

Voltammetric and Amperometric Detection of Nitrated Explosives (A Review)

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Abstract: In this article, possibilities of electrochemical detection of various explosives containing electrochemically active nitro group are reviewed. Attention is paid both to the use of traditional mercury electrodes and non-traditional, recently developed electrodes based on mercury amalgams, bismuth films, boron-doped diamond films and carbon films in voltammetric and amperometric mode. Screen-printed, chemically modified and/or biologically modified electrodes are discussed as well. Advantages and disadvantages of electroanalytical techniques are briefly discussed together with their possible combination with a preliminary separation and preconcentration using liquid-liquid extraction or solid phase extraction. Electrochemical detection of reducible explosives in flowing media using above mentioned electrodes is briefly disused, attention being paid to wall-jet, thin-layer, tubular and cylindrical arrangement of the detection system.

Keywords: Explosives; Mercury electrodes; Amalgam Electrodes; Bismuth film electrodes; Boron-doped diamond film electrodes; Carbon film electrodes; Voltammetry; Amperometry.

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Introduction

There is an ever increasing demand for sensitive and selective methods capable to detect trace amounts of nitrated explosives ([1,2]; see Fig. 1); the typical examples of such methods being summarized in Table I.

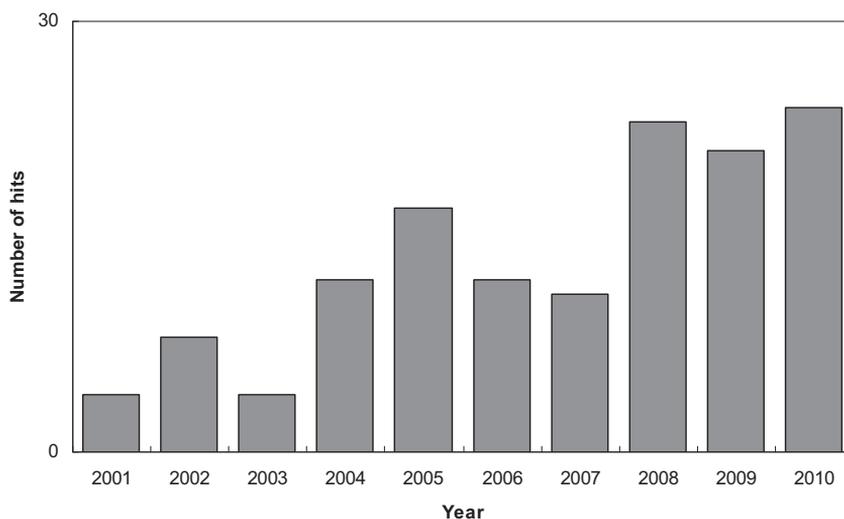


Fig. 1: *The number of publications related to voltammetry or amperometry of explosives in the database SciFinder of Chemical Abstracts Service (CAS).*

Electroanalytical methods are uniquely qualified for the determination of nitro group containing explosives because of easy electrochemical reduction of nitro group [3] connected with the exchange of 2, 4, or even 6 electrons resulting in high sensitivity of appropriate voltammetric or amperometric detection. From the broad spectrum of available electroanalytical methods [4], differential pulse voltammetry [5], square wave voltammetry [6] and adsorptive stripping voltammetry [7] are most frequently exploited for the determination of organic compounds containing nitro group.

The most suitable electrode for voltammetric detection of nitro compounds is the hanging mercury electrode (HMDE [8]) because of its atomically smooth and easily renewable surface and broad cathodic potential windows. However, unsubstantiated fears of mercury toxicity initiated a large scale search for new – more environmentally friendly and less toxic - electrode materials [9,10].

Another advantage of electroanalytical methods is easy miniaturization of corresponding instrumentation. In connection with recent advances in microelectronics and microfabrication, it can result in construction of easily portable, low cost, compact, and 'user-friendly' apparatus with low power demands suitable for low cost field detection of nitrated explosives [2] and for addressing security and environmental problems connected with the occurrence of nitrated explosives.

