

Electrochemical Determination of N-Guanylurea Dinitramide (FOX-12) Using a Poly(Methyl Orange)-Modified Carbon Nanotube Electrode

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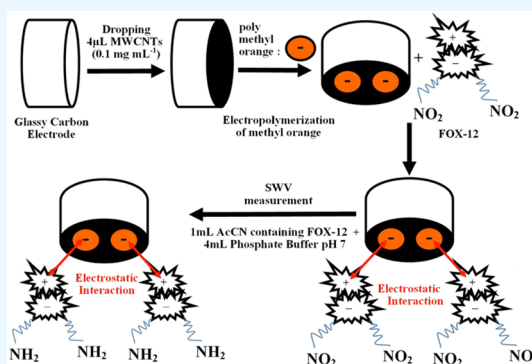
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ABSTRACT: This study introduces a novel electrochemical method and a sensor electrode designed for the first time to enable the selective and sensitive quantification of N-guanylurea dinitramide (FOX-12) via square-wave voltammetry (SWV). A glassy carbon (GC) electrode was surface-modified to create the new working electrode using poly(methyl orange: MO), which was altered by electropolymerizing the acid/base indicator MO using cyclic voltammetry and dripping well-dispersed multiwalled carbon nanotubes solution onto the electrode surface. The current intensity was correlated to the concentration of FOX-12, and the calibration line was built between 10 and 100 mg L⁻¹ of FOX-12. The limit of detection (LOD) and the limit of quantitation (LOQ) for FOX-12 were 1.5 mg L⁻¹ and 5.0 mg L⁻¹, respectively, and its distinctive reduction peak potential was determined to be around -1.25 V. Additionally, the modified GC/MWCNTs/pMO electrode was effectively used to measure FOX-12 in the presence of synthetic and real mixtures of energetic substances. Furthermore, FOX-12 (50 mg L⁻¹) was quantitatively recovered at 40-fold concentrations of common soil ions and 10-fold concentrations of camouflage materials. The proposed method was applied to clay soil samples polluted with FOX-12 and validated against an HPLC method using the statistical *t*- and *F*-tests.



1. INTRODUCTION

Energetic (explosive) substances are chemical compounds or mixtures that decompose rapidly when exposed to external influences such as heat, vibration, friction, and ignition. 2,4,6-Trinitrotoluene (TNT), 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazosine (HMX) are often used for military purposes, by keeping in mind that these substances could spontaneously explode during their manufacture, transportation, storage, and use.¹ Therefore, global research has focused on the development of energetic materials that are close to performance but insensitive to the potential risks of these materials. In this regard, the high-energy/low-sensitivity explosive N-guanylurea dinitramide (FOX-12 or GuDN) was synthesized by researchers at the Swedish National Defense Research Institute in 2002.² It is a white crystalline solid explosive, commonly known as FOX-12, which is an acid-stable salt of dinitramide with a high energy and excellent thermal stability.^{3–11} Its activation energy (E_a) is 277 kJ mol⁻¹, apparent crystal density is 1.7545 g cm⁻³, ignition temperature is 192 °C, detonation velocity is 8210 m s⁻¹, and heat of formation (ΔH_f) is -355 kJ mol⁻¹.^{2,10} FOX-12 has an intermediate energy level between those of RDX and TNT, and a sensitivity level close to that of triaminotrinitro benzene (TATB). It is nonhygroscopic and insoluble in cold water.^{5,12} Its decomposition produces major

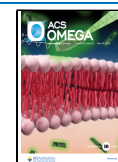
products such as CO₂, N₂, H₂N₂, and NH₃ and byproducts such as H₂O and HN₂.¹³ It combines very easily with certain additives used for energetic materials.¹³ It is soluble in some organic solvents such as *N*-methylpyrrolidone (NMP), dimethyl sulfoxide (DMSO), acetonitrile (AcCN), and *N,N*-dimethylacetamide (DMA) and also in some binary solvent mixtures.^{5,11,12} FOX-12 is used in the military field for the production of explosives. In this context, FOX-12 is used as a propellant in firearms and high-explosive melt-cast formulations.⁶ It can also be used in insensitive warhead fillings, i.e., artillery, bombs, mortar rounds, and tanks.² The release of FOX-12 into water and soil may have adverse effects on living species. The synthesis, solubility, applications, and pyrolysis of FOX-12 have been extensively studied in the literature.^{3,5,7,14} Because of the difficulties in quantifying FOX-12, few methods have been developed for its analysis, mainly comprising thermal, chromatographic, and spectroscopic analysis.^{1,8,15} However, these complex techniques are comparatively

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expensive, time- and solvent-consuming, and demanding. Electrochemical methods constitute a good alternative to these methods as being more selective, sensitive, rapid, easy to use, and inexpensive,^{16–18} but such electrochemical detection of FOX-12 has not been reported.

Different working electrode types, including GCEs, carbon fiber electrodes, and screen-printed carbon electrodes, have been described for the electrochemical measurement of various explosives.^{19,20} In addition, these base materials can be modified by polymers and nanomaterials (multiwalled carbon nanotubes (MWCNTs), gold nanoparticles, *etc.*), due to their valuable properties such as huge surface area and unique physicochemical characteristics. Furthermore, because of their superior electrical conductivity, chemical stability, and ease of functionalization, conducting polymers are frequently used in electrode modification. These polymers provide active sites for analyte interaction and facilitate electron transport, which improves the sensitivity and selectivity of the electrochemical sensors. To further enhance sensor performance, a variety of components have been added to these polymer matrices, such as metal nanoparticles, graphene derivatives, and metal–organic frameworks.^{21–24}

