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# Anodic Stripping Voltammetry of Heavy Metals at Nanocrystalline Boron-Doped Diamond Electrode

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## Abstract

Boron-doped Diamond (BDD) electrode has become one of the important tools for heavy metal detection. By studying some analytical parameters of DPASV method, like deposition time and potential in different electrolyte concentrations (acetate buffer), the conditions for detecting very low metal ion levels (Zn, Cd, Pb, and Cu) could be chosen. Diluted electrolyte (0.01 M buffer) was one of the factors favoring low detection and quantification limits, but its quantification range is short in comparison to more concentrated media. For  $-1.7$  V deposition potential, the detection of single metal at ppb levels was reached in 60 s deposition time. Understanding different metal-metal interactions shows the limits to the simultaneous determination of heavy metals at BDD. Quantification was possible for the simultaneous determination of Zn, Cd and Pb despite the overlapping of Zn and Cd peaks. The performance of the BDD was compared with that of another C-based solid electrode: the glassy carbon electrode (without mercury plating). A lower base line current, wider potential range, higher sensitivity (3 to 5 times higher than GC) and longevity of the material were noticed for the BDD.

**Keywords:** Boron-doped diamond (BDD), Glassy carbon electrode (GCE), Differential pulse anodic stripping voltammetry (DPASV), Heavy metals, Simultaneous detection

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## 1. Introduction

The determination of heavy metal ultra-traces is a tough challenge for analysts. Human activity, principally during the last two centuries, has released these toxic metals into the environment and now the impact on the health of humans, animals and plants is obvious.

Spectroscopic and electroanalytical techniques have been widely used, but the principal difference between them being the instrumental cost. Electroanalytical techniques are easy to use in situ and the apparatus is easy to handle for measurements in rivers or lakes.

ICP-AES and ICP-MS and related techniques have been widely used in the recent past and nowadays to determine low levels of heavy metals in pharmaceutical drugs [1], in food and fish [2], in wine [3], in highly concentrated salt water [4], or marine microalgae *Fucus* [5]. Detection limits are frequently about 1 ppb or less.

Electroanalytical techniques may compete with spectral methods for selected heavy metals such as copper, lead, cadmium and zinc because these four metals are so called reversible (rapid electron exchange), a real advantage since their signals are wide even at low concentration. In the past, mercury used as a dropping or a hanging electrode was the preferred working electrode, because of the surface renewal of the drop and the low noise current. Associated to pulse or

square-wave techniques, the mercury electrode was one of the best for trace analysis [6–7]. Nowadays it is highly recommended not to use mercury and to choose other kinds of electrodes whose toxicity is low or nil. Carbon electrodes were then used like graphite [8–9], glassy carbon [10–13], carbon paste electrodes [14] and screen printed carbon electrodes SPCE [15] and their efficiency has been demonstrated for anodic stripping analysis.

Recently, a diamond film carbon electrode has been developed. It consists of a thin film of carbon (with a preponderance of  $sp^3$  carbon geometry) deposited by chemical vapor deposition (CVD), on an inert substrate such as silicon for example. This carbon is doped with boron which has a high conductivity value. The boron doped diamond (BDD) electrode has several qualities, such as a large electroactivity range in water, allowing species difficult to reduce or oxidize to be studied [16–17] and a low background current (one magnitude lower than the one generated by glassy carbon electrode) [16]. Furthermore, chemical and mechanical robustness of this electrode made it suitable for working in corrosive media [18, 19] and resistant to ultrasonic probes which have beneficial effects in general for stripping analysis by increasing mass transport, enhancing sensitivity, and better electrode cleaning from electrodeposited species or adsorbed organics [20–28].

