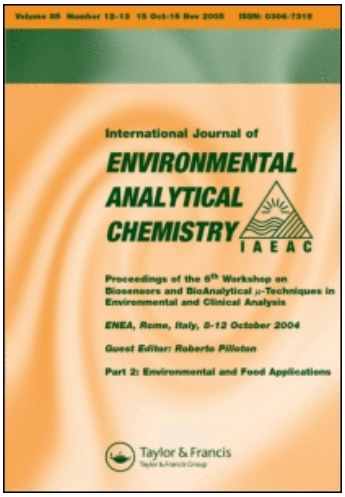


## International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

# Electroanalysis of some nitro-compounds using bulk bismuth electrode

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Online publication date: 09 December 2009

**To cite this Article** Tall, Omar El , Beh, Daniel , Jaffrezic-Renault, Nicole and Vittori, Olivier(2010) 'Electroanalysis of some nitro-compounds using bulk bismuth electrode', International Journal of Environmental Analytical Chemistry, 90: 1, 40 — 48

**To link to this Article: DOI:** 10.1080/03067310902871265

**URL:** http://dx.doi.org/10.1080/03067310902871265

*Intern. J. Environ. Anal. Chem.*
Vol. 90, No. 1, 15 January 2010, 40–48

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# Electroanalysis of some nitro-compounds using bulk bismuth electrode

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(*Received 18 September 2008; final version received 2 March 2009*)

Nitro compounds were usually determined electrochemically using the mercury drop with DPP technique. An alternate way to toxic mercury is the increasing use of the bismuth electrode as thin film electrodeposited on glassy carbon or copper for example, or as bulk bismuth disc. In the present paper several nitrocompounds were investigated: mononitrophenols, dinitrophenol, nitrobenzoic acid, nitrobenzaldehyde and a well known pesticide, parathion, which has a nitro group in para position on a phenyl cycle. Bulk bismuth electrode was a disc (cross section of a rod of 5 mm diameter embedded in Teflon®) polished with silicon carbide disc (P2400) and sonicated to remove any abrasive particle. The supporting electrolyte was the acetic buffer (pH 4.7), which was found suitable for all these compounds. Using cathodic sweep differential pulse voltammetry, it was noticed that according to the position of the nitro group on the cycle, the peak potentials might range between −300 to −750 mV vs. SCE. Limits of detection (LOD) and limits of quantification (LOQ) were determined for each compound whose response for increasing concentration was linear in the ~3–50 μmol $L^{-1}$ whatever the considered molecule. Adsorptive differential pulse voltammetry was found very efficient to determine parathion, because this molecule adsorbs on bismuth at −0.2 V vs. SCE. Bulk bismuth electrode was compared to the hanging mercury drop electrode and led to an identical behaviour.

**Keywords:** bismuth electrode; nitrophenols; nitrobenzaldehyde; nitrobenzoic acid; parathion



## 1. Introduction

During the last decade bismuth electrodes have received strong attention as an alternative to mercury drop for heavy metals electroanalysis [1]. Bulk bismuth electrodes have been used less frequently than bismuth film electrodes easily made by electrodeposition of $Bi^{3+}$ ions from acidic solutions [1]. Bismuth electrodes present a rather interesting working potential range, because the oxidation of the surface occurs at potential more positive than −0.2V/SCE, leading to a $Bi_2O_3$ growing layer, and the cathodic range is limited at −1.2 V/SCE by hydrogen evolution. Glassy carbon was frequently used as conducting support for the electrodeposited bismuth film [2–6]. Carbon paste was also used [7] as well as graphite epoxy composite mix [8]. Copper, platinum, gold and carbon fibre have been also described as base conducting materials [9,10]. Bismuth films on copper substrate have been covered with Nafion® to increase the sensitivity [9,10]. The major part of

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ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310902871265
http://www.informaworld.com

previous works deals with the anodic stripping of metals in very dilute solutions, such as cadmium [2,5,9,11–17], lead [2,3,5,7,14,16,17] zinc [2,5–11,15], tin [18,19], cobalt and nickel [3,6,20–23], molybdenum [24], uranium [25,26], chromium [27], vanadium [28], thallium [2] and indium [12,16].