Methyl orange (MO) is an organic indicator dye that contains both hydrophilic and hydrophobic groups along with a molecular cavity. While its aromatic rings contribute to its hydrophobic nature, they also provide chemical stability and make MO an electroactive, conductive molecule. In the literature, the analysis of various analytes has been carried out using electrodes fabricated by electropolymerizing methyl orange. For example, methyl orange was electropolymerized onto a metal–carbon–polymer nanocomposite using cyclic voltammetry, and the electrochemical determination of cholesterol was carried out.²⁵ Sahara and colleagues used a pencil graphite electrode modified with poly(methyl orange) to achieve a sensitive and selective voltammetric measurement of aminotriazole.²⁶ In another study, a carbon paste electrode modified with poly(methyl orange) and a shape memory alloy was used to successfully perform the electrochemical measurement of dopamine.²⁷ In a different work, an effective electrochemical sensing platform for the detection of 4-nitrophenol was created using a glassy carbon electrode modified with poly(methyl orange); 4-nitrophenol was detected at nanomolar concentrations thanks to this modification.²⁸

In this work, the rapid, selective, and sensitive electrochemical detection of FOX-12 was achieved with a novel square-wave voltammetric (SWV) method. Multiwalled carbon nanotubes (MWCNTs) and poly(methyl orange) (pMO) were used for modifying the surface of GCE. Thus, a novel working electrode was developed for selectively sensing FOX-12 in the presence of various types of energetic including nitramines and nitro-aromatics. Numerous detection parameters, including buffer pH, solvent type and composition (acetonitrile), MWCNTs concentration, and electrolyte type, were carefully examined. In addition, the suggested SWV approach was tested using a high-performance liquid chromatographic (HPLC) process using the statistical *t*- and *F*-tests and did not react to common soil ions or electroactive substances.¹ Najafi & Darabi showed, in a single paper, the electroreducibility of dinitramide (as ammonium salt: ADN form)—but not of FOX-12—on a graphene film-modified GC electrode, but in this study, only a limited number of ions were studied as potential interferents and spiked water was used for

simulating a real sample.²⁹ Thus, this work is the first report of an electrochemical method for the detection of FOX-12.

2. EXPERIMENTAL SECTION

2.1. Chemicals, Solutions, and Instruments. Various explosive substances, such as TNT, 2,4-dinitrotoluene (DNT), RDX, HMX, 3-(nitrooxy)nitrate-2,2-bis[(nitrooxy)methyl]-propyl (PETN), 2,4,6-trinitrophenylmethyl nitramine (tetryl), Comp B composite explosive (including 60% RDX, 39% TNT, and 1% wax), Comp C (including 91% RDX and a binder) and Octol (including 70% HMX and 30% TNT), and FOX-12 (target analyte), were used, which were provided by the Machinery & Chemistry Industries Institution (MKEK) of Turkey in earlier projects (explosives were only used in very dilute solutions mg L^{−1} range). NaCl, LiClO₄, NaNO₃ (Sigma-Aldrich), and 0.1 mol L^{−1} phosphate buffer (PB) (pH: 7) were used as electrolytes. Alumina slurry (Baikowski International 0.05 mm, BaikaloX 0.05 CR), acetone, and ethanol (all of which are technical grades) were used to clean the electrodes. Methyl orange (MO) (Merck) and multiwalled carbon nanotubes (MWCNTs) (Sigma-Aldrich) were used as working electrode modifiers, and Merck (Darmstadt, Germany) supplied the other chemicals.

In extra pure acetonitrile (AcCN), various basic stock solutions of specific explosives, as well as actual explosive combinations, were created at concentrations of 1000 mg L^{−1}. Similarly, 1000 mg L^{−1} of NH₄NO₃ was made in 0.1 mol L^{−1} PB (pH: 7). The stock solutions of various camouflage substances at concentrations of 10,000 mg L^{−1} and of common soil ions at 2500 mg L^{−1} were prepared in PB at 0.1 mol L^{−1} and pH 7. Resin for cation exchange (Lewatite S1468) was used to eliminate Cu²⁺ and Fe³⁺ interferences. Chromafil PET-45/25 (a 0.45-μm filter) (Macherey-Nagel) was used to filter electroactive camouflage substances.

Five mmol L^{−1} of [Fe(CN)₆]^{3−/4−} solution was prepared in 0.1 mol L^{−1} HCl containing 0.1 mol L^{−1} KCl (as supporting electrolyte), used for impedance measurements and the CV characterization. Voltammetric experiments were carried out with the help of a Metrohm Autolab Potentiostat/Galvanostat (PGSTAT204, Switzerland). As working, auxiliary, and reference electrodes, the GCE (BASi stationary voltammetry electrodes; 1.6 mm, surface area of 0.02 cm²), a platinum electrode (Pt), and an Ag/AgCl electrode (containing 3 M NaCl) were utilized. For SEM measurements of the GC/MWCNTs/pMO electrode, the FEI model Quanta 450 FEG instrument was used. In polluted clay soil samples containing FOX-12, the suggested SWV technique was statistically verified against the HPLC method.¹ The HPLC system was equipped with a 1525 pump (Waters), a 2998 photodiode array detector, and a Hypercarb column (Thermo Scientific).

2.2. Method Optimization. Certain characteristics, such as the kind of working electrode and the type of supporting electrolyte (Figure S1), the pH of the measurement medium (Figure S2), the amount of acetonitrile used for the SWV analysis (Figure S3), the amount of MWCNTs used in the preparation of the working electrode (Figure S4), and the cycle number of MO electropolymerization in the preparation of the working electrode (Figure S5), were investigated. The SWV procedure and potential ranges (0 to −2.1 V) were selected, PB was employed as a supporting electrolyte, and the mixture of PB/AcCN at a volume ratio of 8:2 (v:v) was used as the baseline solution for SWV measurements.

