



## Voltammetric determination of trinitrotoluene (TNT) at antimony-modified glassy carbon paste electrode in polluted soil sample collected in an industrial area

Ivan Švancara<sup>1\*</sup>, Barbora Dellingerová-Perinajová<sup>1</sup>,  
and Hanna Ingrid Sopha<sup>2</sup>

<sup>1</sup> *Department of Analytical Chemistry, The University of Pardubice, Studentská 573, CZ–532 10 Pardubice, Czech Republic*

<sup>2</sup> *Center of Materials and Nanotechnologies – CEMNAT, The University of Pardubice, nám. Čs. legií 565, CZ–530 02 Pardubice, Czech Republic*

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*2,4,6-trinitrotoluene (TNT) in polluted soil sampled in the area of a factory producing industrial explosives could be determined using an antimony film pre-plated ex-situ onto a glassy carbon paste electrode (SbF-GCPE) in combination with square-wave cathodic stripping voltammetry (SWCSV). For electrochemical measurements in Britton-Robinson buffer (BRB, pH 9), the substance of interest had to be transferred from solid sample into the solution by extracting with aqueous or water / methanolic media of chosen composition and adjusted pH, in some cases, followed by neutralising the extracts with solid NaHCO<sub>3</sub>. A comparison of the results from analyses of four different solutions has allowed us to evaluate the most effective extracting agent, which was the case of a mixture of 0.5 M CH<sub>3</sub>COOH in 30% CH<sub>3</sub>OH neutralised with solid NaHCO<sub>3</sub>, and further diluted with BRB (pH 9) in order to yield pH ~ 8. In this medium, the SWCSV analysis with SbF-GCPE has resulted in the content of 3.77 μg TNT in 10 mL extract, which corresponded to the same contents in mg per 1 kg of dried soil. This has represented ca. 85% recovery with the result obtained with GC-MS, which can still be considered as acceptable agreement.*

**Keywords:** Antimony film; Glassy carbon paste electrode; Cathodic stripping voltammetry, Trinitrotoluene (TNT); Determination; Polluted soil.

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\* Corresponding author, ✉ Ivan.Svancara@upce.cz

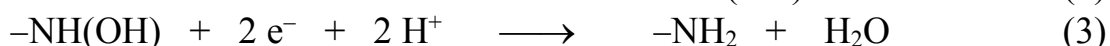
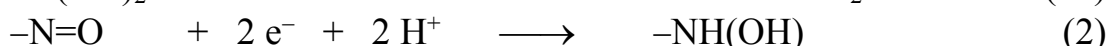
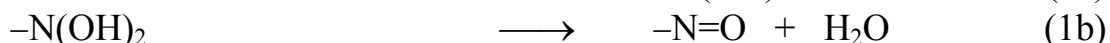
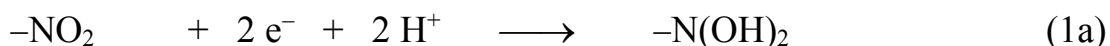
## Introduction

Nearly two decades, the so-called *non-mercury* (or also *mercury-free*) *metal film plated electrodes* (MeFEs) represent one of the most popular topics in modern electroanalysis [1]. The respective research activities had begun on the verge of a new millennium, when Hočevar et al. reported for the first time on a novel type of the working electrode for electrochemical stripping analysis (ESA) based on a thin bismuth film deposited onto the glassy carbon electrode [2], since then known as the BiFE type [3]. Their configuration, together with similar variants (e.g. [4–6]), had soon attracted electrochemists and electroanalysts worldwide, resulting in a real boom of a myriad of related electrodes, sensors, and detectors, including some multi-electrode systems.

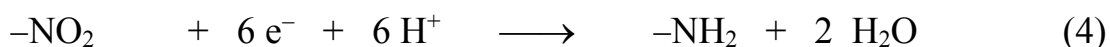
Among fundamental types of MeFEs, one can also classify the antimony-modified configurations; mainly, antimony film electrode (SbFE) co-discovered by our electroanalytical group [7]. In ESA, it offers the analytical performance comparable to the BiFE although there are some specifics [7–9] limiting its practical applicability; mainly, for detection of organic compounds.

However, this is not the case of polynitrated aromates known mainly as the highly effective (secondary) explosives with both industrial and military use [10] and of permanent interest with respect to analysis in various samples [11]. Due to the presence of highly electroactive groups  $-\text{NO}_2$ , these substances belong amongst readily electroreducible species, giving rise to distinct and well-developed signals at a relatively high sensitivity [12,13]. Moreover, their residua have to be monitored in the environment as organic pollutants with potentially high (cyto)toxicity (see e.g. [14]).