Organic compounds have received more limited attention:

- daunomacyn, an antibiotic, has been studied on bulk bismuth electrode
- picric acid presenting three electro reducible nitro groups [29,30]
- an insecticide, thiamethoxam [31], presenting a nitro group and several heteroatoms
- metallothionein playing important biological and environmental roles that has been also investigated at bismuth film electrode and exhibits two anodic peaks due to cadmium and zinc [32].

Recently 2- and 4-nitrophenol, as well as 2,4-dinitrophenol, have been investigated by Hutton *et al*. [33] at bismuth film electrode (BiFE) for an application to flow analysis. The BiFE was obtained by electrodeposition of $Bi^{3+}$ from an acetate buffer onto a glassy carbon electrode. In a second paper, Pauliukaite *et al*. [34], using bulk bismuth electrode, have shown that 2-nitrophenol was reduced irreversibly in a Britton Robinson buffer.

In the present paper, reinvestigation of the bulk bismuth electrode (BBiE) was undertaken with several nitrocompounds having a phenol, an acidic or an aldehydic group. The objectives were to prove that a rather simple electrode, polished carefully, was able to work as well as a BiFE. An application to parathion, a common pesticide with a nitro group, is presented. The number of electrons involved in the reduction of the nitro group was measured for 4-nitrophenol and for parathion. At least a comparison of the responses for parathion at the hanging mercury drop electrode (HMDE), at the BBiE and at the BiFE is presented proving the efficiency of the BBiE.



## 2. Experimental

### 2.1 *Reagents*

All the reagents were of analytical grade. 2-, 3- and 4-nitrophenols and 2,4-dinitrophenol were purchased from ALDRICH (France). 3-nitrobenzoic acid was purchased from ACROS (France). Picric acid was a PROLABO compound (France), and parathion (Phosphorothionic acid, O, O diethyl, O-(4-nitrophenyl) ester) was obtained from Cluzeaux (France). All the compounds were used without further purification. Bismuth (shot, 99.9%) was purchased from ALDRICH (France).

### 2.2 *Apparatus*

All the measurements at the BBiE and at the BiFE were performed using a PALMSENS Potentiostat (IVIUM technologies, the Netherlands). The cell was a classical three-electrode device, with a bismuth working electrode, a platinum wire as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode (Radiometer Analytical, France). For differential pulse polarography (DPP) measurements with a mercury drop electrode, a POL 150 + MDE 150 polarograph were used, associated to the Voltamaster® software (Radiometer Analytical, France). Oxygen was removed by careful nitrogen bubbling.

### 2.3 *Bismuth electrode*

The bismuth electrode was made filling a warm glass tube (inner diameter: 5 mm) with molten bismuth up to 4 cm high. A copper wire was immersed at only 5 mm from the top of the melt bismuth in order to obtain a good electrical contact. After cooling, the glass tube was broken with care and the bismuth rod was embedded with a Teflon® tape to allow only a 5 mm diameter disk as the active surface of the electrode.

Then the bismuth disk was polished on SiC 1200 polishing disk (ESCIL, France) with a rotating polishing machine (250 rpm). Then a final polishing was made carefully on SiC 2400 polishing disk. The electrode was cleaned for 5 minutes in an ultrasonic bath filled with distilled water before use to remove SiC particles.

### 2.4 *Conditions for electrochemical measurements*

Before any experiment, the electrode was conditioned in $0.01\,mol\,L^{-1}$ acetic buffer (pH = 4.7) by applying 5 cycles from 0 to $-1.2$ V/SCE at a sweep rate of $100\,mV\,s^{-1}$. Then the rest potential was fixed at $-1.0$ V/SCE. All the experiments were made in $0.01\,mol\,L^{-1}$ acetic buffer which appeared as a suitable medium for the reduction of the nitro-compounds. Increasing the compound concentration was made by small standard additions of a stock solution of the compound dissolved in the acetic buffer.

The major part of the experiments was made using the differential pulse voltammetry (DPV) with a pulse width of 40 ms, pulse amplitude of $-50$ mV and a scan rate of $50\,mV\,s^{-1}$, in the cathodic direction. DPP was also used with the HMDE, with the same parameter values.

