

Document downloaded from:

<http://hdl.handle.net/10251/143322>

This paper must be cited as:

Domenech-Carbo, A.; Domenech Carbo, MT.; Valle-Algarra, FM.; Gimeno-Adelantado, J.; Osete Cortina, L.; Bosch-Reig, F. (07-2). On-line database of voltammetric data of immobilized particles for identifying pigments and minerals in archaeometry, conservation and restoration (ELCHER database). *Analytica Chimica Acta*. 927:1-12.  
<https://doi.org/10.1016/j.aca.2016.04.052>



The final publication is available at

<https://doi.org/10.1016/j.aca.2016.04.052>

Copyright Elsevier

Additional Information

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

**On-line voltammetry of immobilized particles database of pigments and minerals for archaeometry, conservation and restoration (ELCHER database)**

Antonio Doménech-Carbó<sup>\*a</sup>, María Teresa Doménech-Carbó<sup>\*b</sup>, Francisco Manuel Valle-Algarra<sup>a</sup>, José Vicente Gimeno-Adelantado<sup>a</sup>, Laura Osete-Cortina<sup>b</sup>, Francisco Bosch-Reig<sup>a</sup>

<sup>a</sup> Departament de Química Analítica. Universitat de València. Dr. Moliner, 50, 46100 Burjassot (València) Spain.

<sup>b</sup> Institut de Restauració del Patrimoni, Universitat Politècnica de València, Camí de Vera 14, 46022, València.

\* Corresponding authors. E-mail: [antonio.domenech@uv.es](mailto:antonio.domenech@uv.es) and [tdomenec@crbc.upv.es](mailto:tdomenec@crbc.upv.es).

Keywords: Voltammetry; Pigments; Database; Archaeometry; Conservation and restoration.

**Abstract**

A web-based database of voltammograms is presented for characterizing artists' pigments and corrosion products of ceramic, stone and metal objects by means of the voltammetry of immobilized particles methodology. Description of the website and the database is provided. Voltammograms are, in most cases, accompanied by scanning electron microphotographs, x-ray spectra, infrared spectra acquired in attenuated total reflectance Fourier transform infrared spectroscopy mode (ATR-FTIR) and diffuse reflectance spectra in the UV-Vis-region. For illustrating the usefulness of the database two case study involving identification of pigments and a case study describing deterioration of an archaeological metallic object are presented.

**Keywords:** Voltammetry of immobilized particles; Database; Pigments; Corrosion products.

## 1. Introduction

1  
2  
3  
4 The elucidation of the composition of artist's materials and their alteration products is  
5 an essential analytical target in archaeometry and conservation of cultural heritage.  
6  
7 These analytical studies are particularly important in regard to pigments. Relevant  
8  
9 information for authentication, dating and provenance studies, identification of  
10  
11 repainting and testing deterioration degree can be obtained from the study of pigments  
12  
13 present in paintings, polychromed sculptures and decorative elements [1,2]. Most  
14  
15 coloring materials historically used by artists are natural products such as minerals,  
16  
17 often chemically treated, and organic extracts and exudates from plants (more rarely  
18  
19 from animals) rather than chemically pure substances. Accordingly, the interpretation of  
20  
21 the analytical data provided by available instrumental techniques requires the disposal  
22  
23 of a wide reservoir of case-sensitive standards. This has motivated the recent  
24  
25 appearance of libraries containing UV-visible spectra, FTIR/Raman spectra and X-ray  
26  
27 diffraction data for minerals and artist's pigments [4-17].

28  
29 On the other hand, available techniques for pigment analysis have been expended by the  
30  
31 development of the voltammetry of immobilized particles (VIMP), a methodology  
32  
33 developed by Scholz *et al.* prompting the electrochemical characterization of solid  
34  
35 materials, early applied to minerals [18-21] and pigments [22]. As recently reviewed,  
36  
37 the VIMP can be applied to the identification, mineralogical and oxidation state  
38  
39 speciation and quantification of selected analytes in a variety of materials [23-25] and  
40  
41 applied to the study of works of art [26-28] using amounts of sample in the microgram-  
42  
43 nanogram range.

44  
45 The special requirements of the analytical procedures when they are applied to works of  
46  
47 art and archaeological artifacts makes VIMP particularly useful because of its inherently  
48  
49 high sensitivity, requirement of minimal amounts of sample, no need of sample  
50  
51 pretreatment and partial sample recuperation and use for multiple analysis. Since its first  
52  
53 application for identifying inorganic pigments [29], the VIMP methodology has been  
54  
55 increasingly used in the analysis of pigments in works of art [30-38], their alteration  
56  
57 products [36,38], as well as metal corrosion products [40-44]. The scope of this  
58  
59 technique in the archaeometric field has been enhanced by the use of 'graphite pencil'  
60  
61 sampling [45-48], local [49,50] and layer-by-layer analysis [51]. The analytical  
62  
63  
64  
65

1 capabilities of VIMP have been expanded to provide relevant information for the  
2 authentication [52,53], tracing and dating [54-57] of archaeological metal. Hybrid  
3 inorganic-organic pigments of historical relevance such as Maya blue have also been  
4 studied by VIMP [58-64].  
5  
6  
7

8  
9 The purpose of the current report is to present a web-based database “Electrochemistry  
10 for Heritage” (ELCHER) covering the VIMP response of artist’s pigments and products  
11 of alteration of stone, ceramics, metals and pigments and discuss the capabilities and  
12 constraints associated to the same, illustrated by selected case studies. The  
13 voltammograms database is complemented with scanning electron microphotographs  
14 and x-ray spectra, IR absorption spectra obtained by ATR-FTIR and UV-vis diffuse  
15 reflectance spectra. A complementary set of data from SECM and AFM coupled to  
16 electrochemical measurements is presented. Such data are of interest for applying them  
17 in the conservation and restoration field where these analytical techniques have been  
18 recently applied for the localization of proteins in paint layers [65] and the identification  
19 of pigments and corrosion products at the nanoscopic scale [37,66].  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29

