variables step. The other six real variables with non-significant effects were fixed at the most experimentally convenient level (namely stoichiometric molar ratio between [Hmim][Cl] and LiNTf_2 ; ionic

strength: 0% NaCl; extraction time: 0.5 min; centrifugation speed: 4000 rpm; centrifugation time: 5 min; and purge time: 20 min).

Optimization of significant variables. Central composite design (CCD) was employed in this optimization step. This design combines a two-level full factorial design (2^k) with $2k$ star points, where k is the number of variables being optimized, and one point at the center of the experimental region, that can be run n times. In order to ensure the rotatability of the model, star points were set at $\alpha=\sqrt{k}=1.41$ whereas the central point was repeated five times to provide an orthogonal design [26]. CCD was used to evaluate and optimize main effects, interaction effects and quadratic effects of the two considered variables. Table 2 shows the low and high levels, the central and star points of the considered variables in the optimization step. Thirteen experiments were carried out using aqueous standards of $100 \mu\text{g L}^{-1}$.

The data obtained were also evaluated using an ANOVA test and the results were visualized with the Pareto chart shown in Figure S1(b) (Electronic Supplementary Material). As can be seen, both the amount of [Hmim][Cl] and sample volume were significant variables, with a 95% probability, confirming the predicted importance of sample volume effect. One of the quadratic effects was also significant, assuming the curvature of the system and fitting the second-grade polynomial model proposed. The response surface obtained using the CCD is shown in Figure 2. The surface graph shows a pronounced increase in the analytical signal as the amount of [Hmim][Cl] decreases and sample volume increases.

In summary, the results obtained from the optimization process lead to the following experimental conditions: amount of [Hmim][Cl], 32 mg; sample

volume, 11 mL; molar ratio [Hmim][Cl]:LiNTf₂, 1:1; ionic strength, 0% NaCl; extraction time, 0.5 min; centrifugation speed, 4000 rpm; centrifugation time, 5 min; and purge time before electrochemical measurements, 20 min.

Electrochemical study of TNT in [Hmim][NTf₂] at SPGEs. DPV of a blank and four TNT standards of 10, 30, 50 and 70 mg L⁻¹ prepared in commercial [Hmim][NTf₂] were carried out using SPGEs in order to study the electrochemical behavior of the analyte. According to previous studies [30,31], using ILs as electrolytes generally leads to three consecutive reduction peaks of TNT, which are believed to correspond to each nitro group at the aromatic ring. Figure 3 shows DPV curves obtained in this study. As can be observed, a well-defined cathodic peak appears at -0.80 V, corresponding to the reduction of one of the three nitro groups in the molecule, whereas the two peaks corresponding to the remaining nitro groups cannot be clearly distinguished. The current peak at -0.80 V displayed a good linearity, between 10 and 70 mg L⁻¹, with a correlation coefficient (r) of 0.996. The repeatability of the electrochemical response was also evaluated for five repeated analyses of the 70 mg L⁻¹ standard and a coefficient of variation (CV) value of 2% was found.

Secondly, the electrochemical behavior of TNT in [Hmim][NTf₂] generated *in situ* was studied. As shown in Figure 4, the reduction peaks of the three nitro groups are perfectly well-defined and, as in commercial [Hmim][NTf₂], an identical peak appears at -0.80 V. Nevertheless, the reductive peaks at -1.06 V and -1.27 V are not well-defined at lower concentrations, therefore the current peak at -0.80 V was finally chosen for evaluation of the proposed method.