At the end of any experiment, the electrode was held at a rest potential of $-1.0$ V/SCE. This procedure allowed the electrode working perfectly for more than 10 consecutive hours. Nevertheless, every day the cleaning procedure was renewed to be sure to keep a similar behaviour.



### 2.5 *Limit of detection (LOD) and limit of quantification (LOQ)*

In the present case, the LOD and LOQ were estimated according to the definitions given by AFNOR [35]. The LOD value was taken as three times the standard deviation of the mean value of the current of the blank (recorded 5 times), divided by the slope of the straight line of the curve current versus concentration. Then the LOQ was three times the LOD.

### 2.6 *Pre-concentration procedure*

As for usual chromatographic analysis, pre-concentration of the compound was tested here. The selected adsorption cartridge was an Envicarb cartridge (Supelco, USA) which contains non-graphitised carbon particles with the following specifications: specific area: $100\,m^2$, pore diameter: 6 nm and porous volume: $0.8\,mL\,g^{-1}$. The Envicarb cartridge was first conditioned with 4 mL of $CH_2Cl_2$, 4 mL of $CH_3OH$ and 4 mL of milli-Q water. Then 1 L of the spiked solution containing a known amount of parathion (0.1 μmol) was passed through the cartridge. The elution was made with 2 mL of $CH_2Cl_2$ three times. Then the solvent was evaporated up to a dry residue. The residue was dissolved in 2 mL of $CH_3OH$ and 8 mL of acetic buffer, leading to an enrichment factor of 100.

## 3. Results and discussion

### 3.1 *Study of several nitrophenols*

Here were studied successively the three isomers of mono nitrophenol, the 2,4-dinitrophenol and picric acid or 2,4,6-trinitrophenol. The three mono nitro phenols exhibited a well-defined reduction peak. The peak potential value was related to the position of the nitro group on the cycle. The reduction was totally irreversible and the peak width was always close to 200 mV. As shown in Table 1, the reduction of 2-nitrophenol is easier and the reduction of 3-nitrophenol is more difficult. Figure 1 gives the typical shape of the reduction peaks of 2-nitrophenol with increasing concentration.

The reduction of the 2,4-dinitrophenol was in accordance with the above observations for mono nitrophenols, since the nitro group in ortho position had quite the same peak potential as for 2-nitrophenol, meanwhile the peak potential of the para nitro group was more negative by about 75 mV than for 4-nitrophenol (Figure 2).

To complete these observations, 2,4,6-trinitrophenol (picric acid) was tested. In this case only two peaks were obtained, at −255 mV and −735 mV/SCE. It was noticed that the

Table 1. Nitrophenols: peak parameters.

| Nitrocompound | Peak potential mV/SCE | Half-peak width mV | Sensitivity μA μmol$^{-1}$ |
|---|---|---|---|
| 2-Nitrophenol | −360 ± 10 | 190 ± 5 | 38.7 |
| 3-Nitrophenol | −529 ± 2 | 190 ± 4 | 32 |
| 4-Nitrophenol | −675 ± 4 | 210 ± 4 | 28.7 |
| 2,4-Dinitrophenol | −306 ± 20 (1st peak) | 140 ± 5 | 54.5 |
| | −747 ± 20 (2nd peak) | 200 ± 5 | 26.9 |
| 2,4,6-Trinitrophenol | −255 ± 20 (1st peak) | 165 ± 5 | 133 |
| | −735 ± 20 (2nd peak) | 220 ± 5 | 28.2 |



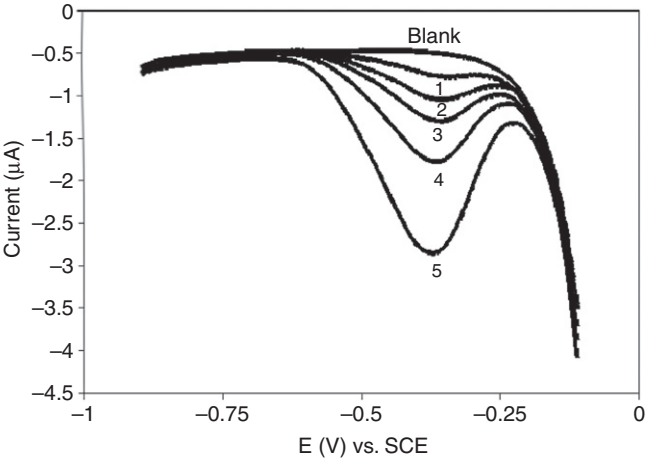


Figure 1. Peak of 2-nitrophenol in acetic buffer for: (1) 5, (2) 10, (3) 15, (4) 25 and (5) 50 μmol L$^{-1}$. Parameters for DPP: $\Delta E = -50$ mV, $t_m = 40$ ms, interval between two pulses: 0.1 s, sweep rate: 20 mV s$^{-1}$.