Perhaps, the most frequent substance from the family of polynitroaromates is *2,4,6-trinitrotoluene*,  $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{CH}_3$ , notoriously known under the abbreviation "*TNT*". Also this yellowish compound offers a very fine electrode behaviour, giving rise to a cascade of three reduction signals during the voltammetric detection at most common electrodes [15,16]. The respective mechanism, almost redrawn from the latter report [16], can be described by the following consecutive steps,



as well as by the overall reaction scheme,



both indicating the six-electron transformation.

And if one considers the molecule of TNT as a whole, the full reduction process, taking place in aqueous solutions at a mild alkaline pH, involves 18 electrons plus 18 protons [13–16], making the TNT particularly electroactive compound. Although there have been also some proposals of alternate reaction pathways (see e.g. commentary in [15]), the ECEE mechanism illustrated by equations (1)–(3) and summarised in (4) prevails as a majority consensus. Otherwise, the TNT is undoubtedly the most frequently determined polynitroaromate in practical electroanalysis, which can be documented on a collection of reports dedicated to this explosive and presenting the methods published in last two decades and employing various carbonaceous electrodes and sensors [17–24].

As the working electrodes of choice for voltammetric determination of TNT, the above-introduced MeFEs have also been tested recently; namely, bismuth- and antimony-film based configurations, both incorporating carbon-paste based electrodes as relatively often selected supports (see e.g. [3,25] and refs. therein). Regarding their use for the determination of TNT, both carbon paste mixtures had been made from a special glassy carbon powder (with spherical particles [26]), resulting in two similar configurations: (i) BiF-GCPE [27,28] and (ii) SbF-GCPE [29]. Similar were also the respective measurements performed in the stripping voltammetric mode and representing initial studies with both BiF-GCPE and SbF-GCPE in order to develop simple methods for analysis of real samples. However, in the reports cited above [27–29], all the experiments of quantitative nature were carried out with model solutions only. Analyses of truly real samples were completed later on and the corresponding experiments added extra into a diploma thesis [30].

In the following sections, this additional material is for the first time reported in the form of a standard scientific paper, offering all the important observations and results from analyses of authentic real specimens – polluted soil and a blank sample collected in the area of a factory manufacturing industrial explosives and related products.

## Materials and methods

### Chemicals and reagents

All chemicals used were of analytical reagent grade and purchased from Sigma-Aldrich or Merck; namely, 96% acetic acid ( $\text{CH}_3\text{COOH}$ ; diluted as required prior to use), methanol ( $\text{CH}_3\text{OH}$ ), and the stock solutions of the acids and hydroxide for universal *Britton-Robinson buffer* ("BRB", [31]), prepared by mixing the solution "A" ( $0.04 \text{ M H}_3\text{BO}_3 + 0.04 \text{ M H}_3\text{PO}_4 + 0.04 \text{ M CH}_3\text{COOH}$ ) with solution "B" ( $0.2 \text{ M NaOH}$ ) at the given ratio and eventually diluted with water in order to yield the desired pH. In this work, if not stated otherwise, a typical mixture of BRB was that with  $\text{pH} \sim 9$ .

A stock solution with  $1000 \text{ mg L}^{-1}$  2,4,6-trinitrotoluene (TNT) was prepared by dissolving the appropriate amount of solid substance in pure  $\text{CH}_3\text{OH}$ , similarly like a solution of 1-nitrobenzene (NB) utilised in one special study and containing 10 mg substance in 10 mL  $\text{CH}_3\text{OH}$ .

For preparation of the *ex-situ* (pre-plated) antimony film, an appropriate amount of  $\text{Sb}^{\text{III}}$  standard for AAS (with  $c_{\text{Sb}} = 1000.0 \pm 0.1 \text{ mg L}^{-1}$ ) was taken, mixed with 10 mL 0.2 M sodium/potassium tartrate and diluted up to 100 mL with 0.01 M HCl. Deionised water obtained by passing distilled water through a Milli-Q purification unit (Millipore, USA) was used throughout the work.

## Apparatus and other instrumentation

Voltammetric measurements were carried out using a modular electrochemical system AUTOLAB (model "PGSTAT 30"; Ecochemie, Utrecht, Holland) operated via the Nova 1.10 software (Metrohm / Autolab B.V.).

A common three-electrode configuration was employed with the working electrode specified below, a Ag/AgCl/3M KCl as the reference, and with a Pt-plate ( $5 \times 3 \text{ mm}$ ) counter electrode completing the cell. During the deposition and conditioning steps, the solutions were stirred using a magnetic stirrer rotated at *ca.* 300 rpm. All the experiments were carried out at room temperature of  $22 \pm 1 \text{ }^\circ\text{C}$  in an ordinary voltammetric vessel (with a working capacity of 20 mL).