Table I: Structural formulas of typical nitro group containing explosives

Name	CAS#	CAS name	Structure
6-Methyl-2-nitroaniline	570-24-1	Benzenamine, 2-methyl-6-nitro-	
Trinitrotoluene	118-96-7	Benzene, 2-methyl-1,3,5-trinitro-	
Pentrit	78-11-5	1,3-Propanediol, 2,2-bis[(nitro-oxy)methyl]-, 1,3-dinitrate	
RDX, Hexogen	121-82-4	1,3,5-Triazine, hexahydro-1,3,5-trinitro-	
HMX, Octogen	2691-41-0	1,3,5,7-Tetrazocine, octahydro-1,3,5,7-tetranitro-	
Picric acid	88-89-1	Phenol, 2,4,6-trinitro-	
Tetryl	479-45-8	Benzenamine, N-methyl-N,2,4,6-tetranitro-	
2,6-Dinitrotoluene	606-20-2	Benzene, 2-methyl-1,3-dinitro-	
9-Nitroanthracene	602-60-8	Anthracene, 9-nitro-	
1-Nitronaphthalene	86-57-7	Naphthalene, 1-nitro-	

Recent activity in our laboratories has led to disposable sensor strips, submersible sensors (on a cable or underwater-vehicle platforms), a voltammetric flow detector, and amperometric detectors for microchip ('Lab-on-Chip') devices for on-site electrochemical measurements of nitrated explosives.

Non-Traditional Working Electrodes for Determination of Nitrated Explosives

Amalgam Electrodes

Amalgam is attractive alternative to mercury as the traditionally best material for electroanalytical cathodic reduction measurements. Amalgam electrodes are nontoxic alternative to mercury electrodes. They have similar size of potential window and similar sensitivity as the hanging mercury drop electrode [11]. Therefore, amalgam electrodes can be used for the determination of explosive agents and for development of electrochemical sensors. Good example of their applicability is sensitive voltammetric determination of picric acid using silver amalgam paste electrode [12]. The developed method was optimized (Britton-Robinson buffer pH 2 as a supporting electrolyte; see Fig. 2, overleaf) and a linear response at AgA-PE was observed over the $2 \times 10^{-6} - 1 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ of picric acid concentration range, with a determination limit of $5.6 \times 10^{-8} \text{ mol}\cdot\text{L}^{-1}$. The method was successfully applied for the direct determination of picric acid in drinking and river water.

Bismuth Electrodes

Another nontoxic substitute for mercury electrodes — bismuth-based electrodes — attained a lot of attention during the last decade. Bismuth film allows one to modify surface of other solid electrodes, broadening thus their applicability in cathodic potential window. Jacobsen et al. suggested directly heated bismuth film electrodes based on gold micro-wires [13]. The gold bismuth alloy modified wire electrode provided the highest sensitivity compared with both plain Au wire and bismuth film electrode. Properties of picric acid were studied by cyclic voltammetry in acid and alkaline media. At optimal conditions, it was possible to detect 3 ppm of picric acid with temperature pulse amperometric measurement in media of $10 \text{ mmol}\cdot\text{L}^{-1}$ NaOH solution containing $5 \text{ mmol}\cdot\text{L}^{-1}$ of tartaric acid.