peak potential of the first peak (−255 mV) was less negative than that observed for the 2-nitrophenol. The second peak (−735 mV) corresponding to the para position was found to have a value close to that found for 4-nitrophenol and 2,4 –dinitrophenol (second peak, Table 1). In Table 2 the parameters of these reductions were given: linear dynamic range, half-height width of the peaks, detection limit, quantification limit, and the standard deviation for 8 successive analysis at a fixed concentration of 25 μmol $L^{-1}$.

### 3.2 *Study of 3-nitrobenzoic acid*

In the same way as above, 3-nitrobenzoic acid was studied. According to its $pK_a$ (3.47) the acid was in the anionic form for about 95% in the acetate buffer. The reduction peak was similar to that of 3-nitrophenol and its peak potential was quite similar, indicating that the position of the nitro group had more influence than the charge of the molecule. In Table 3 the characteristics of the peak are given, and in Table 4, the limit of detection and the dynamic range for the electrochemical detection of 3-nitrobenzoic acid.

### 3.3 *Study of 4-nitrobenzaldehyde*

4-nitrobenzaldehyde was chosen because the molecule was neutral. In this case the peak potential was not at the same value as for 4-nitrophenol. In the present case, the observed value is only −355 mV/SCE, a value close to that of the ortho position for 2-nitrophenol, 2,4-dinitrophenol and 2,4,6-trinitrophenol (Table 1). The inductive effect of the aldehydic group made easier the reduction of the nitro group. In Tables 3 and 4 the analytical parameters for the electrochemical detection of 4-nitrobenzaldehyde are given.



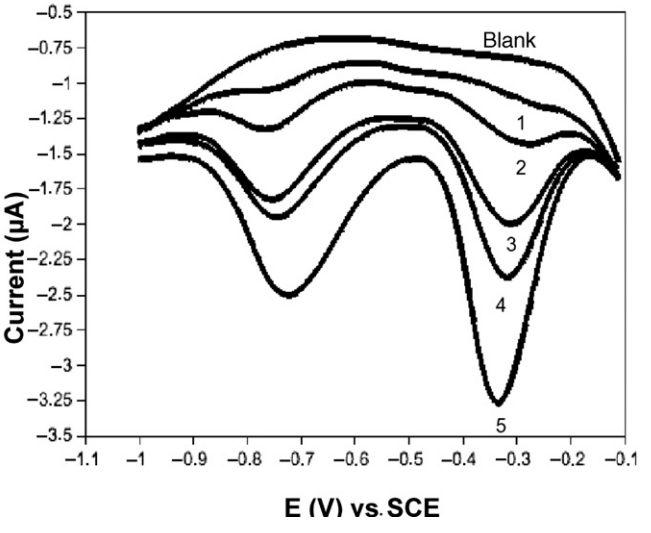


Figure 2. Peaks of 2,4-dinitrophenol in acetic buffer for: (1) 5, (2) 10, (3) 20, (4) 25 and (5) 40 μmol $L^{-1}$. Parameters for DPP: $\Delta E = -50$ mV, $t_m = 40$ ms, interval between two pulses: 0.1 s, sweep rate: 20 mV $s^{-1}$.