Wherever needed, pH values were measured with an InoLab E/pH-meter (model "pH 720"; WT Werke, Germany) with the combined pH-electrode (type "Sen Tix 41") calibrated with a set of commercial standard buffers.

## Working electrode

### *Glassy carbon paste electrode (GCPE)*

The native carbon paste for the support electrode was prepared by thoroughly hand-mixing of glassy carbon powder ("Sigradur-G" product; HTW Maitingen, Germany) with 20% (v/v) paraffin oil (mixture of alkanes, a solvent for UV spectroscopy; Merck).

The resultant mixture was homogenized using a pestle and mortar until it had resembled a tough plastic mass, and subsequently filled into a piston-driven electrode holder with the active surface of *ca.*  $7 \text{ mm}^2$  and of own construction (for details see [32]). Prior to a series of new measurements, the surface of GCPE was renewed by extruding approximately 0.5 mm layer of carbon paste out of the holder and smoothed with a wet filter paper.

### *Antimony-film glassy carbon paste electrode (SbF-GCPE)*

The metallic film was generated *ex-situ*, when the bare GCPE support was (pre)plated in 0.01 M HCl + 5 mg Sb<sup>III</sup> (as the complex antimonyl tartrate; pH ~ 2), by applying a potential of –1.0 V vs. ref. for 60 s under stirring.

Before the film preparation, the electrode surface of the GCPE support was occasionally renewed mechanically (see above), but always regenerated / conditioned electrochemically at +0.5 V vs. ref for a period of 30 s.

### Real sample(s)

The specimen of polluted soil was obtained from a factory producing industrial explosives\*. The soil was sampled from sand-like earth forming the bed of a shooting range located inside the area of the factory and serving for testing the newly synthesised explosives. Collected amount of the sample (*ca.* 50 g) was cleaned from mechanic impurities, dried in desiccator, transferred into a small vial, tightly closed and, prior to analysis\*\*, stored (in dark) in a refrigerator at 4 °C. For comparative measurements, a blank sample was also collected in the area of the factory and, after cleaning and drying, stored in the same way.

Both polluted soil and blank samples were grinded into fine powders and two equal portions of 10 g (weighted with analytical precision) extracted with 100 mL of one from the four solvent chosen (see below). The extraction took place under moderate stirring for 60 min, as well as by keeping the vessels with extracts in water bath at a temperature of 40 °C. At the end, both extracts were left to cool down and all the undissolved matter removed by filtration.

Three different media were selected as extraction-enabling solvents\*\*:  
(1) 0.5 M CH<sub>3</sub>COOH; (2) 30% CH<sub>3</sub>OH; (3) 0.5 M CH<sub>3</sub>COOH + 30% CH<sub>3</sub>OH, together with (4) pure BRB (pH 9). In all cases, polluted-soil and blank samples were extracted in parallel.

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\* In Czech Republic, the production of explosives belongs amongst domains with a special status controlled by the state. Hence, in this article, the factory supplying the soil polluted by industrial explosives is anonymised and no further specified.

\*\* A special regime applies also to some details associated with the analysis of polluted-soil and blank samples performed yet before both specimens were offered for voltammetric analysis as truly real samples (see ref. [33]). Both samples had been analysed in the factory's control laboratory by GC-MS in order to identify TNT plus other residua and, in combination with the method of internal standard, to quantify the individual items and their mutual abundance. More specifically, the polluted-soil sample from the shooting-range bed contained (i) 4.45 mg TNT per 1 kg dried soil, (ii) *ca.* three-fold less amount of two major degradation products: 2,6,-dinitro- and 4,6-dinitrotoluenes, DNTs, and (iii) little traces of *p*-toluidine; other minor species like mono-nitrotoluenes, had not already been identified.

In blank sample, only negligible traces of TNT and DNTs had been found out; in all cases, close to the detection limit(s). Herein, it should also be noted that both polluted soil and blank samples were analysed *ca.* two years ago and then stored — as conserved — for later control assays. Due to the emphasised special regime, more updated and therefore "fresher" sample(s) could not be supplied.

Whereas the extracts (2) and (4) were ready for use in voltammetric analysis, the acidic solutions (1) and (3) had to be neutralised by  $\text{NaHCO}_3$  in solid state to attain a weak alkalinity within pH 7.5–8.0, before mixing with BRB (pH 9) prior to voltammetric analysis. So processed extracts were yet filtered to remove the undissolved carbonate salt.