2.3. Glassy Carbon Electrode Pretreatment. The GC working electrode was burnished in circular motions with an alumina for a short time before being rinsed and sonicated in distilled water for 5 min. The electrode was then sonicated continuously for five min in isopropanol-AcCN solution (1:1, v:v). Because there was no peak visible in the baseline during the SWV scan, it was thought that this method was sufficient to clean the electrode.³⁰

2.4. Preparation of the Working Electrode. To alter the working electrode's surface, MWCNTs and pMO were used. MWCNTs solution at 0.1 mg mL⁻¹ was made using a 1:1 suspension of EtOH and water, whereas 0.1 mol L⁻¹ PB at pH 7 was used to make 0.1 mmol L⁻¹ MO. Following this, the working electrode was coated with 4 μ L of the MWCNTs suspension, which was then allowed to dry at room temperature for 30 min. For the electropolymerization of MO, the GC/MWCNTs electrode was inserted into the electrochemical cell containing 5 mL of MO (at 0.1 mmol L⁻¹) via the CV procedure in a potential range between -0.6 and 1.4 V, cycle number 40, and scan rate 50 mV s⁻¹ (0.1 mol L⁻¹ of PB at pH 7 was used as the supporting electrolyte).³¹ The made electrode was identified as a GC/MWCNTs/pMO electrode after air drying for 10 min before SWV measurements.

2.5. Electrochemical Determination of FOX-12. The proposed sensor electrode was submerged in a FOX-12-containing 5 mL of electrochemical cell, 0.1 mol L⁻¹ PB, pH 7 (4 mL), and 1 mL of AcCN solution. The SWV was used in a potential range of 0 to -2.1 V, at a frequency of 25 Hz, with an amplitude modulation of 20 mV and a step of 5 mV. To evaluate the interference effects of the nitroaromatic and nitramine-type energetics, AcCN was added to the measurement media to compensate for the insufficient solubility of these energetic materials in the phosphate buffer medium.

2.6. Analysis of Mixtures of Synthetic and Real Energetic Materials. FOX-12 was detected at 50 mg L⁻¹ via the suggested SWV procedure in the presence of 50 mg L⁻¹ of each of the following: nitroaromatic energetic substances (TNT, DNT, and Tetryl), nitramine-type energetic substances (HMX and RDX), NH₄NO₃, real energetic mixtures (Comp B, Octol, and Comp C4), as well as nitrate ester type energetic materials (25 mg L⁻¹ PETN). All synthetic and actual energy materials were made up to a volume with AcCN to a concentration of 1000 mg L⁻¹ (except NH₄NO₃, which was prepared in 0.1 mol L⁻¹ aqueous PB at pH 7).

2.7. Analysis in the Presence of Electroactive Camouflage Materials. Some electroactive camouflage materials in the presence of FOX-12 (due to their color and similar appearance) were investigated as possible interferents.

Preparation of camouflage materials for analysis: Half a vermidon (analgesic drug) tablet (containing 250 mg of paracetamol and 15 mg of caffeine) was dissolved in 25 mL of 0.1 mol L⁻¹ PB (at pH 7) for 15 min in an ultrasonic bath. After filtering through a Chromafil PET-45/25 (0.45- μ m filter), the solution was diluted to the proper concentration in a 25 mL flask containing 0.1 mol L⁻¹ PB (the stock solution's last concentration was 600 mg L⁻¹ of caffeine and 10,000 mg L⁻¹ of paracetamol). As previously mentioned, 250 mg of D-glucose, 14 Canderel tablets (each having 250 mg of aspartame), and half of an aspirin tablet (which included 250 mg of acetylsalicylic acid) were made. These stock solutions had ultimate concentrations of 10,000 mg L⁻¹. In the absence of 500 mg L⁻¹ concentrations for each of these electroactive

camouflage materials, 50 mg L⁻¹ of FOX-12 was measured using the SWV technique.

2.8. Potential Interferences of Certain Soil Ions. FOX-12 at 50 mg L⁻¹ was evaluated in the presence of possibly interfering ions like Cl⁻, CO₃²⁻, SO₄²⁻, NO₃⁻, Na⁺, K⁺, NH₄⁺, Mg²⁺, Ca²⁺, and Pb²⁺ at concentrations of 2000 mg L⁻¹. As Fe³⁺ and Cu²⁺ interfered at a 40-fold concentration of the analyte, Lewatit S1468 was utilized to eliminate the adverse effects of these cations separately.

Usage of the cation exchange resin for Fe³⁺ and Cu²⁺: Two grams of the resin were put in an Erlenmeyer flask containing 100 mL of distilled water, which was then incubated for a day. Afterward, the flask was decanted of its water content. The resin was treated with 250 mg L⁻¹ of FOX-12 and 10-fold concentration levels of Fe³⁺ (the total volume was preserved at 10 mL), and the solution's pH was fixed at 2.5. The substance was moved into a centrifuge tube and spun at 1000 rpm for 90 min. It was then transferred to a volumetric flask after being filtered through Chromafil PET-45/25. For the SWV application, the measurement cell was filled with 1.0 mL of AcCN, 1 mL of the centrifugate solution, and 3.0 mL of 0.1 mol L⁻¹ PB (the last concentrations were 50 mg L⁻¹ of FOX-12 and 500 mg L⁻¹ of Fe³⁺). The potential interference effect for Cu²⁺ was investigated by using the same procedure.