Table 2. Nitrophenols: LOD, LOQ and dynamic range.

| Nitrocompound | LOD, Limit of detection $\mu mol\,L^{-1}$ | LOQ, Limit of quantification $\mu mol\,L^{-1}$ | Linearity range µmol $R^2 > 0.997$ | Standard deviation[a] % |
|---|---|---|---|---|
| 2-Nitrophenol | 1.2 | 3.6 | 4–50 | 1.5 |
| 3-Nitrophenol | 0.8 | 2.4 | 2.5–50 | 0.8 |
| 4-Nitrophenol | 0.7 | 2.1 | 2.2–50 | 0.75 |
| 2,4-Dinitrophenol | 2 (1st peak) | 6 (1st peak) | 7–50 | 2.9 |
| | 1.8 (2nd peak) | 5.4 (2nd peak) | 6–50 | 2.1 |
| 2,4,6-Trinitrophenol | 0.8 (1st peak) | 2.4 (1st peak) | 2.6–30 | 1 |
| | 1.3 (2nd peak) | 3.9 (2nd peak) | 4.5–30 | 1.8 |

Note: [a]For 8 identical independent measurements at $25\,\mu mol\,L^{-1}$.

Table 3. Reduction peak parameters for nitrobenzoic acid, nitrobenzaldehyde and parathion.

| Nitrocompound | Peak potential mV/SCE | Half-peak width mV | Sensitivity $\mu A\,\mu mol^{-1}$ |
|---|---|---|---|
| 3-Benzoïc acid | $-583 \pm 3$ | $170 \pm 4$ | 28.2 |
| 4-Nitrobenzaldehyde | $-355 \pm 7$ | $190 \pm 5$ | 21.7 |
| Parathion | $-495 \pm 10$ | $170 \pm 4$ | 48 |



Table 4. Nitrobenzoic acid, nitro benzaldehyde and parathion: LOD, LOQ and dynamic range.

| Nitrocompound | LOD, Limit of detection $\mu mol\,L^{-1}$ | LOQ, Limit of quantification $\mu mol\,L^{-1}$ | Linearity range $R^2 > 0.997$ $\mu mol\,L^{-1}$ | Standard deviation[a] % |
|---|---|---|---|---|
| 3-Benzoic acid | 1 | 3 | 3.3–50 | 1 |
| 4-Nitrobenzaldehyde | 1.5 | 4.5 | 5–50 | 1.9 |
| Parathion (after 60 s of adsorption) | 0.05 | 0.15 | 0.15–25 | 1 |

Note: [a]For 8 identical independent measurements at $25\,\mu mol\,L^{-1}$.

### 3.4 *Study of parathion*

To complete this study, some attention was done to parathion, an insecticide, widely used in large-scale cultivation. The molecule has an alkylthiophosphate located in para position to a nitro group on a benzene ring. The peak potential was observed at −495 mV/SCE (see Figure 3), a value less negative than for the para position observed for the corresponding 4-nitrophenol (Tables 3 and 4).

The alkyl thiophosphate group has certainly an inductive effect on the nitro group. In addition it was found that parathion molecule adsorbed on bismuth at −0.2 V/SCE. This was specific to parathion, because adsorption was not noticed for the other nitrocompounds under study here. This adsorption step increased the parathion peak

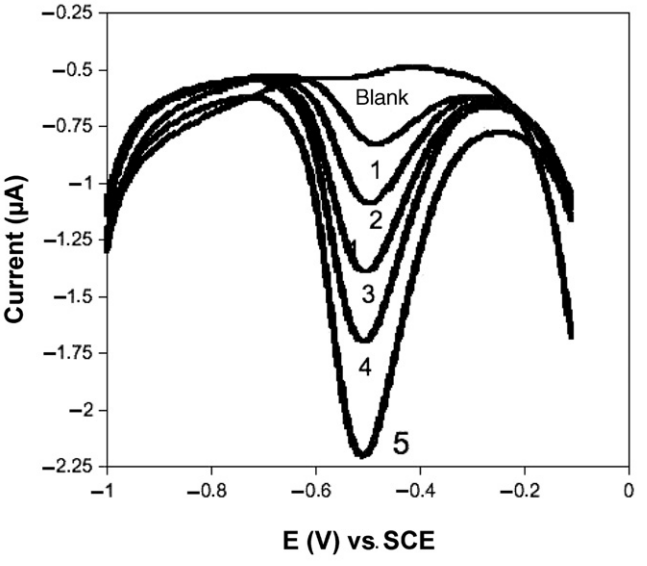


Figure 3. Peaks of parathion in acetic buffer for: (1) 5, (2) 10, (3) 15, (4) 20 and (5) 30 μM $L^{-1}$.



intensity, nevertheless a rest period longer than 30 s did not lead to higher peak intensity. For the bismuth disk electrode, the linear range was 0.15 to 25 μmol $L^{-1}$ with $R = 0.9987$ and the equation: $I = 1.0206$ [parathion] + 0.0609 (concentration of parathion is expressed in μmol $L^{-1}$).