## Procedures

### *Square-wave cathodic stripping voltammetry (SWCSV)*

Typical measurements were carried out in a mixture of 10 mL sample solution + 10 mL BRB (pH 9) as the supporting electrolyte. Under stirring, the pre-concentration was performed at  $-0.3$  V vs. Ag/AgCl ("ref.") for 60 s or 180 s; then, stirring was stopped and after the equilibrium period for 10 s, the stripping curve recorded in the cathodic voltammetric mode within a potential range from  $-0.3$  V to  $-1.3$  V vs. ref. Based on previous optimisation [19], the square-wave voltammetric potential ramp was selected and the following instrumental parameters set up: step potential,  $E_{\text{SW}} = 4$  mV; frequency,  $f_{\text{SW}} = 25$  Hz; the pulse height,  $\Delta E_{\text{SW}} = 50$  mV. If not stated otherwise, the sample solution was purged by bubbling with inert gas (argon, 99.99%; Linde) to remove dissolved oxygen; usually, this additional step required 5 min, in some cases even 10 min.

### *Evaluation of measurements and processing the data*

All the stripping signals of interest were measured as the current intensities — typically, in  $\mu\text{A}$  — using software and the included procedure for the peak-height evaluation.

### *Analyses of real samples and computing the results*

After checking procedure on a model solution (for details, see [30]), the samples with real specimens were analysed by the method of multiple standard addition. Namely, the respective sample solution was analysed by measuring the sample itself followed by three consecutive aliquots of the TNT standard. The results of analyses were obtained by evaluating the resultant regression plot(s); again, by using the software.

## Results and discussion

### Principles of the method

As already emphasised, TNT is readily reducible at all common electrodes, including classical mercury drop-based electrodes (DME [34] and HMDE [35]). Moreover, rather voluminous molecule of TNT tends to be accumulated onto the electrode surface — probably, via adsorption [16,28] —, which allows one to utilise the principles of electrochemical stripping analysis with the pre-concentration step and subsequent voltammetric detection.

Otherwise speaking, cathodic stripping voltammetry (CSV) was the technique of choice, when most of experimental conditions could be adopted from the previous studies with the BiF-GCPE [27,28] or SbF-GCPE [29], respectively, including the square-wave voltammetric (SWV) potential ramp and the corresponding instrumental parameters. In a few cases, some additional optimisation had to be performed, which was mainly the case of re-checking calibration plots and the corresponding linear ranges (for details, see [29,30]).

### Choice of the working electrode with metallic film

First, the determination of TNT had been of interest in studies with BiF-GCE, BiF-CPE, and finally with BiF-GCPE [27,28], when related configurations of SbF-GCE, SbF-CPE, and SbF-GCPE were examined afterwards [29,30]. Although the antimony-based variants exhibited some nuances in behaviour, in the case of TNT, their performance was found very similar to the bismuth-based counterparts, including the proper function in mild alkaline Britton-Robinson buffer chosen as the supporting medium.

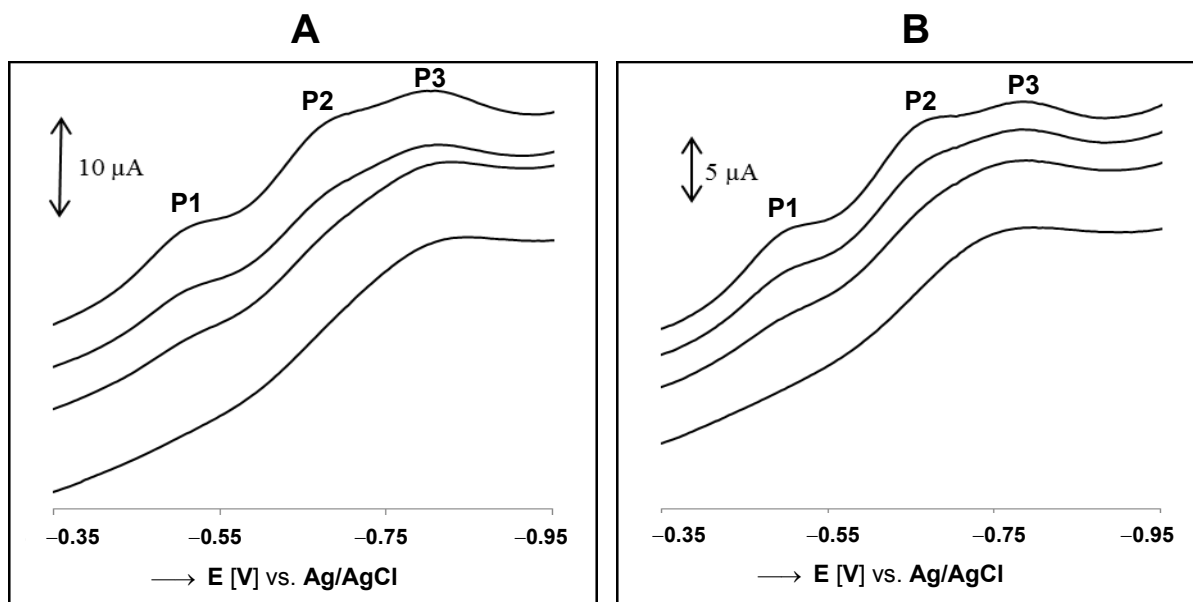
### Sample preparation by extraction into aqueous and methanolic solutions

