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THE IMPORTANCE OF THE CORK (BARK) OF *QUERCUS SUBER* IN THE ENVIRONMENTAL MONITORING OF HEAVY METALS

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KEYWORDS

Heavy metals, Pb(II), cork (bark), *Quercus suber*, environment, DPASV

ABSTRACT

The recent absence of Lead element as catalyst in internal explosion motors, being an extremely important action for the stop of this environmental aggression, has no effect in the minimization of the harm this element does in the positions where its deposition now lays. The impact of the ubiquity of pollution, in this case Lead pollution, needs to have monitoring tools. The greatest of the tools one can have is the analysis of the content of a strong indicator. One that stands for a long time in one place, for which it is able to receive the marks of the analyte passage. *Quercus suber* (Cork Oak) tree is such a case. Having a life expectation ranging from 200 to 500 years (depending on the cork extraction intensity) and with a capability of regeneration of its cork coverture, it concentrates the amounts of Lead, with which it had contacted through its life, in successive layers, corresponding, the larger ones, to the high temperatures season, and the thinner ones to the low temperatures season. So, the analysis of the content of the element in a layer of cork with a given amount of years in the tree, will be a good estimator of how the content of Lead as evolved in the area. And a correct distribution of sampling trees will show much more about a greater area. The possibility of choosing years by choosing layers of cork, and the fact that the sampling will not harm the tree, if properly done, make this procedure a novel and powerful tool in the monitorization of the dispersion of heavy metals in areas populated by *Quercus suber*, as it is the case of big areas in Portugal, the great of the greatest in everything related with this tree, namely economically, and, in general, in the area of the Mediterranean basin. This paper announces how the electroanalytical determination of Pb(II) by Differential Pulse Anodic Stripping Voltammetry (DPASV), recently done in the Department of Chemistry of the University of Évora, already accepted for publication in *Portugaliae Electrochimica Acta*, has proven to allow a deeper insight into the previously discussed problematic.

INTRODUCTION

The vocation of the entire area of Portugal, when seen at the Mediterranean basin scale (Fig. 1), in 1950 by Vieira Natividade, Vieira Natividade (1990), is tendencially subericultural. This panoramic view is possible only because of the used scale. Even so, in a closer look, possible in Gil (1998), it can be seen that the distribution of *Quercus suber*, according to a 1991 work, is quit frequent in Portugal (Fig. 2). On the other hand, the growing behaviour of the bark of this tree, in which one layer of cork means a low temperatures season or a high one, whether it is a small or a big layer (Fig. 3), Vieira Natividade (1990), allows us to look for a chronological concentration pattern, for a certain analyte, through those layers. Differential Pulse Anodic Stripping Voltammetry (DPASV) is the analytical tool already expected to be

ideal for the test needed, once it allows rather good evaluations of the Pb(II) content of the cork from *Quercus suber*, Ponte e Sousa (2003), as is shown in this work.

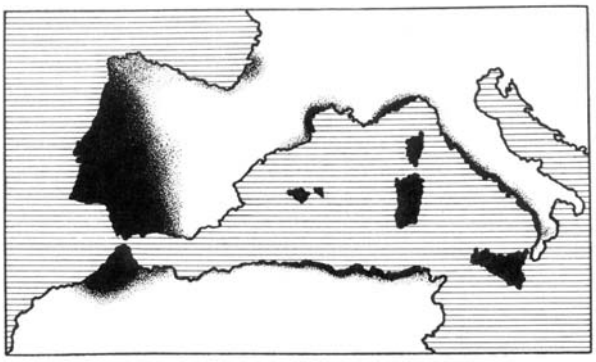

Figure 1 - Quercus suber distribution in the Mediterranean basin, Vieira Natividade (1990) p 35.

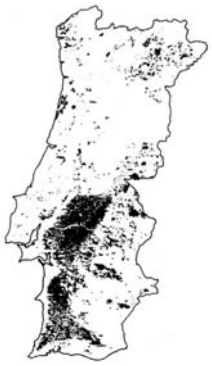

Figure 2 - Quercus suber distribution in Portugal, as shown in Gil (1998) p 63.