## 30 **2. The ELCHER database**

31  
32 The ELCHER database is available on the internet website: <http://www.elcher.info>. The  
33 website was developed using HTML 4.0, CSS 2.0, PHP 4.0 and JavaScript  
34 programming languages. The voltammograms as well as microphotographs, x-ray, IR  
35 and reflectance spectra are available online. The whole database has, at this moment,  
36 100 voltammograms, 30 x-ray spectra, 50 ATR-FTIR spectra (spectral range: 600-4000  
37  $\text{cm}^{-1}$ ) and 50 UV-vis spectra (spectral range: 200-800 nm) of 70 different materials  
38 specifically used by artists from prehistoric times until nowadays.  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48

49 The home page contains a banner with graphs and photographs of a selection of  
50 pigments from the database. The web page is organized in seven areas (Fig. 1a). Tabs in  
51 the header allow the user to move from one major content area to another. The first area  
52 includes general information on the electrochemistry for heritage (ELCHER) research  
53 group (background, organization chart and facilities and equipments). The second area  
54 is a summary of the main results obtained by the ELCHER group in the last years (R+D  
55 projects, papers and books). The main results of a case study of relevance are shown in  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

1 the fourth area. The fifth area contains the ELCHEM database. The sixth to seventh  
2 areas are target frames containing all the links, news and contact information on the web  
3 page and the research group. Instrumentation and other details of voltammograms and  
4 spectra contained in the database may be obtained by clicking on “About Elcher  
5 Database” in the pull-down menu of the database tab in the main page. To start  
6 navigating through the database, users must click on the “search” button on the pull-  
7 down menu of the database tab after ticking the box “accept terms of use and legal  
8 conditions” (see Fig. 1b). Access to the voltammogram and spectra of a specific  
9 pigment or mineral is possible by writing the name of the pigment in the keyword box  
10 (Figure 2a). Restricted search can be carried out by selecting the option “common  
11 name”, “material type” or “data type” in the box “search by”. Then the page of the  
12 material selected appears. This page contains the following: voltammogram, filename,  
13 the pigment’s common name in English and Spanish languages, supplier or provenance  
14 data, chemical composition, acquisition conditions of the voltammogram. If available,  
15 x-ray, backscattered electron photograph, IR and UV-vis spectra are shown (Figure 2b).  
16 To a magnified view of the desired voltammogram, spectrum or microphotograph, users  
17 must click on the “voltammogram” or spectrum box which then opens a pop-up  
18 window with the image requested.  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33

### 34 **3. Experimental**

#### 35 *Reagents and reference materials*

36 Data presented here correspond to Kremer pigments (Aichstetten, Germany). Sodium  
37 acetate, acetic acid, hydrochloric acid (Panreac), acetone (Sigma) and Paraloid B72  
38 (Rhöm & Haas) were used as chemical reagents.  
39  
40  
41  
42  
43  
44  
45  
46

#### 47 *Instrumentation*

48 VIMP experiments were performed at 298 K in a three-electrode cell under argon  
49 atmosphere using a CH I660C device (Cambria Scientific, Llwynhendy, Llanelli UK)  
50 and Ivium CompactStat (Ivium Technol. B.V., Eindhoven, The Netherlands) portable  
51 equipment. A platinum wire counterelectrode and a saturated calomel reference  
52 electrode (SCE) completed the three-electrode arrangement. Aqueous 0.25 M sodium  
53 acetate buffer and 0.10 M HCl were used as electrolytes after being deoxygenated by  
54 bubbling Ar during 15 min. Cyclic and square wave voltammograms (CVs and SWVs)  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

1 were obtained using conventional abrasive VIMP protocols [18,19]. Commercial  
2 graphite leads Staedtler, Alpino, Hoc-i-noor and Disnak, all of HB type (68 %wt  
3 graphite) were used. Importantly, the electrolyte solution was renewed after each  
4 electrochemical run to avoid contamination due to metal ions eventually released to the  
5 solution phase during electrochemical turnovers. Prior to the series of runs for each  
6 material or sample, a conditioning protocol was used to increase repeatability. The  
7 electrode surface was polished with alumina, rinsed with water and polished by pressing  
8 over paper. In conventional ‘scratching’ VIMP for reference materials, an amount of 1-2  
9 mg of the solid was previously powdered in an agate mortar and pestle, was extended  
10 on the agate mortar forming a spot of finely distributed material. Then the lower end of  
11 the graphite electrode was gently rubbed over that spot of sample and finally rinsed with  
12 water to remove ill-adhered particles. Sample-modified graphite bars were then dipped  
13 into the electrochemical cell so that only the lower end of the electrode was in contact  
14 with the electrolyte solution.  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26

27 For field emission scanning electron microscopy X-ray microanalysis, cross-sections  
28 prepared from samples excised of paintings by embedding in polyester resin and polishing  
29 with SiC abrasive disks. Cross-sections were examined under a Zeiss model ULTRA 55  
30 field emission scanning electron microscope, which operated with an Oxford-X Max X-  
31 ray microanalysis system. Image acquisition was done at the 3 kV accelerating voltage.  
32 The chemical composition of pigments was obtained at the 20 kV accelerating voltage  
33 and 6-7 mm was the working distance for the X-ray detector. Samples were carbon-  
34 coated to eliminate charging effects. A semiquantitative microanalysis was carried out  
35 by the ZAF method to correct interelemental effects. The counting time was 100 s for  
36 major and minor elements alike. Element percentages were generated by the ZAF  
37 method on the Oxford-Link-Inca EDX software, which was performed to exclude C to  
38 avoid erroneous quantification because the signal detected for this element mainly came  
39 from the C coating applied to samples to suppress charge effects.  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52