An attempt to reveal the analytical importance of this material in electrochemistry has been made by Peilin et al. They demonstrated that BDD has a slight advantage for sensitivity (2.99 nA/mm<sup>2</sup> ppb for Pb) in comparison to GCE (2.41 nA/mm<sup>2</sup> ppb for Pb) with in situ plated mercury for both [29]. The same comparison between BDD (without mercury plating) and Hg-coated GC showed sensitivity three to five times lower for BDD [30]. In an analytical application of anodic stripping voltammetry at BDD electrode, Manivannan et al. reported that for 15 min deposition time at  $-1$  V, Pb is detectable at sub-ppb levels [31]. Similar study was made in tap water giving sub-ppb detection of Pb too [32]. Other studies treating single metal analysis of Pb and Cd at BDD have mentioned 10 ppb quantification limit for both metals for 5 min accumulation at  $-1$  V (Pb) and  $-1.1$  V (Cd) with 0.1 M KCl as electrolyte [33]. Microwave enhanced anodic stripping detection of Pb seems to have advantageous effects on the sensitivity of analysis [34]. A rotating disk technique has also proved its efficiency in detecting ppt level of Hg at BDD [35]. Further individual metal analysis at BDD electrode was done for Zn, Cd, Pb, Cu, Ag [36] and Hg [37, 38]. Introducing sonoelectrochemical analysis to metal detection at BDD was found to be beneficial for stripping analysis of Pb [25], Ag [26], Mn [27] and Cd [28]. Array of BDD microdisks electrode had also been tested for single metal analysis of Cu and Ag. The analysis reached 20 ppb as limiting quantification level for both metals with a 5 and 10 min accumulation times for Cu and Ag [39]. Other diamond conducting films like N-DLC (Nitrogen Diamond Like carbon) were fabricated but gave no better detection than BDD [40]. Simultaneous detection of heavy metals was made for Pb, Cd and Ag at nanocrystalline BDD and resulted in 10 ppb quantification limit for 3 min and  $-0.9$  V accumulation time and potential [41]. Electrolyte was 0.1 M acetate buffer. An interaction Pb-Cd study was also done at BDD electrode and gave, in simultaneous detection, 50 ppb detection limit for Cd in presence of Pb and 72 ppb for Pb in presence of Cd [42]. At last a Bi-film modified BDD was described, giving for Pb detection in human blood 19 ppb detection limit (non sonicated analysis) for 1 min deposition time and at  $-1.5$  V deposition potential [43].

This study aims at finding parameters that allow the values of detection and quantification limits of four heavy metals Zn, Cd, Pb, Cu at BDD to be lowered separately and simultaneously. A short analysis time is recommended. Care has to take into account the variation of electrolyte concentration and its effect during the whole study so that the measuring conditions are closer to the reality of natural water samples.

## 2. Experimental

### 2.1. Reagents

All the reagents were of analytical grade. Cadmium nitrate was purchased from ALFA AESAR, zinc nitrate and lead

nitrate were purchased from Fluka, and hemipentahydrate lead nitrate from Aldrich. Acetate acid and sodium acetate were purchased from ACROS. Water was first deionized and second distilled ( $\sigma = 2$   $\mu$ S/cm). Oxygen was removed by pure nitrogen bubbling (Linde).

### 2.2. Apparatus

A PalmSens PC system (Eindhoven, the Netherlands) was used to apply pulse techniques to the carbon electrodes. It was connected to a PC computer loaded with specific software. The electrochemical cell is a 100 mL cylindrical shaped one, having a circular neck shaped opening on its inferior lateral side, allowing the solution to be in contact with diamond film side of BDD plane electrode. An O-ring tap rubber is placed to ensure sealing. The diameter of the o-ring rubber defines the diameter of effective disk BDD surface. The electrical back side contact of BDD electrode was made with an aluminum foil. To fix well the cell-electrode system, it was pressed with screw device. A magnetic bar could thus be placed at the bottom of the cell ensuring stirring in the accumulation stage of the analysis.

### 2.3. Electrodes

The glassy carbon electrode was the V25 type with 4500  $\mu\Omega$  cm resistivity and was a typical 3 mm diameter disk obtained with a 1 cm long rod embedded in a cylindrical 1 cm long Teflon rod, Le Carbone Lorraine (France). BDD electrodes were purchased from ADAMANT technologies (Switzerland). They consist in very thin, nanocrystalline ( $1.8 \mu\text{m} \pm 0.5 \mu\text{m}$ ), carbon film (2.26  $\mu\text{m}$  thickness) deposited by CVD on one side of a 1 mm thick polycrystalline silicon ( $10 \times 10$  mm or  $50 \times 5$  mm) plate. The diamond film was doped with boron up to 1300 ppm. Average roughness of substrate was 0.32  $\mu\text{m}$ . The electrical resistance of the film was 12  $\Omega$  and the  $\text{sp}^3/\text{sp}^2$  ratio 88% (measured by Raman spectroscopy). The reference electrode was a classical calomel electrode, saturated with KCl, and the auxiliary one was a platinum wire.