2.9. Validation of the SWV Method Against the Reference HPLC Method. One gram of clay soil was blended with 12.5 mL of a 500 mg L⁻¹ FOX-12 solution to create a suspension of contaminated clay soil, which was then allowed to dry at room temperature. The dried soil was extracted with two (10 mL) successive portions of AcCN, followed by a final 5 mL portion of the same solvent with 5 min of ultrasonic agitation after each extraction. The entire mixture was then put into centrifuge tubes and centrifuged for 5 min at 5000 rpm. Following a filtering process using Chromafil PET-45/25, the centrifugate was added to a 25 mL flask with dilution to the mark (the final concentration was 250 mg L⁻¹ of FOX-12). In order to determine FOX-12 using the recommended SWV method, the working cell received 1 mL of the solution and 4 mL of 0.1 mol L⁻¹ (pH 7) PB. For the validation of the developed method, the literature HPLC-DAD procedure was slightly modified.¹ The analyses were performed with the Hypercarb (100 \times 4.6 mm, 7 μ m particle size) column, which had different dimensional properties from those of the literature method, and the mobile phase contained 90% 0.01% trifluoroacetic acid in water and 10% acetonitrile. Isocratic flow was applied at 1 mL min⁻¹, and the injection volume was set to 50 μ L. The detector was programmed to monitor the wavelengths between 190 and 400 nm, and the absorbance at 210 nm was evaluated for quantitative analyses (for two peaks of N-guanyllurea and dinitramide, as dissociated from FOX-12, with different retention times). Analyses were performed in a 1:1 (v:v) acetonitrile/water medium as solvent. The suggested FOX-12 technique was validated against the standard HPLC technique utilizing the Student *t*- and *F*-statistical tests.

3. RESULTS AND DISCUSSION

3.1. Characterization of the GC/MWCNTs/pMO-Modified Electrode. The developed GC/MWCNTs/pMO-modified electrode was investigated using cyclic voltammetric scans (CV scans), scanning electron microscopy (SEM) images, and impedance measurements. The CV scans were performed on the GC, GC/MWCNTs, and GC/MWCNTs/

pMO electrodes in 5 mmol L⁻¹ of [Fe(CN)₆]^{3-/4-} solution prepared in 0.1 mol L⁻¹ HCl containing 0.1 mol L⁻¹ KCl (as supporting electrolyte) at a 50 mV s⁻¹ scan rate (Figure S6). As a result of CV measurements, it was observed that three electrodes had electroactivity, and using the obtained results, the active surface areas of these electrodes were calculated using the Randles–Sevcik equation.³² All obtained results are given in detail in the Supporting Information section.

Using FEI Model Quanta 450 FEG equipment, the SEM picture of the prepared GC/MWCNTs/pMO was captured, and MWCNTs were clearly visible in Figure 1.

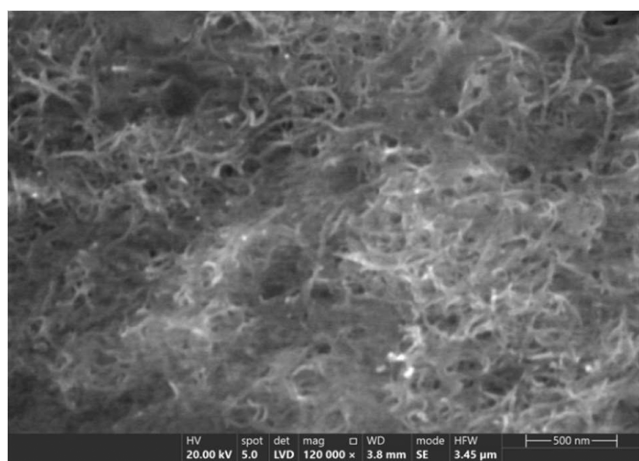


Figure 1. 120,000-fold zoomed SEM images of the GC/MWCNTs/pMO electrode.

The EIS method was used to evaluate the impedance of the GC, GC/MWCNTs, and GC/MWCNTs/pMO electrodes in a 5.0 mmol L⁻¹ [Fe(CN)₆]^{3-/4-} solution (including 0.10 mol L⁻¹ KCl and 0.10 mol L⁻¹ HCl). The points/decade was 10 mV, and the frequency range included 10 mHz to 0.1 MHz. The resistance to electron transport is known as R_{ct} (charge transfer resistance). After measuring impedance, the R_s (solution resistance) and ($R_s + R_{ct}$) values were calculated by using the “electrochemical circle fit” function in Metrohm Autolab’s Nova 2.1.6 program to the acquired semicircle. By subtraction of the R_s value from the ($R_s + R_{ct}$) value, the R_{ct} value was found. In this paper, the values of the R_{ct} were determined to be 141.3 and 93.5 Ω for the GC electrode and GC/MWCNTs/pMO, respectively. The semicircle could not be formed because the R_{ct} value of the GC/MWCNTs electrode was very low. Due to the low charge transfer resistance value (R_{ct} value), the GC/MWCNTs and GC/MWCNTs/pMO electrodes had high electrical conductivity. For the purpose of measuring the impedance of the GC, GC/MWCNTs, and GC/MWCNTs/pMO electrodes, the “fit and simulation” feature of the Nova 2.1.6 software was also used to generate the Randles equivalent circuit. The fitted data are shown in Figure 2.

3.2. Fabrication of the GC/MWCNTs/pMO Electrode.

The experimental section describes the two steps that were used to prepare the GC/MWCNTs/pMO working electrode. First, the GC working electrode surface was covered with 4 μ L of the MWCNTs (0.1 mg mL⁻¹) suspension, which was then dried for 30 min at ambient temperature. The GC/MWCNTs electrode was then placed in an electrochemical cell containing

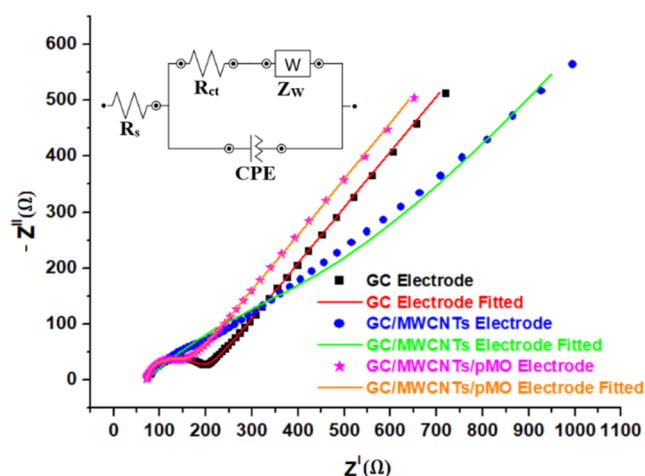


Figure 2. Impedance measurements of the GC, GC/MWCNTs, and GC/MWCNTs/pMO electrodes using the Potentiostat EIS method in 0.1 mol L⁻¹ HCl medium containing 5 mmol L⁻¹ [Fe(CN)₆]^{3-/4-}, and the Randles equivalent circuit was given as inset figure (constant phase element (CPE) and Z_w are Warburg impedance).