#### 53 **4. Operating database**

##### 54 **4.1. Voltammetric response**

55 Generation of a practical database for artists’ pigments and corrosion products of art  
56 objects involves several analytical problems. The first one is the variability in the  
57 possible standard materials, because natural pigments or pigments prepared from natural  
58  
59  
60  
61  
62  
63  
64  
65

1 materials have been typically used until recent times. This means that materials with  
2 source-dependent composition rather than pure chemicals have to be tested. A second  
3 difficulty derives from the texture and composition of the base electrode to be used.  
4 Textural and chemical properties of the supporting graphite can influence the  
5 voltammetric response of the pigment, at least, in three ways: first, as a result of the  
6 different adherence and porosity of the graphite surface, thus yielding a more or less  
7 effective 'contact' and a more or less extensive three-phase particle/electrolyte/base  
8 electrode junction; second, by producing signals associated to oxygen (hydroquinone,  
9 phthalic anhydride and carboxylic, mainly) functionalities in the graphite surface [67,68];  
10 third, as a result of the more or less extensive surface area exposed to the electrolyte,  
11 determining more or less intense resistive plus capacitive effects on the base line of the  
12 voltammogram. Home-made paraffin-impregnated graphite electrodes are preferentially  
13 used in VIMP literature, but, as demonstrated by an inter-laboratory trial on iron earth  
14 pigments [31], the voltammetric response is sensitive to changes in the carbonaceous  
15 material constituting the base electrode. The more or less conductivity, particle  
16 adherence, and the appearance of surface oxygen functionalities [67,68] can promote  
17 significant changes in the voltammetric response. Additionally, the amount of electrode  
18 modifier determines a slight shift in the peak potentials [7]. To face all these problems,  
19 it is convenient to adopt common, uniform chemical (electrolyte, base electrode,  
20 conditioning protocol) and electrochemical (sweep rate, etc.) conditions and define  
21 shape-dependent quantities to define pigment-characteristic parameters (*vide infra*).  
22 According to that and, in order to facilitate standardization, commercial graphite bars of  
23 uniform graphite content (HB type, see Experimental section) have been used in this  
24 database. The selection of the electrolyte is another important step in the  
25 electrochemical identification of pigments. The use of different electrolytes allows the  
26 introduction of additional criteria for identification [23-28]. Aqueous 0.25 M sodium  
27 acetate buffer and 0.10 M HCl were used as electrolytes in the ELCHER database.  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50

51 Figure 3 shows the CV of a malachite deposit on graphite bar immersed into 0.25 M  
52 HAc/NaAc, pH 4.75. This voltammogram is illustrative of the typical response of  
53 copper pigments (as well as lead and cadmium pigments) in that electrolyte, yielding a  
54 two-electron reduction of the parent copper compound to copper metal in the initial  
55 cathodic scan, followed in the subsequent anodic scan, by stripping peaks associated to  
56 the oxidative dissolution of the metal deposit electrochemically generated to  $\text{Cu}^{2+}$  (aq)  
57  
58  
59  
60  
61  
62  
63  
64  
65

1 ions in solution phase. The electrochemical reduction of metal compounds to the  
2 corresponding metal can involve a topotactic reduction process via formation of an  
3 intermediate hydrated layer, as described by Scholz et al. for lead oxides [69], goethite  
4 [70] and silver halides and sulfide [71].  
5  
6  
7

8  
9 As far as the inorganic pigments consist usually of oxides, hydroxioxides, sulfides, etc.,  
10 for identification purposes, cathodic signals should be used preferentially. This can be  
11 combined with stripping peaks due to the oxidative dissolution of metals, but these  
12 latter cannot, in principle, be used to differentiate between different pigments of the  
13 same metal. Such cathodic signals are dependent on the composition of the pigment and  
14 the electrolyte but are also dependent on the characteristics of the base graphite  
15 electrode and the amount of solid abrasively transferred to the electrode surface.  
16  
17  
18  
19  
20  
21  
22

23 Square wave voltammetry (SWV) was systematically used by its inherently high  
24 sensitivity and reluctance to capacitive effects [72]. SWV experiments at low frequency  
25 carried out with pigments produced, in general, the better results in terms of  
26 compromise between sensitivity and peak resolution. This aspect is of particular interest  
27 keeping in mind the application of this methodology for the analysis of real pictorial  
28 samples, where micro- or nanograins of pigment are accompanied by other components  
29 such as bindings, preparative supports, varnishes and/or alteration products. This can be  
30 seen in Figure 4 where SWV of malachite transferred abrasively to four different  
31 graphite bars immersed into acetate buffer are shown. Anodic stripping peaks are much  
32 less sensitive to changes in the base electrode. In several cases, overlapping stripping  
33 oxidation signals appear, which are attributable to the superposition of different deposits  
34 of the same metal [73,74]. It should be noted, however, that co-electrodeposition of  
35 metals can produce distorted voltammetric responses as a result of the formation of  
36 intermetallic compounds.  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50

51 From the electrochemical point of view, apart from the above family of pigments, those  
52 reducible to metals, a second important group of pigments is constituted by those  
53 experiencing reductive or oxidative dissolution processes [23-25]. The most  
54 representative example is that of iron oxide-based or earth-type pigments, an extensive  
55 family of natural and artificial pigments displaying reductive dissolution processes  
56 [30,31,36]. The rate of such processes is driven by the detachment, via ion diffusion or  
57  
58  
59  
60  
61  
62  
63  
64  
65



1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

complexation reaction, of metal centers from the reduced metal sites in the surface of the solid particles. As a result, the position and shape (roughly, peak width) of the voltammetric peaks depend on the average particle size and the homogeneity of the particle size distribution [75,76]. Figure 5 compares the SWV response of four commercial pigments, Bohemian green, umber, Sienna raw and French ochre immersed into 0.10 M HCl. Although this electrolyte provides better discrimination between different iron oxide-based pigments than acetate buffer, the voltammograms of ochres from different provenances were quite similar, so that chemometric methods are needed for identification purposes [36].