### 2.4. Procedure

Differential pulse anodic stripping voltammetry (DPASV) was used for all experiments. The potential of accumulation was usually chosen at  $-1.7$  V/SCE and applied for 60 s. A rest time of 15 s was always applied after accumulation, the stirring being stopped. The potential scan was performed from  $-1.7$  to  $+0.3$  V/SCE with a scan rate of 50 mV s<sup>-1</sup>, a potential step of 25 mV and a pulse length of 50 ms. After each experiment applying  $+0.5$  V potential for 60 s provided the elimination of eventual deposited species at the working electrode. Quotidian cleaning of BDD was made with concentrated acid then with ethanol and deionized water. For GC, polishing on abrasive SiC disks, with

decreasing granules size (22, 15, 10  $\mu\text{m}$ ), was necessary before the beginning of daily analysis. After polishing, the electrode was sonicated for 2 min in ultrasonic bath to clean surface from polishing residues.

### 3. Results and Discussion

Four currently analyzed heavy metals were selected: copper, lead, cadmium and zinc, whose stripping peak potentials are respectively:  $-0.1$ ,  $-0.5$ ,  $-0.82$  and  $-1.0$  V/SCE. The electrochemical behavior of these metals is known to be that of reversible systems in various electrolytes, which allows the use of anodic stripping for trace analysis. Our study is first focused on finding the best analytical parameters for the method, i.e., the accumulation potential, the deposition time and the supporting electrolyte concentration. Second, analysis of each metal was made and the results were reported. Third, a simultaneous metal ion analysis and interference study show us the difficulties encountered with this sensor. Finally, a comparison between BDD and GC performance is presented.

#### 3.1. Influence of Analysis Parameters

##### 3.1.1. Deposition Potential

All experiments were made with 10 ppb of each metal and the acetic acid-sodium acetate buffer was selected in order to stabilize the pH value of the measured samples (4.8). To obtain an appreciable signal for the anodic stripping peaks, it was rapidly recognized that a much more cathodic deposition potential than the peak value of each metal was necessary. Figure 1 shows typical results, the peak amplitude being plotted as a function of the deposition potential. These results clearly indicate that a potential lower than  $-1.5$  V/SCE is necessary in the absence of zinc, while in the presence of zinc, a  $-1.7$  V/SCE seems more suitable. Because a BDD electrode may operate down to very cathodic potentials, using very cathodic potentials, even lower than that of hydrogen evolution (begins at  $-1.3$  V/SCE in 0.01 M acetate buffer), doesn't affect the material surface or the analysis of the element under study, as will be seen below in following paragraphs.

##### 3.1.2. Accumulation Time

Usually in anodic stripping an increase of the deposition time leads to a proportional increase of the peak current. For BDD this is true for 0.1 M acetate buffer but not really for a ten times diluted buffer. Linear response of Cd anodic stripping peak is observed from 0 to 10 min accumulation time in 0.1 M acetate buffer. For a 0.01 M buffer, proportionality may be limited up to 2 to 3 minutes. The same observation was made for the three other metals.

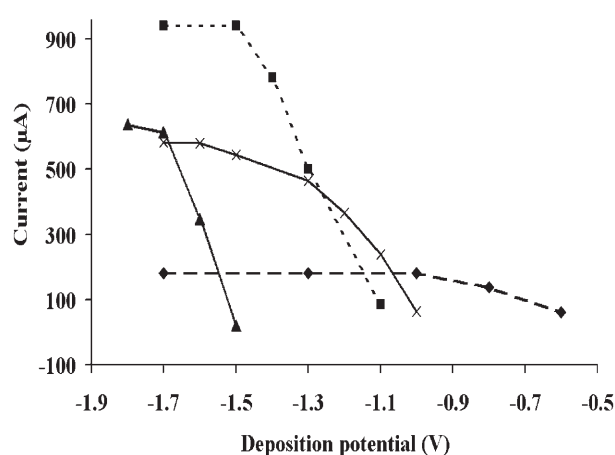


Fig. 1. Influence of deposition potential on the Zn, Cd, Pb, and Cu stripping peak current (DPASV). Analyses were made at BDD ( $\varnothing = 7.2$  mm) in 0.01 M acetate buffer and 60 s deposition time and 400 rpm stirring during accumulation. ( $\blacklozenge$ ) 10 ppb Cu, ( $\blacksquare$ ) 10 ppb Cd, ( $\blacktriangle$ ) 10 ppb Zn + 10 ppb Pb.