5 mL of MO (0.1 mmol L⁻¹) and subjected to the CV technique (Figure 3).

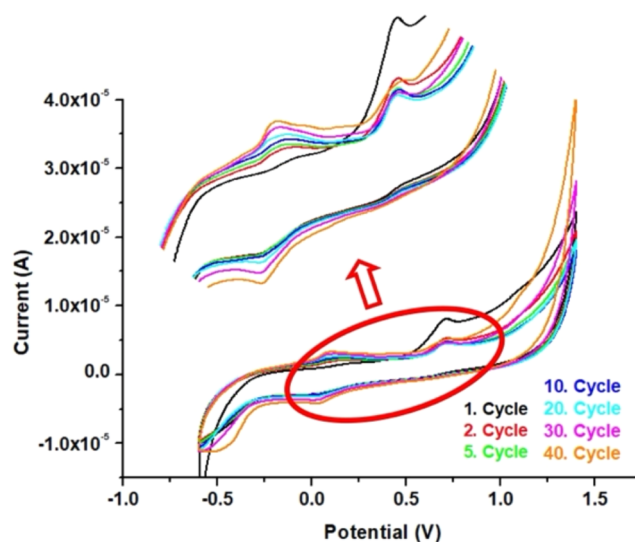


Figure 3. Electropolymerization of MO on the GC/MWCNTs electrode's surface using cyclic voltammetry (0.1 mol L⁻¹ PB (at pH 7) as the supporting electrolyte) (scan rate: 50 mV s⁻¹).

Using 0.1 mol L⁻¹ PB (at pH 7) as the supporting electrolyte, Figure 3 depicts the GC/MWCNTs electrode's surface modification with pMO. The CV cycles began to condense as the polymerization progressed, which was a sign that the pMO layer was depositing on the electrode surface. At the polymerization step, the two oxidation peaks and a reduction peak were obtained at about 0.1, 0.7 and 0.02 V, respectively. After the completion of cycles, the extra methyl orange was removed by using deionized water, leaving behind a thin film of conductive pMO. After the working electrode was air-dried for 10 min prior to SWV measurements, this electrode was named the GC/MWCNTs/pMO electrode.

3.3. Electrochemical Determination of FOX-12. The suggested SWV technique (Step: −0.005 V, Modulation

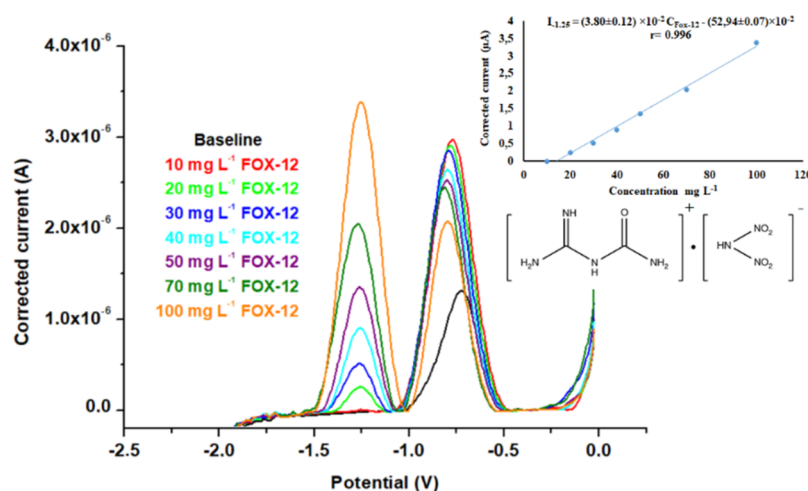


Figure 4. Square-wave voltammograms of FOX-12 taken with the GC/MWCNTs/pMO electrode and FOX-12 structure, and an inset figure depicts the structure and calibration of FOX-12 (Step: -0.005 V, Modulation amplitude: 0.02 V, and Frequency: 25 Hz).

amplitude: 0.02 V, and frequency: 25 Hz) and the GC/MWCNTs/pMO electrode were used to electrochemically determine FOX-12 in a medium containing 1 mL of AcCN and 4 mL of PB, within a potential range of 0 to -2.1 V and a concentration range of 10 to 100 mg L^{-1} . The SWV of FOX-12 is given in Figure 4, where the characteristic reduction peak potential of FOX-12 (originating from its dinitramide constituent) was observed at about -1.25 V and the conversion of O_2 to H_2O_2 may be responsible for the peak appearing at roughly -0.75 V.³³ The voltammetric measurement of FOX-12 was performed using calibration lines ($A = mC + n$) with the appropriate analytical performance parameters [i.e., $\text{LOD} = 3\sigma_{\text{bl}}/m$ and $\text{LOQ} = 10\sigma_{\text{bl}}/m$, where m symbolizes the slope of the calibration line and σ_{bl} the standard deviation of the blank].