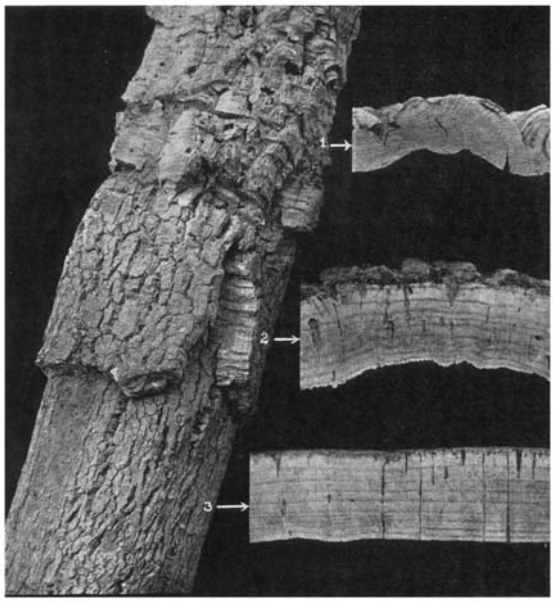

Figure 3 - Layers of growing cork: 1-In never extracted cork. 2- In cork grown after the first extraction. 3- In cork grown after the second extraction. Vieira Natividade (1990) p 139.

EXPERIMENTAL

As in Ponte e Sousa (2003), the experimental was as follows:

Reagents and solutions

Were prepared: A supporting electrolyte solution NaCl 0.1 mol.dm^{-3} dissolving NaCl (Merck p. a.) in Milli-Q water. A HNO_3 0.1 mol.dm^{-3} solution, done by dissolving HNO_3 65% (Merck p.a.) in Milli-Q water. A Pb(II) 1.1x10^{-2} mol.dm^{-3} stock solution, dissolving $Pb(NO_3)_2$ (Riedel) in $HNO_3$0.01mol.dm^{-3}. A standard solution Pb(II) 1.1x10^{-5} mol.dm^{-3}, done diluting the former. Were used as digestor reagents: HNO_3 65% (Merck p. a.) and H_2O_2 30% p/v (Panreac p. a.).

Instrumentation

Differential Pulse Stripping Voltammetry was made using a potentiostat/galvanostat AUTOLAB/PGSTAT 20 (Eco Chemie) associated to a VA Stand 663 (Metrohm). In this equipment were used: a Hanging Mercury Drop Electrode (HMDE), a Glassy-Carbon Rod Counter Electrode, and an Ag/AgCl/KCl 3M Reference Electrode. Software: GPES 4.9 (Eco Chemie).

Voltammetric conditions

Pretreatment: Purge time: 5 s. Deposition potential: -0.650 V. Deposition potential time: 180 s. Stirrer off during deposition: No. Equilibration time: 30 s.

Measurement: Cell off after measurement: Yes. Modulation time: 0.05 s. Interval time: 0.25 s. Potentials: Initial potential: -0.650 V. Final potential: -0.1 V. Step potential: 0.00195 V. Modulation amplitude: 0.03 V. Scanning velocity: 7.8 mV/s.

Other characteristics

Drop Surface: 0.25 mm^2 ± 10%. Agitator rotation velocity: 1500 min^{-1}. Deaeration time: 10-12 min.

Procedure

Digestion: Several tree cork (with no industrial treatment) digestions were made, according to the following scheme: Extraction of Cork Oak bark faces; Granulation with a plastic granulator; Weighing [0.09]g of bark powder from granulation; Addition of 2 ml HNO3 and 0.25 ml of H2O2; Waiting for 2 hours, approximately; Digestion in closed recipient (85-90 ºC) for 8 hours.

Voltammetries: Quantities of 0.1 ml of standard were additionated to 1 ml of cork solution and 20 ml supporting electrolyte. Each measurement was made three times in each addition.

RESULTS

The following results have been achieved, shown in figures 4 (and table 1), 5 (and table 2) and 6.

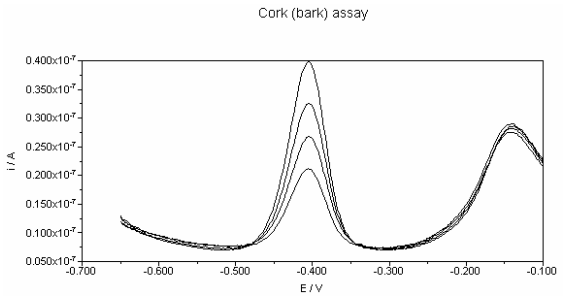

Figure 4 - Superposition of one representative voltammogram for each addition. From bottom up: Cork (bark) solution, 1st, 2nd and 3rd standard addition. Standard additions were of 0.1 ml 1.1x10-5M Pb(II) to 21 ml (20 ml NaCl 0.1M and 1 ml Cork Solution). Three replicas were made for each addition.