In fact, extractions in the individual media acted as a sample pre-treatment, transferring the analyte(s) into the aqueous environment required for electrochemical measurements. This was accomplished with the aid of three different media selected upon recommendation [33] plus a solution of BRB. In this set, two extraction media were purely aqueous: 0.5 M CH<sub>3</sub>COOH and BRB (pH 9) and such a selection possible because of a slight solubility of TNT in water. Other two represented the water / methanol mixed solutions; namely, 30% CH<sub>3</sub>OH and 0.5 M CH<sub>3</sub>COOH in 30% CH<sub>3</sub>OH.

Although the aqueous extracts seemed more suitable for voltammetric measurements, mixed media with methanol were anticipated as more effective due to a 10-fold higher solubility of TNT in this solvent compared to pure water (*ca.* 0.13 g L<sup>-1</sup> in water versus 2.1 g L<sup>-1</sup> in alcohol; see ref. [10]).

### Voltammetric analyses of the extracts

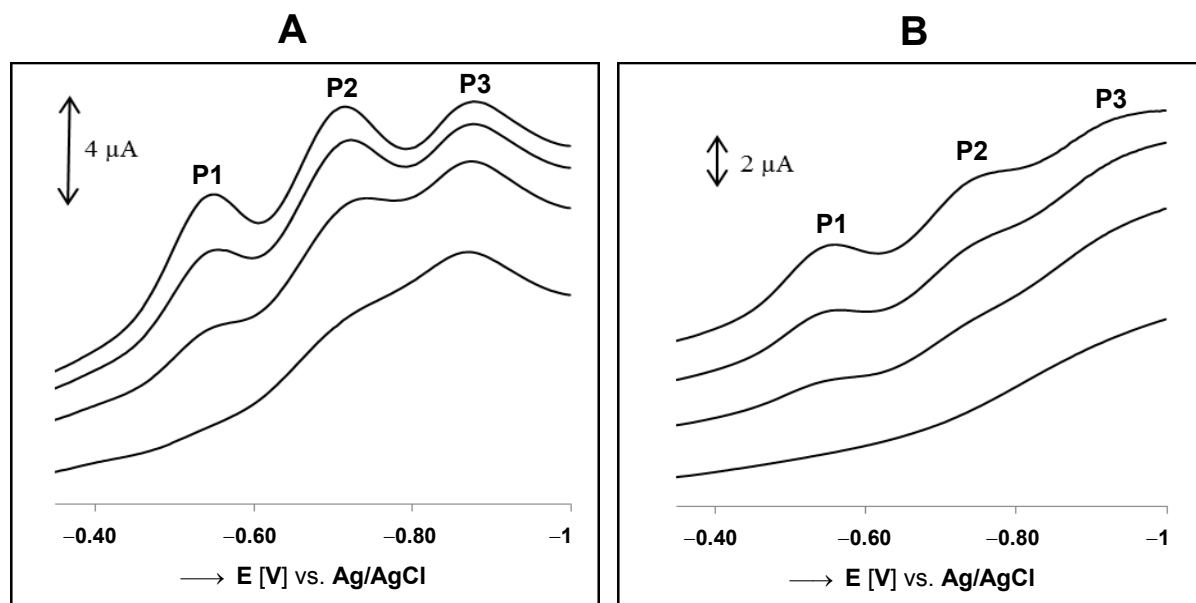
The results of the extraction efficiency for all four extracting media used are documented on a quartet of Figs 1–4, illustrating the respective analyses of polluted soil (images "A") and blank sample (images "B") by SWCSV with the SbF-GCPE. In each figure, the individual sets of voltammograms show the measurement of the sample extract (on bottom) together with three subsequent experiments performed after the corresponding addition of TNT standard aliquot (a set of three curves drawn above that of sample).