##### 3.1.3. Supporting Electrolyte

In electroanalysis, the concentration of the supporting electrolyte is always a critical problem. When analyzing traces, it is necessary to have as little pollution as possible coming from the reagents. In order to add a minimum amount of supporting electrolyte to natural water we observed the stripping of Cu, Pb, Cd and Zn in 0.01, 0.05, 0.1 M acetate buffer. For the four metals it was noticed that the response increases as the supporting electrolyte is diluted. For example, Figure 2 shows data for  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$ . This is interesting since detection is better and since the pH of the samples will be adjusted without a great change of volume.

Table 1 shows data for the four metals analysis in 0.01 M and 0.1 M acetate buffer.

Detection limit and quantification limit have been calculated from the following formulae: [44]

$$L_D = 3 Rh$$

$$L_Q = 10 Rh$$

with  $h$  = amplitude of noise signal,  $R$  = response factor quantity/peak height

We can realize from data in Table 1 that the detection limit of heavy metals is slightly in favor of diluted buffer. This is probably due to the electrolyte's ionic force that generates a higher residual current in more concentrated media. The Zn peak being very close to the hydrogen evolution, it is all the more affected by this phenomenon. The calculated detection limits and quantification limits were close to what had been observed experimentally. On the other hand concentrated media provides wider detection ranges. Sensitivity was not dramatically affected by the change of media. For a one-minute accumulation time, ppb

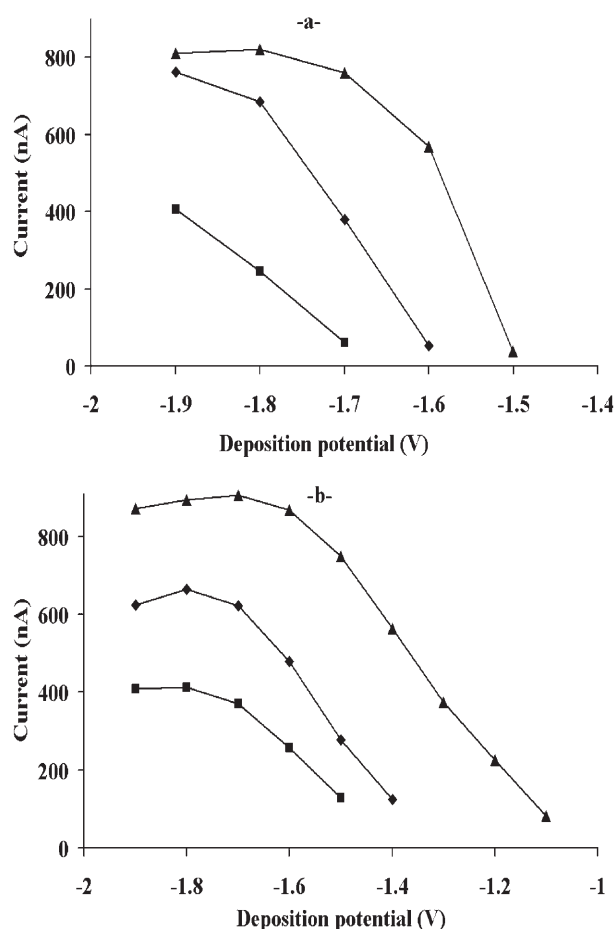


Fig. 2. Influence of electrolyte concentration on stripping peak current of a) Zn (10 ppb) and b) Cd (10 ppb) (DPASV). Stripping peak current vs. accumulation potential is presented for each electrolyte concentration; (▲) 0.01 M, (◆) 0.05 M, (■) 0.1 M acetate buffer. Analyses were made at BDD ( $\varnothing = 7.2$  mm). Accumulation time: 60 s and stirring 400 rpm during accumulation.

metal detection is possible at BDD ( $\varnothing = 7.2$  mm) in 0.01 M acetate buffer medium.

Comparing these results with those obtained previously at BDD in the literature shows the improvement in detection, quantification and time that this method brings [29–43].

### 3.2. Interference and Simultaneous Determination

Single metal detection is a particular case that we may not encounter in real sample analysis, simultaneous metal detection is needed for samples in polluted sites, and thus metal-metal interaction study must be taken into consideration before any quantification study specially, as known, that solid electrodes presents difficulties for simultaneous metal detection in general. Part of most frequent interactions will be presented discussed and compared to some literature approaches.