The mechanism of FOX-12 determination is based on the electrostatic interaction between the polymerized form of the anionic indicator dye poly(methyl orange) and the cationic constituent of FOX-12, guanyluarea. Poly(methyl orange) bears functional groups such as amino ($-\text{NH}_2$), azo ($-\text{N}=\text{N}-$), and sulfonate (SO_3^-) that increase the hydrophilicity and electroactivity of this indicator dye that is responsible for various interactions with the analyte, particularly the electrostatic interaction between the anionic terminating sulfonate groups of pMO³⁴ and the cationic analyte (i.e., N-guanyluarea constituent of FOX-12). Another possible interaction is intermolecular hydrogen bonding, as confirmed by FTIR measurements shown in Figure 5. By using the developed electrode in conjunction with the SWV technique, the electroreduction of NO_2 groups of the dinitramide part of FOX-12 was measured at -1.25 V.²⁸

FOX-12 calibration equation (at -1.25 V) revealed a linear relationship between corrected current and FOX-12 concentration; $I_{-1.25} = (3.80 \pm 0.12) \times 10^{-2} C_{\text{FOX-12}} - (52.94 \pm 0.07) \times 10^{-2}$ ($r = 0.996$), where $I_{-1.25}$ is the corrected current (μA) at -1.25 V and $C_{\text{FOX-12}}$ is the concentration of FOX-12 (mg L^{-1}). The LOD and LOQ were 1.5 and 5.0 mg L^{-1} , respectively. The created GC/MWCNTs/pMO electrode may be used all day without needing to be cleaned, and its service life is a single week. Furthermore, the intra- and interassay coefficients of variation were 2.24 and 6.61% , respectively (Figures S7–S8).

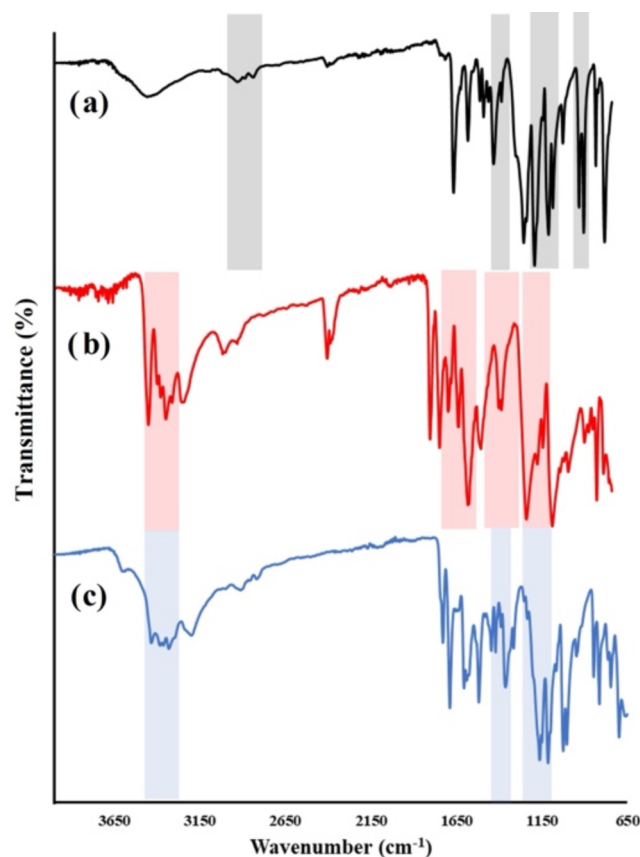


Figure 5. FTIR spectra of pure MO (a), FOX-12 (b), and MO+FOX-12 (c).

In the infrared spectrum of MO in Figure 5a, the C–H stretching peak of the aromatic benzene ring at 3010 cm^{-1} and the C–H stretching peak of the aliphatic chain at 2950 – 2900 cm^{-1} are seen. In addition, the peak observed at around 1420 cm^{-1} is the S = O stretching peak of the sulfonate group. The peaks observed at around 1150 cm^{-1} can be assigned to aliphatic C–H bending, and those at around 900 cm^{-1} can be assigned to aromatic C–H bending. The characteristic primary amine in the guanyluarea group of FOX-12 is seen at 3400 cm^{-1} , and the secondary amine of FOX-12 is seen at 3300 and

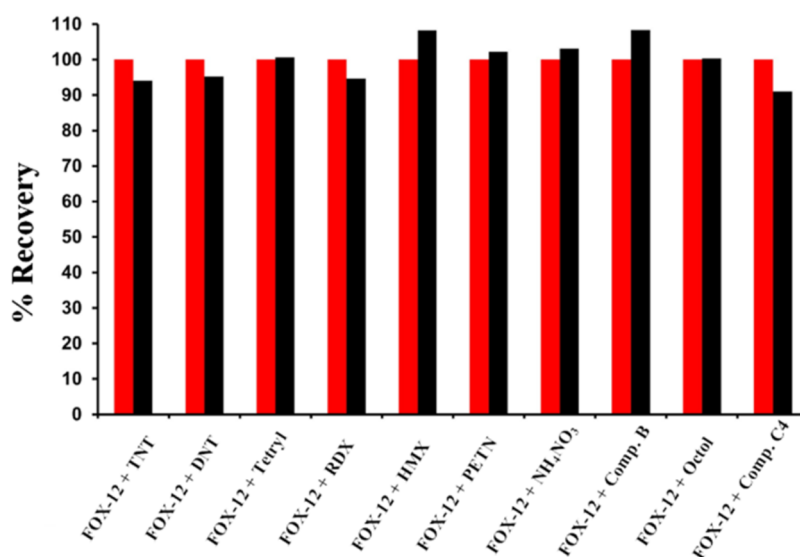


Figure 6. Recovery (%) values of 50 mg L^{−1} FOX-12 in the presence of one-fold concentrations of TNT, DNT, Tetryl, RDX, HMX, PETN (25 mg L^{−1}), NH₄NO₃, and Comp. B, Octol, Comp. C4.