The third important group of pigments is constituted by those displaying solid-state ion insertion (or de-insertion) processes, the typical case being the Prussian blue [23,24,77-79], whereas much organic pigments experience solid state redox processes involving proton insertion/release [32-35,80,81]. This type of processes would be also involved in the electrochemistry of organic-inorganic hybrid materials [58-65,82].

Finally it is pertinent to note that: i) application of VIMP in the fields of archaeometry and conservation of heritage is complementary to the existing techniques; in general multi-technique approaches are needed for properly elucidating the composition of work of art samples; ii) the presented database can be viewed as a flexible tool for aiding to other more conventional in the identification of pigments; ‘historical’ pigments, however, can have a composition differing from their contemporary counterparts of the same nominal composition; iii) data analysis should take into account that pigment association to supports and bindings can distort the voltammetric response, as recently studied by the case of Egyptian blue in wall paintings [83].

#### 4.2. Application of ELCHER database to problem solving

To illustrate the suitability of the ELCHER database for analyzing pictorial samples, it is shown the analyses of a blue-greenish sample from the canvas painting “*La Degollación de los Inocentes*” painted by the Valencian painter Miguel March (17<sup>th</sup>-18<sup>th</sup> century) (Fig. 6) and the analyses of a red sample from the canvas painting “*Desposorios místicos de Santa Margarita*” painted by the Italian painter Girolamo Francesco Maria Mazzola (Il Parmigianino) (1503-1540) (Fig. 7). Cross-section

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

obtained in the first sample shows a paint layer of blue-greenish color applied over a red earth ground. X-ray spectra obtained by means of spot analyses performed with FESEM-EDX in different grains (see Fig. 1S-4S in supplementary electronic material) enabled identification of a copper blue pigment (probably azurite), white lead and, present at lesser extent, lead-tin yellow.

Figure 8 depicts the voltammograms corresponding to the blue-greenish layer of sample S1 from the painting “*La Degollación de los Inocentes*”. In the negative-going potential scan, a cathodic signal at  $-0.10$  V precedes a prominent signal at  $-0.55$  V. Such signals are typical of copper and lead pigments, respectively, whose presence was confirmed by the appearance of stripping peaks at  $-0.50$  V (lead) and  $+0.10$  V (Cu). The shoulders at ca.  $+0.40$  V recorded in both voltammograms can be attributed to the presence of tin, suggesting the presence of the pigment lead-tin yellow. This was confirmed upon comparing the profile of the lead-centered signal with that of the pigment, shown in Figures 9a,b. The copper pigment in the blue-greenish paint layer was identified as azurite, as denoted upon comparison with the corresponding reference material, subsequently confirmed by means of the Tafel analysis of the voltammetric curves [42,47]. The detail of such voltammograms are depicted in Figures 9,c,d. It is of worth mention that X-ray microanalysis was unable to identify this mineral as this technique provides the elemental composition of the pigment.

In the red sample (S2) of the painting “*Desposorios místicos de Santa Margarita*”, a mixture of lead white and vermilion, was identified by VIMP and FESEM-EDX (see Fig. 5S-7S in supplementary electronic material) [29]. This combination of pigments is frequently used by painters in flesh and in the lighted up parts of the draped red robes. The presence of lead white was denoted by the characteristic profile of the cathodic signal at ca.  $-0.55$  V (Figures 10a,b) whereas vermilion was detected by the anodic signal between  $0.0$  and  $+0.2$  V which can be seen in Figures 10c,d.

The application of the database to the study of metals and alloys and their corrosion products is illustrated in Figure 11, where the voltammograms of golden and silver bracelets from the *Camí de la Bola* archaeological site of the caliphal period (Xàtiva, Spain) are shown. Remarkably, this study was performed using a portable equipment

1 (see Experimental section). To detect the presence of gold, HCl media was preferred  
2 due to the favorable oxidation to  $\text{AuCl}_4^-$  [84]. On comparing the SWV of a sample from  
3 a golden bracelet (Fig. 11a) and a polycrystalline gold electrode (Fig. 11b); one can see  
4 that the gold-characteristic signal at ca. +1.0 V is accompanied by signals at +0.45,  
5 -0.10 and -0.40 V representative of the stripping peaks of silver, copper and lead,  
6 respectively, denoting the complex composition of the sample. In the case of the  
7 negative-going scan voltammogram for a silver bracelet depicted in Figure 11c, now  
8 recorded in contact with acetate buffer, the reduction of AgCl at ca. 0.0 V is  
9 accompanied from that of silver tarnish ( $\text{Ag}_2\text{S}$ ) at more negative potentials, thus  
10 denoting the presence of both alteration products. The first signal is overlapped with the  
11 reduction of any copper corrosion products, as denoted by the positive-going scan  
12 voltammogram (Fig. 11d), where the stripping of copper at +0.10 V is accompanied by  
13 two Ag stripping signals at +0.25 and +0.45 V, a feature previously observed in Ag  
14 coins [48].  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26

#### 27 **4. Conclusions**

28  
29  
30  
31 The VIMP methodology can be used for identifying electroactive pigments and  
32 minerals in art and archaeological objects. Attachment of microsamples of commercial  
33 pigments and minerals to commercial graphite leads and aqueous electrolytes provide  
34 well-defined voltammetric responses under conditions accessible to conventional  
35 equipment. The ELCHER database, which includes voltammograms and ATR-FTIR,  
36 diffuse reflectance and X-ray spectral data, is presented as a tool for facilitating  
37 practical application of the VIMP in the domain of conservation and restoration of  
38 heritage as a technique that complement the non-electrochemical methodologies more  
39 extensively used in this field.  
40  
41  
42  
43  
44  
45  
46  
47  
48