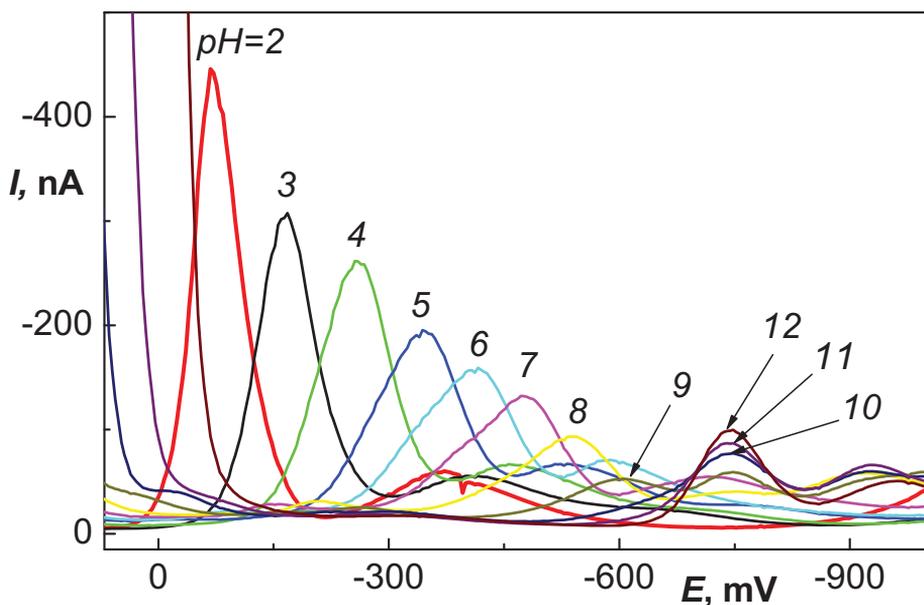


Fig. 2: Differential pulse voltammograms of picric acid ($100 \mu\text{molL}^{-1}$) at silver amalgam paste electrode in Britton-Robinson buffer (pH 2-12). Note: As indicated, numbers inscribed above the curves correspond to the pH given. (From authors' archives)

Boron-Doped Diamond Film Electrodes

Diamond present exciting material with very specific properties and in the case of boron-doped diamond (BDD) modification obtains sufficient conductivity for electrochemical use. Diamond based electrodes offer many advantages compared to other solid electrodes usually used: low and stable background current over a wide potential range, corrosion resistance, high thermal conductivity and high current densities. Usually no mechanical or electrochemical pretreatment of BDD film electrode is needed. Therefore, BDD film electrodes find use also in the area of environmental analysis and for organic explosives determinations [14]. The next advantage of BDD is that it enables indirect oxidation by electrogenerated active intermediates, such as hydroxyl radicals, which can be used for degradation of nitrated explosives [15].

BDD based electrochemical detector allowed amperometric detection in 15 mM borate buffer (pH 9.2, containing 15 mM sodium dodecyl sulfate) of TNT, 1,3-dinitrobenzene and 2,4-dinitrotoluene over the 200–1400 ppb range, with detection limits at the 100 ppb level [16].

In this case the diamond electrode offers enhanced sensitivity, lower noise levels, and sharper peaks in comparison with thick-film carbon detector for several groups of important analytes (nitroaromatic explosives, organophosphate nerve agents, phenols).

Screen-Printed Electrodes

Disposable screen-printed electrodes (SPEs) present direction of development to single use sensors for routine analysis. Method of screen printing allows one to construct the whole electrode systems. It could be important for analysis in complex matrix or in the case of risk of cross sample contamination. Otherwise, the SPEs seem to be the optimal supporting material for electrode modifications in routine analysis.

Screen-printed carbon thick film electrodes were demonstrated as suitable sensors to measure TNT by square wave voltammetry in as little as 50 μL sample volume [17]. This assay was coupled with a solid phase extraction. The preconcentration factor of 1:500 yielded a 100-fold higher sensitivity, giving finally a calibration range of 2 ppb – 2 ppm for TNT.

A polyphenol-coated screen-printed carbon electrode was used for highly sensitive voltammetric measurements of TNT in the presence of surface-active substances [18]. After this modification the high levels of gelatin, humic acid and sodium dodecyl sulfate (up to 50 mgL^{-1}) had negligible effects upon the square-wave voltammetric TNT response in 0.5 molL^{-1} sodium chloride. Detection limit was around 1 ppm TNT.

Measurement in single 20 μL drop of sample was proposed for three electrode screen printed system based on preanodized carbon electrode [19]. The preanodization treatment of working electrode — *i.e.*, application of highly positive potentials — makes the peak sharper and hence provides a precise way to identify the substituent effect on nitroaromatic compounds. The method allowed square-wave voltammetric determination of TNT in lake water at the micromolar level.