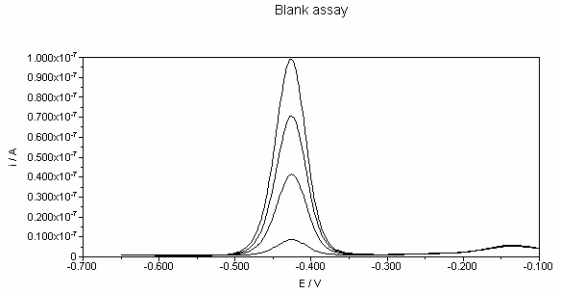

Figure 5 - Superposition of one representative voltammogram for each addition. From bottom up: digestor solution, 1st, 2nd and 3rd standard addition. Standard additions were of 0.1 ml 1.1x10-5 M Pb(II) to 21 ml (20 ml NaCl 0.1M and 1 ml Digestor Solution). Three replicas were made for each addition.

Table 1 - E and i were measured three times for supporting electrolyte and for each addition. Standard additions were of 0.1 ml 1.1x10-5 M Pb(II) to 21 ml (20 ml NaCl 0.1M and 1 ml Cork Solution). E- Peak Potential (Versus Ag/AgCl/KCl 3mol.dm-3. In NaCl 0.1 mol.dm-3); i- Peak Current Intensity; SD- Standard Deviation; Med- Average Value; Cp- Standard Concentration; icr = i ((Ves+Va+ΣVp) / (Ves+Va))- Corrected Peak Intensity Current; Ves- Supporting Electrolyte Volume; Va- Sample Volume; Vp- Standard Addition Volume.

	E med/V ± 10^3 SD/V	**10^9 i med/A ± 10^{10} i SD/A**	**10^9 icr med/A ± 10^{10} icr SD/A**	**10^8 Cp/M**
Cork Solution	-0,405 ± 1	13,95 ± 6,029	13,95 ± 6,029	0
1st Standard Addition	-0,405 ± 1	19,39 ± 1,484	19,49 ± 1,491	5,213
2nd Standard Addition	-0,405 ± 1	25,53 ± 4,148	25,77 ± 4,187	10,38
3rd Standard Addition	-0,404 ± 0	32,37 ± 4,285	32,83 ± 4,346	15,49

Table 2 - E and i were measured three times for supporting electrolyte and for each addition. Standard additions were of 0.1 ml 1.1x10-5 M Pb(II) to 21 ml (20 ml NaCl 0.1M and 1 ml Digestor Solution). E- Peak Potential (Versus Ag/AgCl/KCl 3mol.dm-3. In NaCl 0.1 mol.dm-3); i- Peak Current Intensity; SD- Standard Deviation; Med- Average Value; Cp- Standard Concentration; icr = i ((Ves+Va+ΣVp) / (Ves+Va))- Corrected Peak Intensity Current; Ves- Supporting Electrolyte Volume; Va- Sample Volume; Vp- Standard Addition Volume.

	E med/V ± 10^3 SD/V	**10^9 i med/A ± 10^{10} i SD/A**	**10^9 icr med/A ± 10^{10} icr SD/A**	**10^8 Cp/M**
Digestor Solution	-0,426 ± 0	7,745 ± 0,540	7,745 ± 0,540	0
1st Standard Addition	-0,426 ± 0	40,48 ± 0,346	40,67 ± 0,348	5,213
2nd Standard Addition	-0,426 ± 0	70,15 ± 8,411	70,82 ± 8,490	10,38
3rd Standard Addition	-0,426 ± 0	98,77 ± 17,91	100,2 ± 18,20	15,49