**Fig. 1** Analysis of the extract in 0.5 M CH<sub>3</sub>COOH. Square-wave cathodic stripping voltammograms obtained at ex-situ plated SbF-GCPE for polluted soil (A) and blank sample (B), in both cases, followed by three successive standard additions of TNT

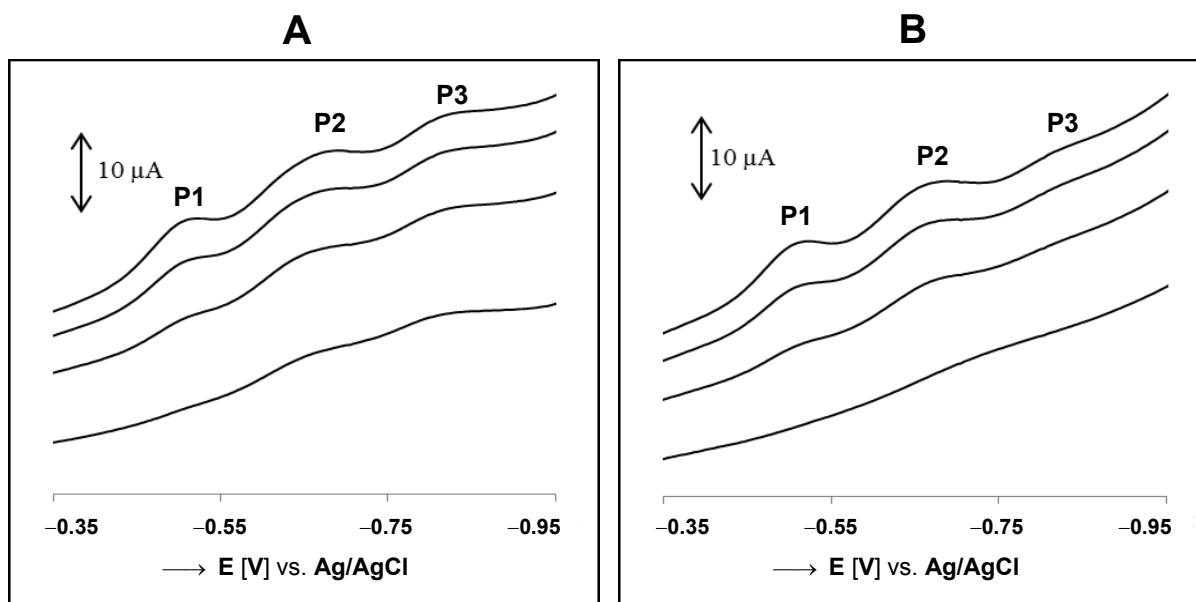
Experimental conditions: sample **A**: 10 mL soil extract + 10 mL BRB (pH 7.74), sample **B**: 10 mL blank extract + 10 mL BRB (pH 7.54); TNT standard solution: aliquot of 0.3 mg L<sup>-1</sup>. For instrumental parameters, see Materials and methods.





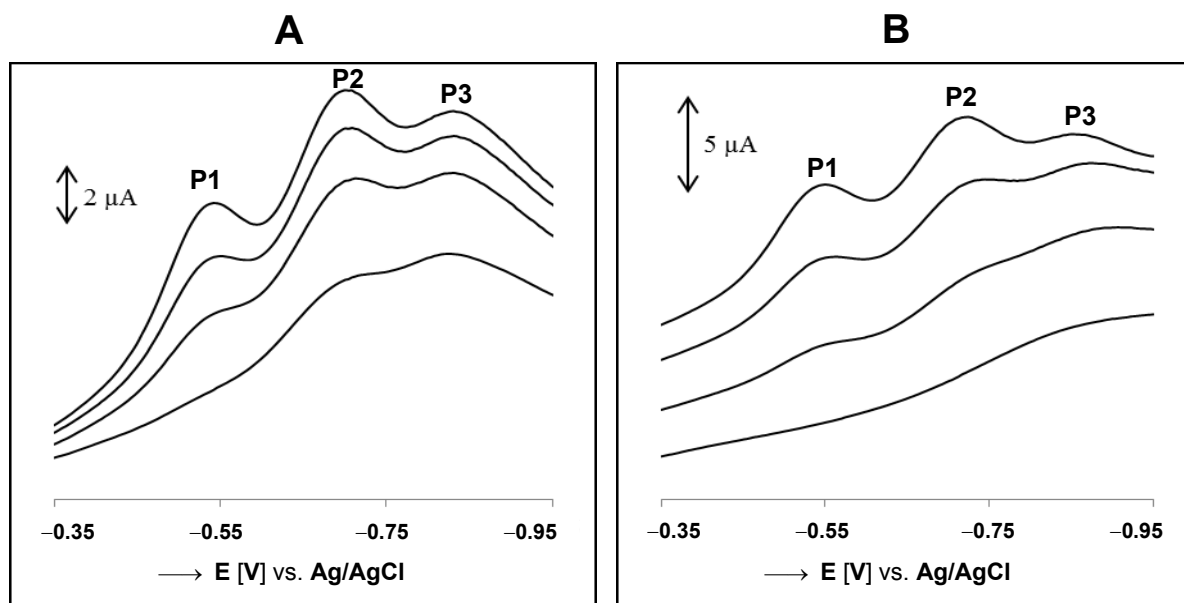
**Fig. 2** Analysis of the extract in 30%  $\text{CH}_3\text{OH}$ . Square-wave cathodic stripping voltammograms obtained at ex-situ plated SbF-GCPE for polluted soil (A) and blank sample (B), in both cases, followed by three successive standard additions of TNT

Experimental conditions: sample A: 10 mL soil extract + 10 mL BRB (pH 8.72), sample B: 10 mL blank extract + 10 mL BRB (pH 8.20); TNT standard solution: aliquot of  $0.3 \text{ mg L}^{-1}$  as aliquot. For instrumental parameters, see Materials and methods.