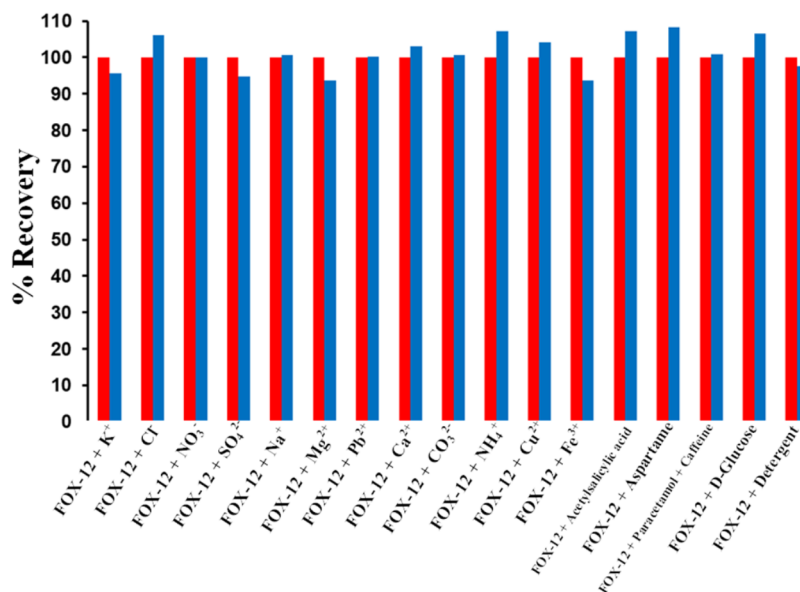


Figure 7. Recovery % of FOX-12 in the presence of electroactive camouflage substances and common soil ions.

3260 cm^{−1} (Figure 5b). While the characteristic peak of the amide-carbonyl group is located at 1650 cm^{−1}, there is an N–O stretching peak at 1490 cm^{−1}. N–H bending peaks are seen as double peaks at 1330 and 1313 cm^{−1}. When the infrared spectrum of MO+FOX-12 given in Figure 5c is examined, the intensity of the primary amine (3400 cm^{−1}) and secondary amine (3300 cm^{−1} and 3260 cm^{−1}) peaks of FOX-12 decreases due to the interaction between the dye and analyte. Proportionally, changes in N–H bending peaks are also observed (the peak at 1313 cm^{−1} becomes sharper and the peak at 1330 cm^{−1} almost disappears). It is clearly seen that the intensity of the S = O stretching mode of the sulfonyl group of MO observed around 1420 cm^{−1} as a characteristic band of the sulfonate group has decreased. All of these data confirm the possible hydrogen bonding and electrostatic interactions between the sulfonyl groups of MO and the amine groups of N-guanyurea of FOX-12.

The developed method was applied to a pure ADN sample to support the proposed detection mechanism. ADN responded at a more negative potential (−1.71 V) than FOX-12, with a smaller peak without any overlap of the peaks. While the determination of ADN is based on the electroreduction of the −NO₂ group of dinitramide, FOX-12 (having the ADN constituent) can be determined at a more positive potential (−1.25 V) than ADN. The negatively charged dinitramide by itself is repelled by the terminal −SO₃[−] groups of pMO on the prepared electrode.

3.4. Analytical Results for Synthetic Mixtures of Energetic Materials and Analysis of Real Samples. The suggested SWV approach was used to quantify FOX-12 at 50 mg L^{−1} in the presence of 50 mg L^{−1} quantities of TNT, DNT, RDX, Tetryl, PETN, HMX, NH₄NO₃, Comp B, Octol, and Comp C4 for binary/multicomponent synthetics and real energetic materials. FOX-12 recoveries were between 91.0 and

108.4% for all mixtures (five repeated experiments; $N = 5$), the results of which are depicted in Figure 6.

3.5. Interferences of Electroactive Camouflage Materials and Common Soil Ions to the Electrochemical Determination of FOX-12. Certain electroactive substances, including caffeine, paracetamol, D-glucose, acetylsalicylic acid, aspartame, and detergents, were used as camouflage substances, and their interference effects were investigated due to their comparable look and color. These materials did not interfere with the analysis of FOX-12 (50 mg L^{-1}) at 10-fold concentrations of the analyte, and the recoveries were found to be 97.7 to 108.2% (Figure 7). Additionally, the common soil ions' interfering effects were also examined, and no interference was observed in the quantification of FOX-12 (50 mg L^{-1}) in the presence of 40-fold of ions such as Cl^- , CO_3^{2-} , SO_4^{2-} , NO_3^- , Na^+ , K^+ , NH_4^+ , Mg^{2+} , Ca^{2+} , and Pb^{2+} . Due to their strong electroactivity, Fe^{3+} and Cu^{2+} ions were found to interfere at comparable concentration levels. To eliminate the interference caused by these ions, we employed Lewatit S1468 for cation exchange. Subsequently, 50 mg L^{-1} of FOX-12 was measured in the presence of Fe^{3+} and Cu^{2+} at 10-fold concentrations, and the recoveries lay between 93.6 and 108.2% for all ions studied (Figure 7).