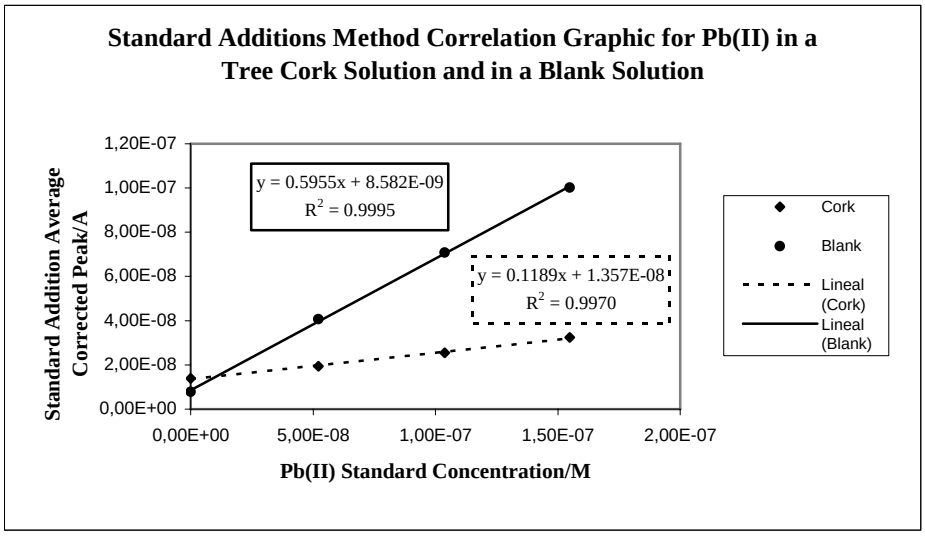

Figure 6 - Correlation analysis by the Minimum Square Method using data according to tables 1 and 2.

Final result assessment

Having the corrected average current intensity peak height (icr) and the known Lead standard concentrations used, in the voltammetric cell, it was done the adjust of a line to points icr versus C_p using the Minimum Square Method, fulfilled its conditions (namely, deterministic knowing of concentration). This was done for both Digestor and Cork Solutions. Subtracting the Digestor value from the Cork value, it is found the amount of Lead in Cork.

So, we have the following connected equations, Equation 1 for Cork, and Equation 2 for Digestor (Pb_C- Lead from Cork analysis. Pb_R: Lead from Digestor analysis):

$$i = 0 = 0.1189\ (Pb_C + Pb_R) + 1.357x10^{-8} \quad (1)$$

$$i = 0 = 0.5995\ Pb_R + 8.582x10^{-9} \quad (2)$$

From which we found:

$$PbC = (PbC + PbR) - PbR = 1.357x10\text{-}8/0.1189 - 8.582x10\text{-}9/0.5995 \quad (3)$$

So: The concentration in Pb(II), from the digested Cork sample, in the voltammetric cell is $1.14x10^{-7}$ M, and the concentration in Pb(II), from the Digestor sample, in the voltammetric cell, is $1.43x10^{-8}$ M.

From which we may accept the estimation that the Lead concentration, in the voltammetric cell, coming from Cork is in the concentration of $9.97x10^{-8}$ M.

So, once the analyzed sample was diluted from 1 ml/21 ml, that this 1 ml was retired from one aferition of the Cork digestion with 5 ml, that the molar mass of Lead is 207.2 g/mol and that was digested 0.09 g of Cork, it is concludable that, in the sample there was 24.1 μg Pb(II)/ (g of used Cork).

(mPb(II)/mCork) = $9.97x10^{-8}$ M x 21 x 5 ml x (207.2g/mol)/0.09g=24.1μgPb(II)/(g of used Cork) (4)

CONCLUSIONS

The main conclusions of this work is the capability DPASV, still on study, keeps on showing of allowing a inexpensive and straightforward way for the determination of the Lead content of Cork, as exposed in the main text of this article (24.1 μg Pb(II)/ (g of used Cork), (Gil (1998), p 255, refers values from 10 to 50 μg/g)), and also the opportunity it poses for a deeper environmental monitoring approach to the capability of assessing the environmental Lead distribution (following the way Nriagu seems to defend, Nriagu (1978)), once seen that the layerly way of the growing of Cork allows us to dispose of a renewable, non harmful for the tree, natural material, for analysis, that works like an undoubtly steady state probe. In a nine years cycle extraction, or using ancient monumental trees, the use of such a

Potential Vegetation tree, so Mediterranean, to find the distribution of Lead in Mediterranean countries, like Portugal, is right in front of the investigation.

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