49 **Acknowledgements:** Research was conducted within the “Grupo de análisis científico  
50 de bienes culturales y patrimoniales y estudios de ciencia de la conservación”  
51 Microcluster of the University of Valencia Excellence Campus. Financial support is  
52 gratefully acknowledged from the MINECO Projects CTQ2014-53736-C3-1-P and -2-P  
53 which are also supported with ERDF funds. The authors would like to thank to Gonzalo  
54 Gironés Sarrió manager of GongDissey Co. by the technical support for building the  
55 site structure and the structure of the database, Archbishop of Valencia, Dr. Ignacio  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

1 Bosch Reig and Dr. Pilar Roig Picazo directors of the intervention project in the  
2 Basílica de la Virgen de los Desamparados de Valencia as well as Estrella Arcos Von  
3 Haartman and City Council Town of Málaga, as well as the Museum of Archaeology of  
4 Xàtiva, the curators Isabel Martínez Lázaro and Betlem Martínez and its director Angel  
5 Velasco for facilitating access to samples and Manuel Planes Insausti and Dr Jose Luis  
6 Moya López technical supervisors of the Electron Microscopy Service of the  
7 Universitat Politècnica de València where were carried out SEM-EDX analyses.  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

## References

- [1] T. J. Reedy, Ch.L. Reedy, *Statistical Analysis in Art Conservation Research*, The Getty Conservation Institute, Los Angeles, 1988.
- [2] F. Mairinger, M. Schreiner *New methods of chemical analysis-a tool for the conservator*, Science and Technology in the service of conservation, IIC, London, 1982, pp. 5–13.
- [3] A. Wangm, J. Han, L. Guo, J. Yu, P. Zeng, *Database of standard Raman spectra of minerals and related inorganic crystals*, *Appl. Spectrosc.* 48 (1994) 959–968.
- [4] I.M. Bell, R.J.H. Clark, P.J. Gibbs, *Raman spectroscopic library of natural and synthetic pigments*, *Spectrochim. Acta* 53A (1997) 2159–2179.
- [5] Silva CE, Silva LP, Edwards HGM, de Oliveira LFC (2006) *Diffuse reflection FTIR spectral database of dyes and pigments*, *Anal. Bioanal. Chem.* 386: 2183–2191.
- [6] P. Vandenabeele, B. Wehling, L. Moens, H.G.M. Edwards, M. de Reu M, G. Van Hooydonk, *Analysis with micro-Raman spectroscopy of natural organic binding media and varnishes used in art*, *Anal. Chim. Acta* 407 (2000) 261–274.
- [7] P. Vandenabeele, L. Moens, H.G.M. Edwards, R. Dams, *Raman spectroscopic database of azo pigments and application to modern art studies*, *J. Raman Spectrosc.* 31 (2000) 509–517.
- [8] L. Burgio, R.J.H. Clark, *Library of FT-Raman spectra of pigments, minerals, pigment media and varnishes*, *Spectrochim. Acta A* 57 (2001) 1491–1521.
- [9] M. Bouchard, D.C. Smith, *Catalogue of 45 reference Raman spectra of minerals concerning research in art history or archaeology, especially on corroded metals and coloured glass*, *Spectrochim. Acta A* 59 (2003) 2247–2266.
- [10] G. Burrafato, M. Calabrese, A. Cosentino, A.M. Gueli, S.O. Troja, A. Zuccarello, *ColoRaman project: Raman and fluorescence spectroscopy of oil, tempera and fresco paint pigments*, *J. Raman Spectrosc.* 35 (2004) 879–886.
- [11] <http://www.irug.org> (1<sup>st</sup> February 2016).
- [12] K. Castro, M. Pérez-Alonso, M.D. Rodríguez-Laso, L.A. Fernández, J.M. Madariaga, *On-line FT-Raman and dispersive Raman spectra database of artist materials (e-VISART database)*. *Anal. Bioanal. Chem.* 382 (2005) 248–258.
- [13] K. Castro, M. Pérez, M.D. Rodríguez-Laso, J.M. Madariaga, *FTIR spectra database of inorganic art materials*, *Anal. Chem.* 75 (2003) 214A–221A.
- [14] <http://www.ehu.es/udps/database/database.html> (1<sup>st</sup> February 2016).