#### 3.2.1. Case of Pb + Cd

To show if metals like Cd and Pb have major effects on each other, we proceeded to the following experiment: Alternating additions of Cd and Pb were made on an initial solution of 15 ppb of Pb in 0.01 M acetate buffer. The first addition of Cd (5 ppb) had no apparent effect on Pb stripping peak comparing it with the initial Pb one. A reverse addition of 5 ppb of Pb was made after that, on the previous solution and had no effect on the Cd stripping peak. Figure 3 represents a 3D overlay stripping voltammograms of three alternating successive additions of Cd and Pb that shows our observation.

In fact, these observations are true but reflect part of reality of Pb–Cd interaction especially if we refer to the work done by Manivannan et al. [42]. For them Pb and Cd interfere one on other but quantification is still possible. By proposing sequence of events occurring during the deposition and stripping from solution containing both metals they tried to give explanation to their claim. One of the most important events proposed was that, during accumulation stage, deposition of Cd could occur at BDD (nucleation and growth) and at Pb nanoparticles (at monolayer level)

Table 1. Analyses (DPASV) of heavy metals ( $L_D$ ,  $L_Q$ , sensitivity, linearity range and correlation coefficient) at BDD ( $\varnothing = 7.2$  mm) in different electrolyte concentrations (0.1 M and 0.01 M acetate buffer) with deposition potential  $-1.7$  V deposition time 60 s solution being stirred at 400 rpm.

Metal/Acetate buffer	Correlation coefficient	$L_D$ (ppb)	$L_Q$ (ppb)	Linearity range (ppb)	Sensitivity (nA/ppb)
<b>Zn</b>					
0.01 M	0.996	1.6	5	5–20	54.8
0.1 M	0.995	9.6	32	32–100	31
<b>Cd</b>					
0.01 M	0.998	0.36	1.2	1.2–25	65
0.1 M	0.998	1	3.2	3.2–70	68
<b>Pb</b>					
0.01 M	0.999	1.15	3.8	3.8–45	71.2
0.1 M	0.999	2.3	7.7	7.7–100	93.9
<b>Cu</b>					
0.01 M	0.999	0.9	3	3–20	12
0.1 M	0.998	2.3	7.5	7.7–100	40

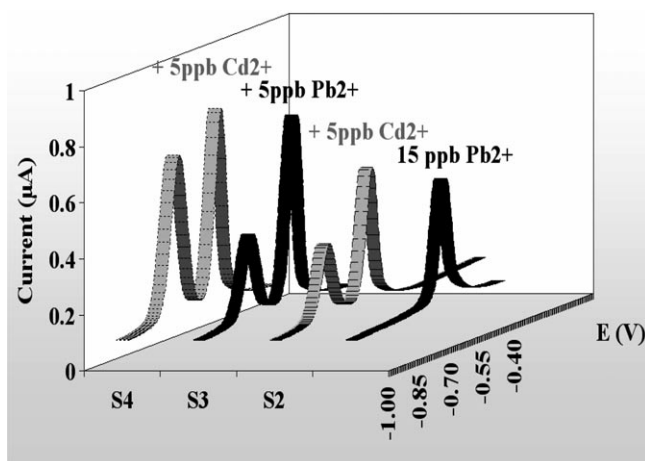


Fig. 3. 3D anodic stripping voltammograms overlay (DPASV) after adding alternating successive amounts of Pb and Cd in 0.01 M acetate buffer at  $-1.9$  V deposition potential and 60 s deposition time. BDD ( $\varnothing = 7.2$  mm). Stirring was at 400 rpm during accumulation.

which are preferentially deposited at BDD surface during this stage (what generally happens for metals with less negative standard potential). Therefore, Cd and Pb stripping peaks will be affected since Cd present at Pb particles as monolayer is stripped along with Pb stripping. But, despite the fact that small amounts of Pb decreases considerably the Cd stripping peak, further addition of Pb has slight effect on the last one (Pb peak being slightly increased for Cd additions). This is in agreement with the no apparent interaction of Cd and Pb in our experiment especially because initial solution, before additions, was the Pb one.