Analytical figures of merit of the proposed method. Quality parameters of the proposed method were evaluated. A concentration range

from 10 to 100 $\mu\text{g L}^{-1}$ was studied and the linear range was finally established from 10 to 80 $\mu\text{g L}^{-1}$. The resulting calibration curve gave a high level of linearity with a correlation coefficient (r) of 0.9990 ($N=4$). The sensitivity of the instrumental measurements estimated by the slope of the calibration curve was $(0.0112 \pm 0.0004) \mu\text{A } \mu\text{g}^{-1} \text{ L}$. The repeatability of the proposed method, expressed as CV, was evaluated at two different spiking levels (20 and 50 $\mu\text{g L}^{-1}$) by extracting five consecutive aqueous standards, and CV values were found to be 7% and 5%, respectively. The enrichment factor of the proposed procedure was 300, defined as the ratio of C_o/C_a , where C_o is the concentration of analytes in the IL phase after extraction and C_a is the original concentration of analytes in the aqueous phase.

The LOD and the limit of quantification (LOQ) were estimated using the mean signal of the blank ($n=$ three replicates) at -0.80 V plus three or ten times its standard deviation. The LOD was found to be 7 $\mu\text{g L}^{-1}$ whereas the LOQ was 9 $\mu\text{g L}^{-1}$. It should be pointed out that the LOD of the developed method is equal or even lower than others recently reported detection limits for the electrochemical analysis of TNT obtained with more expensive and complex electrodes, using carbon nanomaterials, metallic nanoparticles or assembly procedures (Table 3). In addition, our approach combines a simple sample preparation step with unmodified inexpensive SPGEs, thereby providing a lower LOD than those obtained with other SPEs [20-23] reported to date (Table 3); therefore the developed method presents unique benefits.

Real-world water samples analysis. The applicability of the proposed method to determine TNT in real-world water samples was evaluated. Three replicated analyses of both tap water and wastewater were carried out at 40 μg

L⁻¹ spiking level. Wastewater was filtered with a 0.22 µm nylon filter after being spiked. It should be noted that in previous analyses none of the selected water samples had initial detectable TNT concentrations. Relative recoveries were calculated as the ratio of the signals found in real and ultrapure water samples spiked at the same concentration level. Relative recovery for tap water samples was found to be 114% with a CV value of 16%, whereas for wastewater samples the relative recovery was 109% with 18% CV. According to these results, it can be concluded that the matrix effects were not significant in TNT analysis in the two selected water samples. Therefore, the developed method can be successfully applied to clean and complex water sample matrices.

CONCLUSIONS

Screen-printed graphite electrode-based electrochemical detection has been successfully combined with LPME for the first time. The proposed analytical method employs miniaturized systems both in sample preparation and in detection stage, with the advantage of avoiding expensive and bulky or immovable instrumentation. *In situ* IL formation in the microextraction methodology avoids the use of harmful and toxic organic compounds both as extractant and disperser solvents. The incorporation of a simple and fast sample preparation step before the electrochemical measurements with low-cost and disposable SPGEs has yielded a lower LOD than the detection limits previously reported for other SPEs. The multivariate optimization strategy used here enabled us to rapidly and economically find the optimum conditions for the main experimental parameters involved in the sample preparation method, thus providing complete information. Finally, the results have proven the applicability

of the proposed method to determine TNT at trace levels in real-world water samples. Although the use of a nitrogen purge, ice bath and the centrifuge presents a limitation to the portability, this methodology provides a step forward in the development of portable and economical systems available to any laboratory.

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Figure Captions

Fig. 1 *in situ* IL-DLLME coupled with SPGE

Fig. 2 Response surface of CCD

Fig. 3 DPV curves of a blank and four TNT standards prepared in commercial [Hmim][NTf₂]

Fig. 4 DPV curves of a blank and a TNT standard of 80 µg L⁻¹ in ultrapure water after *in situ* IL-DLLME under optimum conditions

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Fig. 1

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Fig. 2

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Fig. 3

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Fig. 4

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445 **Table 1.** Experimental variables and levels of the Plackett-Burman design.

Variable	Level	
	Low (-1)	High (+1)
Amount of [Hmim][Cl] (mg)	34	68
Sample volume (mL)	5	11
Ionic strength (NaCl concentration, %, w/v)	0	10
Molar ratio [Hmim][Cl]:LiNTf ₂	1:1	1:3
Extraction time (min)	0.5	1
Centrifugation time (min)	5	10
Centrifugation speed (rpm)	2000	4000
Purge time (min)	20	30

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447 **Table 2.** Variables, low and high levels, central and star points used in CCD.