- 1 [15] [http:// www.chem.ucl.ac.uk/resources/raman/speclib.html](http://www.chem.ucl.ac.uk/resources/raman/speclib.html) (1<sup>st</sup> February 2016).
- 2 [16] <http://minerals.gps.caltech.edu/> (1<sup>st</sup> February 2016).
- 3
- 4 [17] <http://www.ruff.info> (1<sup>st</sup> February 2016).
- 5
- 6 [18] F. Scholz, L. Nitschke, G. Henrion, A New procedure for Fast Electrochemical
- 7 Analysis of Solid Materials. *Naturwiss.* 76 (1989) 71–72.
- 8
- 9 [19] F. Scholz, L. Nitschke, G. Henrion, F. Damaschun, A New technique to Study the
- 10 Electrochemistry of Minerals. *Naturwiss.* 76 (1989) 167–168.
- 11
- 12 [20] F. Scholz, L. Nitschke, G. Henrion, Identification of solid materials with a new
- 13 electrochemical technique. *Fresenius Z. Anal. Chem.* 334 (1989) 56–58.
- 14
- 15 [21] F. Scholz, L. Nitschke, G. Henrion, F. Damaschun, Abrasive Stripping
- 16 Voltammetry - the Electrochemical Spectroscopy for Solid State: Application for
- 17 Mineral Analysis. *Fresenius Z. Anal. Chem.* 335 (1989) 189–194.
- 18
- 19 [22] B. Lange, F. Scholz, A. Weiss, G. Schwedt, J. Behnert, K.P. Raezke, Abrasive
- 20 Stripping Voltammetry - the Electrochemical Alternative for Pigment Analysis- *Internat.*
- 21 *Lab.* 23 (1993) 23–26.
- 22
- 23 [23] F. Scholz, B. Meyer, Voltammetry of solid microparticles immobilized on electrode
- 24 surfaces. *Electroanalytical Chemistry, A Series of Advances* vol. 20 (1998) 1–86.
- 25
- 26 [24] F. Scholz, U. Schröder, R. Gulabowski, A. Doménech-Carbó, *Electrochemistry of*
- 27 *Immobilized Particles and Droplets*, 2<sup>nd</sup> edit. *Monographs in Electrochemistry Series*, F.
- 28 Scholz, Ed. Springer, Berlin-Heidelberg (2014).
- 29
- 30 [25] A. Doménech-Carbó, J. Labuda, F. Scholz, *Electroanalytical chemistry for the*
- 31 *analysis of solids: characterization and classification (Technical Report)*. *Pure Appl.*
- 32 *Chem.* 85 (2013) 609–631.
- 33
- 34 [26] A. Doménech-Carbó, M.T. Doménech-Carbó, V. Costa, *Electrochemical Methods*
- 35 *in Archaeometry, Conservation and Restoration*. *Monographs in Electrochemistry*
- 36 *Series*, F. Scholz, Ed. Springer, Berlin-Heidelberg (2009).
- 37
- 38 [27] A. Doménech-Carbó, Voltammetric methods applied to identification, speciation and
- 39 quantification of analytes from works of art: an overview. *J. Solid State Electrochem.* 14
- 40 (2010) 363–379.
- 41
- 42 [28] A. Doménech-Carbó, Tracing, authenticating and dating archaeological metal using
- 43 the voltammetry of microparticles. *Anal. Methods* 3 (2011) 2181–2188.
- 44
- 45 [29] A. Doménech-Carbó, M.T. Doménech-Carbó, M. Moyá-Moreno, J.V. Gimeno-
- 46 Adelantado, F. Bosch-Reig, Identification of inorganic pigments from paintings and
- 47
- 48
- 49
- 50
- 51
- 52
- 53
- 54
- 55
- 56
- 57
- 58
- 59
- 60
- 61
- 62
- 63
- 64
- 65

1 polychromed sculptures immobilized into polymer film electrodes by stripping differential  
2 pulse voltammetry. *Anal. Chim. Acta*, 407 (2000) 275–289.

3 [30] A. Doménech-Carbó, M.T. Doménech-Carbó, J.V. Gimeno-Adelantado, F. Bosch-  
4 Reig, M.C. Saurí-Peris, S.Sánchez-Ramos, Electrochemistry of iron oxide pigments  
5 (earths) from pictorial microsamples attached to graphite/polyester composite electrodes.  
6 *Analyst* 126 (2001) 1764–1772.

7 [31] T. Grygar, P. Bezdicka, D. Hradil, A. Doménech-Carbó, F. Marken, L. Pikna, G.  
8 Cepria, Voltammetric analysis of iron pigments, *Analyst* 127 (2002) 1100–1107.

9 [32] T. Grygar, S. Kuckova, D. Hradil, D. Hradilova, Electrochemical analysis of natural  
10 solid organic dyes and pigments. *J. Solid State Electrochem.* 7 (2003) 706–713.

11 [33] A. Doménech-Carbó, M.T. Doménech-Carbó, M.C. Saurí-Peris, J.V. Gimeno-  
12 Adelantado, F. Bosch-Reig, Electrochemical identification of anthraquinone-based dyes in  
13 solid microsamples by square wave voltammetry using graphite/polyester composite  
14 electrodes. *Anal. Bioanal. Chem.* 375 (2003) 1169–1175.

15 [34] A. Doménech-Carbó, M.T. Doménech-Carbó, M.C. Saurí-Peris, Electrochemical  
16 identification of flavonoid dyes in work of art samples by abrasive voltammetry at  
17 paraffin-impregnated graphite electrodes. *Talanta* 66 (2005) 769–782.

18 [35] A. Doménech-Carbó, M.T. Doménech-Carbó, M.C. Saurí-Peris, J.V. Gimeno-  
19 Adelantado, F. Bosch-Reig, Identification of curcuma and safflower dyes by voltammetry  
20 of microparticles using paraffin-impregnated graphite electrodes. *Microchim. Acta* 152  
21 (2005) 75–84.

22 [36] A. Doménech-Carbó, M.T. Doménech-Carbó, H.G.M. Edwards, Identification of  
23 Earth Pigments in Highly Damaged Frescoes by Applying Multivariate Chemometric  
24 methods to Solid State Voltammetry, *Electroanalysis* 19 (2007) 1890–1900.

25 [37] A. Doménech-Carbó, M.T. Doménech-Carbó, X. Mas-Barberá, Identification of lead  
26 pigments in nanosamples from ancient paintings and polychromed sculptures using  
27 voltammetry of nanoparticles/atomic force microscopy, *Talanta* 71 (2007) 1569–1579.

28 [38] A. Doménech-Carbó, M.T. Doménech-Carbó, H.G.M. Edwards, Application of  
29 Tafel analysis for quantitation in solid state voltammetry. Application to the analysis of  
30 cobalt and copper pigments in severely damaged frescoes, *Anal Chem.* 80 (2008)  
31 2704–2716.

32 [39] V. Costa, K. Leyssens, A. Adriaens, N. Richard, F. Scholz, Electrochemistry  
33 reveals archaeological materials, *J. Solid State Electrochem.* 14 (2010) 449–451.