### 3.2.2. Case of Cu, Pb, Cd, Zn

Copper, the first metal to be deposited, seems to have great influence on the responses of the three other metals. Cadmium and zinc peaks dropped when copper was added. Typical behavior for Cd and Zn in the presence of Cu is given in Figure 4. The Cd peak dropped and showed an intermetallic peak tailing with copper, positioned on the Pb stripping potential. The Zn peak was almost suppressed. If we compare these observations with literature, Foord et al. [45] have found in their study of Zn and Cd interaction with Cu at BDD, that accumulation being favorable to copper (most positive redox potential), active sites of BDD are thus occupied by this one blocking Cd and Zn deposition. No further explanations were given for this inhibition. Formation of intermetallic species was also suspected at intermediate Cu/Zn ratio. Cu-Zn intermetallic was noticed in other studies [10, 41], and same for Cu-Cd [33]. This proposal is in agreement with what is observed in figure 4 representing the overlay of stripping voltammograms before and after adding Cu to Cd and Zn initial solution. We can also explain the dramatic dropping of Zn stripping peak in our experiment, compared with Cd one, by the presence of the close hydrogen evolution whose formation is cata-

lyzed by the presence of Cu at BDD and hence perturbs Zn signal.

Along with these kinds of interactions that we mentioned above, there exists a well-known Cu-Pb interaction in literature. The formation of intermetallic oxidation peak is mentioned as a consequence of Cu-Pb alloy formation in the accumulation stage [20, 32–33]. Other studies noticed a formation of misleading extra peak due to hydrogen evolution at freshly exposed copper under stripping conditions at low pH values and high Cu concentrations [46]. This was also noted by other studies [47].

### 3.2.3. Case of Zn + Pb

Because Pb was deposited at less cathodic potentials than zinc, it was observed that it has an influence on the peak magnitude of Zn. Figure 5 clearly illustrates this observation. The analysis of the initial solution (voltammogram n° 1) having a 6 ppb Zn level gives a Zn peak that is perfectly well defined. But after adding increasing amounts of Pb to the solution (voltammograms n° 2, 3, 4), the initial Zn stripping peak dropped and resulted in an indefinite large zone peak, also affecting the stripping potential of Cd. Conversely, the Pb peak was unchanged when increasing amounts of Zn were added (voltammogram n° 5). This observation reveals clearly the formation of intermetallic Zn-Pb species. It could be the result of Zn-Pb alloy formation at BDD, involving very little amounts of Pb, or the nucleation of Zn at Pb deposited particles at BDD sites inducing a shift of the Zn stripping potential (without affecting Pb stripping peak).

After this interaction study between heavy metals of interest, we can say that the simultaneous analysis of those contaminants seems to be complex and not so easy especially in the presence of copper, which is the most disturbing element. For this reason the simultaneous analysis of Cd and Pb will be realized (Sec. 3.2.4) and then

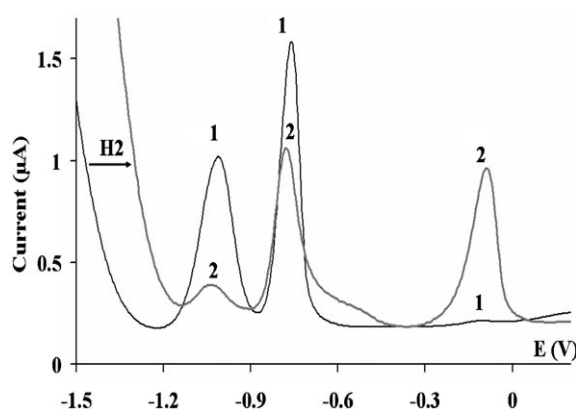


Fig. 4. Anodic stripping voltammograms (DPASV) of simultaneous analysis at BDD ( $\varnothing = 7.2$  mm) of Zn (15 ppb) and Cd (15 ppb) 1) before and 2) after adding 23 ppb  $\text{Cu}^{2+}$ . Electrolyte was acetate buffer 0.01 M,  $E_{\text{dep}} = -1.9$  V and  $T_{\text{dep}} = 60$  s. Stirring 400 rpm.