**Fig. 3** Analysis of the extract in 0.5 M  $\text{CH}_3\text{COOH}$  + 30%  $\text{CH}_3\text{OH}$ . Square-wave cathodic stripping voltammograms obtained at ex-situ plated SbF-GCPE for polluted soil (A) and blank (B), in both cases, with three successive standard additions of TNT

Experimental conditions: sample A: 10 mL soil extract + 10 mL BRB (pH 8.10), sample B: 10 mL blank extract + 10 mL BRB (pH 7.76); TNT standard solution: aliquot of  $0.3 \text{ mg L}^{-1}$ . For instrumental parameters, see Materials and methods.



**Fig. 4** Analysis of the extract in Britton-Robinson buffer (pH 9). Square-wave cathodic stripping voltammograms obtained at ex-situ plated SbF-GCPE for polluted soil (A) and blank (B), in both cases, with three successive standard additions of TNT

Experimental conditions: sample **A**: 10 mL soil extract + 10 mL BRB (pH 8.71), sample **B**: 10 mL blank extract + 10 mL BRB (pH 8.95); TNT standard solution: aliquot of  $0.3 \text{ mg L}^{-1}$ . For instrumental parameters, see Materials and methods.

As seen, all four voltammograms of the sample extracts (images "A") exhibit some response of the analyte although none of them revealing all three peaks "P1", "P2" and "P3"; in complete representation being evident at higher concentrations of TNT after the standard addition(s) applied. Apparently, the most favourably developed response has belonged to the soil samples extracted by a mixture of 0.5 M  $\text{CH}_3\text{COOH}$  in 30%  $\text{CH}_3\text{OH}$  depicted in Fig. 3. Here, one can recognise two peaks P2 and P3 and also, the smoothest base-line with minimal distortion, which is in contrast to the remaining three extracts.

The Figs. 1A, 2A, 3A, and 4A also feature the individual sets of voltammograms used for evaluating the TNT content by means of the method of multiple standard addition having being applied in three aliquots. If not stated otherwise, the second peak P2 was the signal of interest selected for quantification and computing the content / concentration of TNT in each extract and correspondingly, in the dried soil.

The right-positioned images "B" then illustrate that all four blank-sample extracts had not yield a visible response, but still featuring fairly the overall shape of base-line, including its characteristic distortion for each extract.

(i) *Results of analyses of the extracts with 0.5 M CH<sub>3</sub>COOH* (see Figs. 1 A,B). Original extracts were markedly acidic (soil: pH 2.34 and blank: pH 2.52) and had to be neutralised with NaHCO<sub>3</sub>. Although this operation could not provide the desired pH ~ 9 because of limited solubility of solid hydrogencarbonate, the neutralised solutions with pH *ca.* 7.5 have been found applicable to analysis. However, the result of quantification, 1.99 µg TNT / 10 mL (corresponding to 1.99 mg per 1 kg of dried soil), has shown the poorest agreement with the analysis by GC-MS [33], of about 50 % only. Thus, this way of extracting the soil sample was evaluated as the worst amongst the variants tested.

(ii) *Results of analyses of the extracts with 30% CH<sub>3</sub>OH* (Figs. 2 A,B). Due to a slightly acidic pH of both extracts (soil: 6.70 and blank: pH 7.7), the respective solutions were yet treated with the BRB solution in order to increase the pH towards the optimal value, when the mixture of choice with pure BRB was set up to 1 : 1 (v/v). The analysis of so pre-treated soil sample extract then provided the result of 2.09 µg TNT / 10 mL ( $\approx$  2.09 mg kg<sup>-1</sup>), representing also a rather low recovery compared to the determination by GC-MS.

(iii) *Results of analyses of the extracts with 0.5 M CH<sub>3</sub>COOH in 30% CH<sub>3</sub>OH*; (Figs. 3 A,B). In these extracts neutralised again with solid NaHCO<sub>3</sub> to pH ~ 8 (original soil extract had had pH 2.58 and blank extract pH 3.3), the analyses by SWCSV have resulted in the tightest agreement with the control determination, when a content of 3.77 µg TNT / 10 mL ( $\approx$  3.77 mg kg<sup>-1</sup>) found by voltammetric analysis represented *ca.* 85 % of that determined by GC-MS analysis; i.e., a relative error of about  $\pm$ 15 %.