- 1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65
- [40] N. Souissi, L. Bousselmi, S. Khosrof, E. Triki, Electrochemical behavior of an archaeological bronze alloy in various aqueous media: New method for understanding artifacts preservation, *Mater.Corr.*54 (2003) 318–325.
- [41] M. Serghini-Idrissi, M.C. Bernard, F.Z., Harrif, S. Joiret, K. Rahmouni, A. Srhiri, H. Takenouti, V. Vivier, M. Ziani, Electrochemical and spectroscopic characterizations of patinas formed on an archaeological bronze coin, *Electrochim. Acta* 50 (2005) 4699–4709.
- [42] A. Doménech-Carbó, M.T. Doménech-Carbó, I. Martínez-Lázaro, Electrochemical identification of bronze corrosion products in archaeological artefacts. A case study. *Microchim. Acta* 162 (2008) 351–359.
- [43] D. Satovic, S. Martinez, A. Bobrowski, Electrochemical identification of corrosion products on historical and archaeological bronzes using the voltammetry of micro-particles attached to a carbon paste electrode, *Talanta* 81 (2010) 1760–1765.
- [44] F.A. Gholeji, A. Adriaens, Electrochemical quantification of copper-based alloys using voltammetry of microparticles: optimization of the experimental conditions, *J. Solid State Electrochem.* 16 (2012) 535–543.
- [45] D. Blum, W. Leyffer, R. Holze, Pencil-Leads as new electrodes for abrasive stripping voltammetry, *Electroanalysis* 8 (1996) 296–297.
- [46] V. Costa, F. Urban, Lead and its alloys: metallurgy, deterioration and conservation, *Reviews in Conservation, International Institute of Conservation* 6 (2005) 48–62.
- [47] A. Doménech-Carbó, M.T. Doménech-Carbó, M.A. Peiró-Ronda, One-touch' voltammetry of microparticles for the identification of corrosion products in archaeological lead. *Electroanalysis* 23 (2011) 1391–1400.
- [48] A. Doménech-Carbó, M.T. Doménech-Carbó, T. Pasies, M.C. Bouzas-Bello, Application of modified Tafel analysis to the identification of corrosion products on archaeological metals using voltammetry of microparticles. *Electroanalysis* 23 (2011) 2803–2812.
- [49] F. Rodríguez, J. Genescá, J. Uruchurtu, Electrochemical evaluation of patinas formed on nineteenth century bronze bells, *J. Appl. Electrochem.* 40 (2010) 311–320.
- [50] Y.V. Roblinetskaya, E.O. Il'inykch V.V. Slepushkin, A standardless method for the local electrochemical analysis of homogeneous alloys, *J. Anal. Chem.* 66 (2011) 84–87.



- 1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65
- [51] A. Doménech-Carbó, M.T. Doménech-Carbó, I. Martínez-Lázaro, Layer-by-layer identification of copper alteration products in metallic works of art using the voltammetry of microparticles approach. *Anal. Chim. Acta* 610 (2010) 1–9.
- [52] A. Doménech-Carbó, M.T. Doménech-Carbó, M.A. Peiró-Ronda, L. Osete-Cortina, Authentication of archaeological lead artifacts using voltammetry of microparticles: the case of the *Tossal de Sant Miquel* Iberian plate. *Archaeometry* 53 (2011) 1193–1211.
- [53] A. Doménech-Carbó, M.T. Doménech-Carbó, M. Lastras, M. Herrero, 2015. Detection of archaeological forgeries of Iberian lead plates using nanoelectrochemical techniques. The lot of fake plates from Bugarra (Spain). *Forensic Sci. Int.* 247 (2015) 79–88.
- [54] A. Doménech-Carbó, M.T. Doménech-Carbó, M.A. Peiró-Ronda, Dating archaeological lead artifacts from measurement of the corrosion content using the voltammetry of microparticles, *Anal. Chem.* 83 (2011) 5639–5644.
- [55] A. Doménech-Carbó, M.T. Doménech-Carbó, M.A. Peiró-Ronda, I. Martínez-Lázaro, Application of the voltammetry of microparticles for dating archaeological lead using polarization curves and electrochemical impedance spectroscopy. *J. Barrio. J. Solid State Electrochem.* 16 (2012) 2349–2356.
- [56] A. Doménech-Carbó, M.T. Doménech-Carbó, S. Capelo, T. Pasíes, I. Martínez-Lázaro, Dating archaeological copper/bronze artifacts using the voltammetry of microparticles. *Angew. Chem. Int. Ed.* 53 (2014) 9262–9266.
- [57] A. Doménech-Carbó, S. Capelo, J. Piquero-Cilla, M.T. Doménech-Carbó, L. Barrio, A. Fuentes, W. Al-Sekkaneh, Dating archaeological copper using electrochemical impedance spectroscopy. Comparison with voltammetry of microparticles dating. *Mater. Corr.* 67 (2016) 120–129.
- [58] A. Doménech-Carbó, M.T. Doménech-Carbó, M.L. Vázquez de Agredos, Dehydroindigo: a New Piece into the Maya Blue Puzzle from the Voltammetry of Microparticles Approach. *J. Phys. Chem. B* 110 (2006) 6027–6039.
- [59] A. Doménech-Carbó, M.T. Doménech-Carbó, M.L. Vázquez de Agredos, Chemometric Study of Maya Blue from the Voltammetry of Microparticles Approach. *Anal. Chem.* 79 (2007) 2812–2821.
- [60] A. Doménech-Carbó, M.T. Doménech-Carbó, M. Sánchez del Río, M.L. Vázquez de Agredos, E. Lima, Maya Blue as a nanostructured polyfunctional hybrid organic-inorganic

material: the need to change paradigms, *New J. Chem.* 33 (2009) 2371–2379.

[61] A. Doménech-Carbó, M.T. Doménech-Carbó, M.L. Vázquez de Agredos, From Maya Blue to ‘Maya Yellow’: A Connection between Ancient Nanostructured Materials from the Voltammetry of Microparticles. *Angew. Chem. Int. Ed.* 50 (2011) 5741–5744.

[62] A. Doménech-Carbó, M.T. Doménech-Carbó, C. Vidal-Lorenzo, M.L. Vázquez de Agredos, Insights into the Maya Blue Technology: Greenish Pellets from the Ancient City of *La Blanca*. *Angew. Chem. Int. Ed.* 51 (2012) 700–703.