### 3.5 *Pre-concentration of parathion*

Natural water contains less than 50 nM of parathion. Therefore, a pre-concentration step was performed as known from HPLC. One L of spiked natural water, containing a known amount of parathion (0.1 μmol), was passed through the Envicarb cartridge. The residue, dissolved in 2 mL of $CH_3OH$ and 8 mL of acetic buffer was then analysed with the bismuth electrode, after 5 mins' nitrogen bubbling. It was found $9.3 \pm 0.2$ μmol $L^{-1}$ of parathion in the residue, for 3 independent determinations. According to the enrichment factor of 100, the determined initial concentration was $0.093 \pm 0.002$ μmol $L^{-1}$. By doing so, we are able to determine, in natural water, parathion concentrations lower than the determined LOQ (cf. Table 4).

### 3.6 *Determination of the number of electrons involved in the reduction step*

It is well known that nitro compounds are usually reduced according a 4 electrons step, leading to the formation of an hydroxylamine group (−NH(OH)).

It was interesting to determine the number of electrons involved in the reduction at the bulk bismuth electrode. Two independent attempts were made with 3-nitrophenol and parathion, these two compounds having some similitude. As for mercury, glassy carbon and platinum, the $-NO_2$ group leads to a −NHOH group with 4 electrons and 4 protons involved, the use of a buffer during the coulometric measurements is necessary [36–39].

The same procedure was applied. The peak current was firstly measured in 20 mL of a $3.10^{-5}$ mol $L^{-1}$ de-aerated solution of the target compound. The electrode was then held at −0.8 V/SCE, (a more negative value than the peak potential) and the chronoamperometric curve was recorded for about 16 hours, under stirring. (Stirring was performed with a magnetic stirrer, rotating slowly at 200 rpm.) Then the peak current of the non-reduced nitrocompound was measured. From the electrical charge having flowed through the electrode and the two peak intensities, the number of electrons was evaluated. (The chronoamperometric curve of the blank (acetate buffer) recorded with the same procedure was removed.) It was found $n = 3.46$ for para-nitrophenol and 3.58 for parathion. These two average values, repeated three times indicated clearly that the real number of exchanged electrons was 4. The fact that the average values were slightly lower than 4 suggests that the electrode was slightly modified with time, perhaps due to a weak adsorption of the reduction product.

### 3.7 *Comparison of the parathion response at the BBiE, the BiFE and the HMDE*

The linear range using DPP, with the hanging mercury drop, was found to be 0.16 to 25 μmol $L^{-1}$, with a correlation coefficient of $R = 0.999$ and a straight line equation of $i = 0.473$ [parathion] + 0.440 (the parathion concentration is expressed in μmol $L^{-1}$) with a correlation coefficient of $R = 0.999$.

In order to complete this comparison, a bismuth film electrode was made on glassy carbon as previously described, by electrodeposition of Bi from an acidic solution containing $10^{-3}$ mol $Bi^{3+}$ in acetate buffer [33]. Similar results were obtained with this electrode, the linear range being 0.15 to 25 μmol $L^{-1}$ with a correlation coefficient of $R = 0.999$ and a straight line equation of $i = 0.526$ [parathion] + 0.230.

A same dynamic range was obtained for the detection of parathion with the three types of electrodes. The slopes of the intensity peak versus parathion concentrations were quite similar for HMDE and BiFE. Nevertheless a higher slope (×2) was obtained with BBiE. This higher sensitivity could be explained by the observed adsorption effect.



## 4. Conclusion

Despite a slightly limited potential range (−0.2 to −1.2V/Ag/AgCl) compared to mercury drop electrode, bismuth electrode showed a good ability to the reduction of some organic nitro compounds and may be an alternative to toxic mercury in analytical laboratories, since bismuth has been recognised as a quasi non toxic metal. Bulk bismuth electrodes were rather easy to build and they certainly have a promising future, particularly for measurements in rivers or lakes, due to their ease of handling.

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