Voltammetric determination of explosive in gas phase was realized by coating of screen printed three electrode system by hydrogel based on 0.5 molL^{-1} potassium chloride in agarose [6]. The thermally desorbed TNT from a preconcentration device was moved by gas at a flow rate of 500 $\text{mL}\cdot\text{min}^{-1}$ to detection system and concentration was measured using rapid square wave voltammetry. The detection system produced linear signal dependence on quantity of TNT exposed to the preconcentrator from 0.25 to 10 μg . Applicability of the integrated device was successfully demonstrated using a sample of solid TNT located upstream of the preconcentrator.

Electrochemical Detection of Explosives in Flowing Systems

HPLC and Flow Injection Systems with Electrochemical Detection

Chromatographic methods are one of most powerful for separation of analyte from complex samples, but selective electrochemical detection can significantly improve detection ability for electro-active species. In the case of electrochemical detection the complete separation of analytes is also not necessary. The electro-active substance could be determined in presence of other chemicals [20]. Therefore, electrochemical detection is useful for fast flow injection analysis of different samples. This point is important for determination of explosives in complicated environmental matrices.

By coupling reversed phase columns of different selectivity together, baseline resolution of 14 standard explosives was achieved [21]. Additional selectivity of amine-substituted nitroaromatic explosives was achieved by using a photochemical reactor with a 366-nm wavelength lamp. After passing through the photoreactor, the eluent enters a thin-layer electrochemical cell, which is fitted with a 1.0 mm diameter glassy carbon working electrode and a silver-silver chloride reference electrode. For selected explosives, the method had a detection level of around $0.2 \mu\text{g mL}^{-1}$.

Alternative method is a post-column quantitative reduction and reaction with oxidizing agent allowing photoluminescence detection [22]. A porous carbon electrode was used for on-line analyte reduction at potential of $-1500 \text{ mV vs. Ag/AgCl}$ and produced hydroxylamines and nitrosamines react readily with tris(bipyridyl)ruthenium(III) to tris(bipyridyl)ruthenium(II) and this compound was detected by laser illumination and light detection. Detection limits were in the low nanomolar range for $20 \mu\text{L}$ injections of non-preconcentrated nitro explosives.

Lab-On-Chip Systems

“Lab-on-a-chip” technology, particularly micromachined capillary electrophoresis system, offers great promise for obtaining the desired forensic information in a faster, simpler and cheaper matter compared to conventional laboratory-based techniques. Furthermore, consumption of solvents, samples and other chemicals is significantly lower than for common techniques. Therefore, these microchip based method are in agreement with the concept of green analytical chemistry.

Simple crossing of four channels microfluidic device was developed for flow-injection/electrochemical analysis of TNT [23]. This method enabled to perform around 150 assays per one hour and the determination at an amalgam mercury/gold disc electrode at a fixed potential of -600 mV vs. ref. has resulted in the detection limit of about $7.0 \mu\text{g L}^{-1}$; also, sample volume $3 \mu\text{L}$ on assay being negligible, indeed.

Similar arrangement allow also electroforetic separation of the neutral nitro aromatic explosive and nerve agent compounds in the microchip channel and or total assays of explosives. [24] Separation was supported by the presence of sodium dodecyl sulfate. Assays rates of about 360 and 30 per hour can thus be realized for the “total” screening and “individual” measurements, respectively. Thick-film carbon working electrodes at a detection potential of 500 mV allowed determination of DNT and TNT on level 60 ppb.

The end-column amperometric detection with boron-doped diamond film electrode after microchip analysis has shown a strong influence of the electrode material selected for manufacturing [16]. The stability of the signal of interest was much higher than that achieved for the alternatively used thick-film carbon electrode and the optimized method could then offer a linear dynamic range over the concentrations of 200–1400 ppb for both 1,3-dinitrobenzene and 2,4-dinitrotoluene.

Conclusions

Growing requirements for safety controls, contamination of large areas of environment after war conflicts lead to the development of new methods for determination of explosives. Among them, also electrochemistry plays an important role and *e.g.* selective and sensitive voltammetric methods represent one of possible directions in future development. Almost the same can be stated about the amperometric detection in combination with HPLC and capillary electrophoresis; the respective methods and procedures offering a number of interesting applications in modern analysis of explosives and their chemistry as such [25].

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