Within a second series of experiments, the neutralised extracts of soil and blank were additionally mixed with BRB solution to adjust the alkalinity closer to pH 9. In this case, the sample solution had contained: 5 mL extract + 5 mL BRB (as diluting agent) + 10 mL BRB as supporting electrolyte. The respective analysis has resulted in a content of 2.87 µg TNT / 10 mL ( $\approx$  2.87 mg kg<sup>-1</sup>), indicating a worse recovery in diluted and “more aqueous” solution.

(iv) *Results of analyses of the extracts with BRB solution* (see also Figs. 4 A,B). In contrast to the experiments with aqueous acetate solutions, both original and additionally diluted BRB extracts have given a better recovery. After the results obtained with previously commented acetate/methanolic extracts, the SWCSV determination with SbF-GCPE was closest to the control analyses by GC-MS. Determination in the original BRB extract (pH 8.71) has revealed the content of 3.03 µg TNT / 10 mL ( $\approx$  3.03 mg kg<sup>-1</sup>), whereas the subsequent experiment with additional BRB (pH 8.95) resulted in 2.36 µg TNT / 10 mL ( $\approx$  2.36 mg kg<sup>-1</sup>), showing again a certain loss after the dilution with the buffer.

Regarding the control determinations with the blank samples — i.e. a series of measurements depicted in images "B" on the right side —, none of the four extracts analysed had revealed a detectable content of TNT.

Some notes on the determination of TNT using SWCSV with SbF-GCPE in the presence of other nitroaromate(s)

After having performed SWCSV analyses of the TNT extracts with the *ex-situ* (pre)plated SbF-GCPE, this configuration under the same conditions has been examined whether or not it would be capable of detecting TNT in the presence of other nitroaromate(s). Since the standards of the two DNTs, two major degradation products of TNT, had not been at disposal at the time of studies with such model samples, a fundamental member of the family, *nitrobenzene* ( $C_6H_5NO_2$ , NB) was chosen instead. For analysis, the model solution of this substance was prepared analogically as the standard of TNT.

Although the respective experiments had not been completely convincing, they have suggested us that in certain constellation of both TNT and NB — e.g., at comparable concentrations —, the trinitroaromate can be determined in the presence of mononitro-derivative if the peak "P1" from three-step reduction of TNT is followed and used for identification and quantification. On the contrary, the peak "P2" in all previous analyses used as the proper signals of choice, could not be used because of mutual interference with the single reduction peak of NB (for further details, as well as an illustrative set of stripping voltammograms, see the original literature [30]).

## Conclusions

In this article, a recently proposed method for the determination of 2,4,6-trinitrotoluene, TNT [29] at the SbF-GCPE in combination with SWCSV technique has for the first time been examined on the analysis of truly real samples – a polluted soil (and its blank counterpart) collected in the area of a factory producing industrial explosives.

When using the method with re-optimised procedure [30] and after solubilising both samples in aqueous and water / methanolic media, it has been found that the most effective extraction of the analyte and most precise determination of its content can be obtained by analysing the extraction mixture containing 10 mL 0.5 M  $CH_3COOH$  in 30%  $CH_3OH$ , neutralised with solid  $NaHCO_3$ , and diluted with 10 mL Britton-Robinson buffer to a final sample solution with pH ~ 8. In this case, the respective analysis (by using the method of multiple standard addition) has resulted in a content of 3.77 mg TNT per 1 kg

dried soil, representing *ca.* 85 % of that found by the reference GC-MS. The analysis of other three extraction media have given yet lower results – in an interval of 50–80 % with respect to the content known from the control lab.

Among others, these observations indicate the key importance of the proper extracting medium used, because the voltammetric determination itself has been found quite reliable for the concentration distribution in the samples of the polluted soil type. However, there is also one aspect explaining somewhat lower result(s) and associated with the sample itself. Its long time storage for *ca.* two-year period could have led to some changes in composition, resulting in a certain loss of the analyte; e.g., by its partial chemical disintegration. This hypothesis, however, would have required a new control analysis of such a sample by independent reference technique.

Otherwise, apart from the right reason for somewhat lower result(s), the voltammetric determination described in this article can be characterised as quite reliable – at least, for preliminary tests and orientation assays in the samples of polluted soils and similar materials without high demands on precision. On the other hand, still limited performance of the method may be a good motivation for its further improvement to offer a simple and inexpensive alternative to various chromatographic/spectral methods, so-far dominating in determinations of TNT and related explosives in environmental or industrial samples [36–45].

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