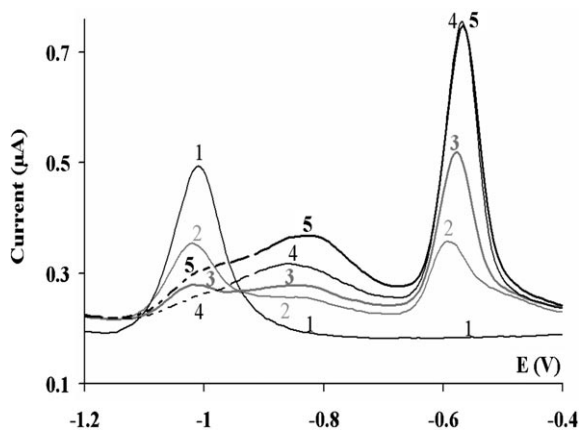


Fig. 5. Overlay of anodic stripping voltammograms (DPASV) for Zn-Pb interaction study. 1) initial solution with 6 ppb  $\text{Zn}^{2+}$ ; 2) first addition of 4 ppb  $\text{Pb}^{2+}$ ; 3) second addition of 6 ppb  $\text{Pb}^{2+}$ ; 4) third addition of 9 ppb  $\text{Pb}^{2+}$ ; 5) fourth addition of 12 ppb  $\text{Zn}^{2+}$ . Analysis was at BDD ( $\varnothing = 7.2$  mm) in 0.01 M acetate buffer, deposition for 60 s at  $-1.9$  V. Stirring was at 400 rpm.

the possibility of calibrating of Zn in the presence of Pb and Cd will also be discussed (Sec. 3.2.5).

### 3.2.4. Cd-Pb Determination

The simultaneous determination of Pb and Cd was made under the following conditions: the supporting electrolyte was a 0.05 M acetate buffer. The buffer concentration was chosen as a compromise between diluted buffer (favoring detection limit) and concentrated buffer (favoring detection range). Deposition potential was  $-1.9$  V giving in this medium, the maximum deposition for Zn (see Fig. 4) if it needs to be detected (later). Deposition time is 60 s and a 400 rpm magnetic stirrer ensures solution stirring. For the simultaneous determination of Cd and Pb we obtained voltammograms presented in Figure 6. For both species we have quantification limits of about 5 ppb, but the linearity range for Pb (5–70 ppb) is wider than that determined for Cd (5–20 ppb). Detection of 1.5 ppb is possible for both metals.

### 3.2.5. Zn Determination in Presence of Cd and Pb

An attempt was then made, to quantify Zn in the presence of Cd and Pb. As predicted, the Zn peak overlapped that of Cd. This is notably due to the presence of Pb as was demonstrated previously in Figure 5 (Sec. 3.2.3) However, and as we can see in Figure 7, adding a quantity of this metal ion produces a shoulder on the cathodic foot of Cd peak. Nevertheless the quantification of zinc is possible. The other two peaks of Cd and Pb were not modified by the addition of Zn, as is shown in figure. For Zn analysis, the sensitivity has dramatically diminished compared to a simple element analysis, but quantification is still possible at levels higher than 4 ppb.

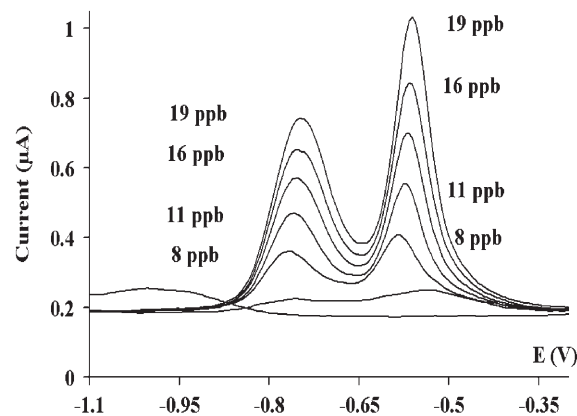


Fig. 6. Overlay of anodic stripping voltammograms for (DPASV) the simultaneous determination of Cd and Pb at BDD ( $\varnothing = 7.2$  mm) in 0.05 M acetate buffer with deposition time 60 s at  $-1.9$  V. Stirring was performed at 400 rpm.

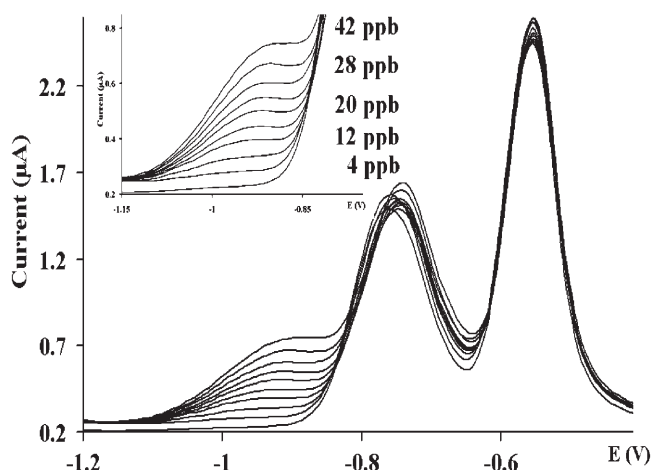


Fig. 7. Anodic stripping voltammograms overlay (DPASV): additions of Zn in the presence of Cd (44 ppb) and Pb (56 ppb). Analyses were at BDD ( $\varnothing = 7.2$  mm) in 0.05 M acetate buffer, deposition for 60 s at  $-1.9$  V. Stirring was at 400 rpm.