3.6. Analytical Results for Contaminated Clay Soil Samples. The HPLC-DAD literature method was carried out for analyzing clay soil samples contaminated with FOX-12 in order to validate the developed method. The retention time for the N-guanylurea constituent of FOX-12 was 1.38 min, while that for the dinitramide constituent was 13.36 min. Analyses were performed in 1:1 (v:v) acetonitrile/water as solvent. Similar to the fact that the nitro groups on dinitramide are reduced to amine groups in voltammetric analysis, the signals obtained for dinitramide were higher in HPLC analysis (details were given in section 2.9), and the peak evaluated in constructing the calibration line and employing statistical tests pertained to dinitramide. First, the linear calibration line of FOX-12 was studied in the concentration range of 10–100 mg L^{-1} in 1:1 (v:v) acetonitrile/water solvent medium under the specified conditions, and the calibration equation for the relationship between FOX-12's peak area and concentration was:

$$\begin{aligned}\text{peak area} &= (3.6 \times 10^4 \pm 6.22 \times 10^2) C_{\text{FOX-12}} \\ &\quad - (6.5 \times 10^3 \pm 3.5 \times 10^4) (r \\ &= 0.9995)\end{aligned}$$

where $C_{\text{FOX-12}}$ was the FOX-12 concentration (in mg L^{-1}) in the final solution. For HPLC tests, the extract from the contaminated clay soil sample (which included 250 mg L^{-1} FOX-12 in the final solution) was diluted five times, it was then used directly for the SWV experiments on $N = 5$ repetitive determinations, the findings produced using the two approaches were statistically compared, and there were no noteworthy variations in the accuracy and precision of the data as presented in Table S1.

4. CONCLUSIONS

FOX-12 is extensively utilized in military applications, including firearms, high-explosive formulations, and insensitive warhead fillings, specifically in artillery, bombs, mortar ammunition, and armored vehicles such as tanks. Due to its water solubility, FOX-12 can be introduced into the environ-

ment through wastewater discharge or detonations, posing significant risks to groundwater, surface water, and soil quality. Although insensitive munitions comprising FOX-12 offer increased safety due to their resistance to unintended detonation relative to conventional formulations, FOX-12 is still toxic to algae, which may adversely affect the food chain of aquatic organisms. Considering the absence of relevant electroanalytical assays, a novel alternative technique for the accurate and practical measurement of FOX-12 in soil and groundwater needs to be developed. By adjusting the surface of a GC electrode with MWCNTs (solution dripped onto the electrode surface) and poly(methyl orange) (pMO) (modified using electropolymerization of MO via cyclic voltammetry), the novel GC/MWCNTs/pMO electrode was created in this work. This allowed for the sensitive and selective detection of FOX-12 in solutions of both synthetic and real mixtures of energetic substances by using the recommended SWV method. The mechanism of the study is based on the electrostatic interaction between the anionic dye, pMO, and the cationic group of FOX-12, N-guanylurea. By using the developed electrode and SWV technique, the reduction of NO_2 groups of the dinitramide part of FOX-12 was evaluated at about -1.25 V . The suitability of the designed electrode for this purpose is also reflected in the observation that FOX-12 behaved as a whole in this electroreduction, meaning that the dinitramide part did not act independently; ammonium dinitramide (ADN) responded at a more negative potential (-1.71 V) than FOX-12 with a smaller peak, without any overlap of the peaks.

The MWCNTs improved the produced electrode's catalytic activity (rapid response) and stabilized the detection potential when added to the GC electrode surface. CV scans, SEM, and electrochemical impedance measurements were used to characterize the designed GC/MWCNTs/pMO electrode before the FOX-12 measurements. Furthermore, a thorough analysis of the method's optimization parameters was conducted. The GC/MWCNTs/pMO electrode, which can be used for up to 1 week without cleaning, was the first that has been developed for the electrochemical determination of FOX-12. Using the fabricated GC/MWCNTs/pMO electrode and the proposed SWV technique, FOX-12 was electrochemically detected and quantified in the presence of common soil ions, synthetic and real mixtures of energetic compounds, and electroactive camouflage materials with good recoveries. The intra- and interassay coefficients of variation were determined to be 2.24% and 6.61%, respectively. The proposed SWV method was further employed for the analysis of clay soil samples contaminated with FOX-12 and subsequently subjected to statistical validation against HPLC using Student's *t*-test and *F*-test. As a result, the established SWV approach is the first in the literature to electrochemically determine FOX-12 using the suggested GC/MWCNTs/pMO electrode and is simple, accurate, repeatable, readily applicable, selective, and sensitive.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.5c01805>.

- Investigation of the supporting electrolyte;
- pH investigation of the phosphate buffer;
- investigation of the acetonitrile amount;
- investigation of

MWCNTs amount for the preparation of the working electrode; (v) examination of the number of cycles used in the electropolymerization stage of MO; (vi) characterization of GC/MWCNTs/pMO-modified electrode and calculation of active surface area; (vii) intra-day and inter-day repeatability results; and (viii) analytical results of method validation experiments (PDF)

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A.K.A.M.: formal analysis and writing—original draft preparation. Ş.S.: formal analysis, investigation, and writing—original draft. Z.C.: validation and writing—original draft. A.Ü.: conceptualization, supervision, and writing—original draft preparation. R.A.: conceptualization, methodology, and writing—reviewing and editing.

Notes

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ABBREVIATIONS

FOX-12, N-guanylurea dinitramide; SWV, square-wave voltammetry; GC, glassy carbon; MO, methyl orange; TNT, 2,4,6-trinitrotoluene; RDX, 1,3,5-trinitroperhydro-1,3,5-triazine; HMX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazosine; TATB, triaminotrinitro benzene; NMP, N-methylpyrrolidone; DMSO, dimethyl sulfoxide; AcCN, acetonitrile; DMA, N,N-dimethylacetamide; MWCNTs, multiwalled carbon nanotubes; HPLC, high-performance liquid chromatography; DNT, 2,4-dinitrotoluene; PETN, 3-(nitrooxy)nitrate-2,2-bis[(nitrooxy)methyl]propyl; tetryl, trinitrophenylmethyl nitramine; PB,

phosphate buffer; CV, cyclic voltammetry; SEM, scanning electron microscopy; R_s , solution resistance; R_{ct} , charge transfer resistance; CPE, constant phase element; LOD, limit of detection; LOQ, limit of quantification

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