Variable	Level			Star points ($\alpha=1.41$)	
	Low (-1)	Central (0)	High (+1)	$-\alpha$	$+\alpha$
Amount of [Hmim][Cl] (mg)	40	60	80	32	88
Sample volume (mL)	4	7	10	3	11

448 **Table 3.** Characteristics of some electrochemical methods developed to determine TNT and
 449 other nitroaromatic explosives.

Electrode	Analytical technique	Analytes	Real samples and spiking levels in parenthesis	TNT LOD	Ref
SPGE	DPV	TNT	Tap water and industrial wastewater (40 $\mu\text{g L}^{-1}$)	7 $\mu\text{g L}^{-1}$	This work
Hydrogel-coated SPEL	SWV	TNT	-	-	[20]
Nafion-coated SPCE	SWV	TNT and other nitroaromatic explosives	Lake water (30 μM ; 6.8 $\mu\text{g mL}^{-1}$)	-	[21]
Textile-based SPEL	SWV	TNT and 2,4-dinitrotoluene	-	1 $\mu\text{g mL}^{-1}$	[22]
SPCE	CV	TNT and 2,4-dinitrotoluene	-	0.4 μM (90 $\mu\text{g L}^{-1}$)	[23]
Mesoporous SiO_2 modified GCE	LSV	TNT and other nitroaromatic explosives	-	< 1.8 nM (4 $\mu\text{g L}^{-1}$)	[32]
GCE functionalized with OMC	AdsSV	TNT and other nitroaromatic explosives	-	0.2 $\mu\text{g L}^{-1}$	[33]
GCE modified with MWCNTs	AdsSV	TNT	Sea water (100-1000 $\mu\text{g L}^{-1}$)	0.6 $\mu\text{g L}^{-1}$	[34]
GCE modified with Cu nanoparticles and SWCNTs	AdsSV	TNT and other nitroaromatic explosives	River and tap water, and soil (50-200 $\mu\text{g L}^{-1}$)	1 $\mu\text{g L}^{-1}$	[35]
GCE modified by LbL self-assembled of {MSU/PDDA} $_n$ films.	DPV	TNT and other nitroaromatic explosives	-	1.5 nM (3.4 $\mu\text{g L}^{-1}$)	[36]
Amalgam Hg/Au electrode	Microchip FIA- ED	TNT	-	7 $\mu\text{g L}^{-1}$	[37]
Electrochemically activated CFMEs	SWV	TNT and other nitroaromatic explosives	Tap and ground water (2 mg L^{-1}); soil samples (200 mg g^{-1})	0.03 $\mu\text{g mL}^{-1}$	[38]
BDD	SWV	TNT	Sea water (20-400 $\mu\text{g L}^{-1}$)	10 $\mu\text{g L}^{-1}$	[39]
Graphene nanoribbon-modified GCE, graphene nanosheet-modified GCE and bare GCE	DPV	TNT	Sea water (4-20 mg L^{-1})	0.140-0.520 mg L^{-1}	[40]

450 DPV, diferential pulse voltammetry; GCE, glassy carbon electrode; LSV, linear sweep
 451 voltammetry; OMC, ordered mesoporous carbon; AdsSV, adsorptive stripping voltammetry;
 452 MWCNTs, multi-wall carbon nanotubes; SWCNTs single-wallet carbon nanotubes; LbL, layer-
 453 by-layer; MSU, mesoporous SiO_2 ; PDDA, poly(diallyldimethylammonium) chloride; FIA-ED, flow
 454 injection analysis with electrochemical detection; CFMEs, carbon fiber microelectrodes; SWV,
 455 square wave voltammetry; CV, cyclic voltammetry; BDD, boron doped diamond.