## 3.3 Comparison Between Glassy Carbon (GC) and BDD

It was interesting to compare the BDD electrode to a classical glassy carbon electrode (GC), which has been recognized as an interesting electroanalytical tool because of its low sensitivity to memory effects and has been widely used for heavy metal detection. To do so, comparable conditions were fixed for both electrodes, and in particular the surface of the sensor was chosen as being 3 mm in diameter in both cases. For the analysis at 3 mm diameter BDD, smaller electrochemical cell than the one for 7.2 mm diameter BDD with smaller opening was chosen. A smaller magnetic bar was used for stirring allowing higher stirring rate to be applied without getting violent agitation of the solution.



Figure 8 shows the overlay of the three metals stripping peaks at GC and BDD. Analysis was made at  $-1.7$  V deposition potential, 2 min deposition time and in 0.01 M acetate buffer electrolyte. We can see that detection is obviously much better at BDD than GC. This observation was ascertained by the results of the analysis at BDD and GC for the four metal ions summarized as  $L_D$ ,  $L_Q$ , and sensitivity in Table 2. We noticed also that the baseline current at BDD is far lower than at GC and the potential range is wider. It is clear that detection and quantification are almost four times lower at BDD and sensitivity is more than two times higher than that at GC in general (Table 2). Furthermore, we can add the longevity of the BDD material that may work for more than six months without a significant change in its quality unlike GC materials that must be frequently polished and cleaned.

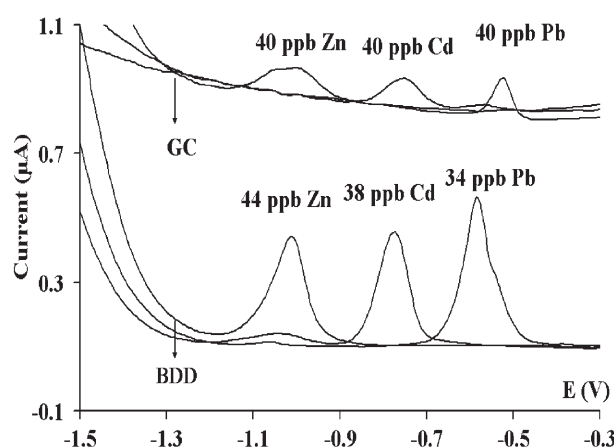


Fig. 8. Overlay of anodic stripping voltammograms (DPASV) of Zn, Cd and Pb at BDD ( $\varnothing = 3$  mm) and GC ( $\varnothing = 3$  mm).  $E_{\text{dep}} = -1.7$  V,  $t_{\text{dep}} = 2$  min, electrolyte: 0.01 M acetate buffer, with stirred solution (900 rpm).

Table 2. Comparison of heavy metals analysis (DPASV) ( $L_D$ ,  $L_Q$  sensitivity) at BDD ( $\varnothing = 3$  mm) and GC ( $\varnothing = 3$  mm) in 0.01 M acetate buffer with  $-1.7$  V deposition potential for 2 min deposition time with solution being stirred at 900 rpm.

Metal/electrode	$L_D$ (ppb)	$L_Q$ (ppb)	Sensitivity (nA/ppb)
<b>Zn</b>			
BDD	2.6	8.5	7.7
GC	8	26	2.6
<b>Cd</b>			
0.01 M	1.9	6.5	9
0.1 M	7.14	23.8	3.7
<b>Pb</b>			
BDD	2.2	7.2	21.4
GC	8.1	27	4.6
<b>Cu</b>			
BDD	1.54	5.15	10
GC	5.8	19.2	3.9

## 4. Conclusion

The simultaneous analysis of heavy metals was the aim of this study. At BDD difficulties were encountered but overcome for Zn, Cd and Pb simultaneous analysis. Copper caused a lot of interference with other metals and was the major problem for the analysis. On the other hand, we saw that working in diluted media favors the detection of these contaminants on this kind of electrode. An ideal deposition time of one minute permitted the detection of a ppb level for the four metals in general.

## 5. Acknowledgements

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