[63] A. Doménech-Carbó, M.T. Doménech-Carbó, C. Vidal-Lorenzo, M.L. Vázquez de Agredos, L. Osete-Cortina, F.M. Valle-Algarra, Discovery of indigoid-containing clay pellets from La Blanca: significance with regard to the preparation and use of Maya Blue. *J. Archaeol. Sci.* 41 (2014) 147–155.

[64] A. Doménech-Carbó, M.T. Doménech-Carbó, F.M. Valle-Algarra, M.E. Domine, L. Osete-Cortina, On the dehydroindigo contribution to Maya Blue. *J. Mater. Sci.* 48 (2013) 7171–7183.

[65] G. Sciutto, S. Prati, R. Mazzeo, M. Zangheri, A. Roda, L. Bardini, G. Valenti, S. Rapino, M. Marcaccio, Localization of proteins in paint cross-sections by scanning electrochemical microscopy as an alternative immunochemical detection technique. *Anal. Chim. Acta* 831 (2014) 31–37.

[66] A. Doménech-Carbó, M.T. Doménech-Carbó, M. Silva, F.M. Valle-Algarra, J.V. Gimeno-Adelantado, F. Bosch-Reig, R. Mateo-Castro, Screening and mapping pigments in paintings using scanning electrochemical microscopy (SECM). *Analyst* 140 (2015) 1065–1075.

[67] H.S. Wang, H.X. Ju, H.Y. Chen, Simultaneous determination of guanine and adenine in DNA using an electrochemically pretreated glassy carbon electrode. *Anal. Chim. Acta* 461 (2002) 243–250.

[68] Y. Tao, Z.J. Lin, X.M. Chen, X.I. Chen, X.R. Wang, Tris(2,2'-bipyridyl)ruthenium(II) electrochemiluminescence sensor based on carbon nanotube/organically modified silicate films. *Anal. Chim. Acta* 594 (2007) 169–174.

[69] U. Hasse, F. Scholz, In situ Atomic Force Microscopy of the Reduction of Lead Oxide Nanocrystals Immobilized on an Electrode Surface, *Electrochem. Commun.* 3 (2001) 429–434.

1 [70] U. Hasse, J. Nieven, F. Scholz, Atomic force Microscopy of the Electrochemical  
2 Reductive Dissolution of Sub-Micrometer Sized Crystals of Goethite Immobilized on a Gold  
3 Electrode. *J. Electroanal. Chem.* 556 (2003) 13–22.  
4

5 [71] U. Hasse, K. Wagner, F. Scholz, Microscopy of the Electrochemical Reduction of  
6 Sub Micrometer Size Silver and Mercury(I) Halide Crystals Immobilized on Gold  
7 Electrodes. *J. Solid State Electrochem.* 8 (2004) 842–853.  
8

9 [72] V. Mirceski, S. Komorsky-Lovirc, M. Lovric, Square Wave Voltammetry –Theory  
10 and Applications- Monographs in Electrochemistry Series, F. Scholz, Ed. Springer,  
11 Berlin-Heidelberg, 2002.  
12

13 [73] S. Komorsky-Lovric, M. Lovric, A.M. Bond, Comparison of the square-wave  
14 stripping voltammetry of lead and mercury following their electrochemical or abrasive  
15 deposition onto a paraffin impregnated graphite electrode. *Anal. Chim. Acta* 258 (1992)  
16 299–305.  
17

18 [74] Zakharchuk, S. Meyer, B. Lange, F. Scholz, A Comparative Study of Lead Oxide  
19 Modified Graphite Paste Electrodes and Solid Graphite Electrodes with Mechanically  
20 Immobilized Lead Oxides, *Croat. Chem. Acta* 73 (2000) 667–704.  
21

22 [75] T. Grygar, Kinetics of Electrochemical Reductive Dissolution of Iron(III) Hydroxy-  
23 Oxides. *Coll Czech Chem Commun* 60 (1995) 1261–1273.  
24

25 [76] T. Grygar, Dissolution of pure and substituted goethites controlled by the surface  
26 reaction under conditions of abrasive stripping voltammetry. *J. Solid State Electrochem.* 1  
27 (1997) 77–82.  
28

29 [77] F. Scholz, A. Dostal, The Formal Potentials of the Solid Metal  
30 Hexacyanometalates, *Angew. Chem.* 107 (1995) 2876–2878 (*Angew. Chem. Int. Ed.*  
31 *Engl.* 34 (1996) 2685–2687).  
32

33 [78] A. Dostal, B. Meyer, F. Scholz, U. Schröder, A.M. Bond, F. Marken, Sh.J. Shaw,  
34 Electrochemical Study of Microcrystalline Solid Prussian Blue Particles Mechanically  
35 Attached to Graphite and Gold Electrodes: Electrochemically Induced Lattice  
36 Reconstruction. *J Phys. Chem.* 99 (1995) 2096–2103.  
37

38 [79] Kahlert, U. Retter, H. Lohse, K. Siegler, F. Scholz, On the Determination of the  
39 Diffusion Coefficients of Electrons and Potassium Ions in Copper(II)  
40 Hexacyanoferrate(II). *J. Phys. Chem. B* 102 (1998) 8757–8765.  
41

42 [80] A. Doménech-Carbó, M.T. Doménech-Carbó, Chronoamperometric study of proton  
43 transfer/electron transfer in solid state electrochemistry of organic dyes. *J. Solid State*  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

Electrochem. 10 (2006) 949–958.

1  
2 [81] A. Doménech-Carbó, M.T. Doménech-Carbó, In situ AFM study of proton-assisted  
3 electrochemical oxidation/reduction of microparticules of organic dyes. Electrochem.  
4 Commun. 10 (2008) 1238–1241.  
5

6  
7 [82] A. Doménech-Carbó, Theoretical scenarios for the electrochemistry of porous  
8 silicate-based materials: an overview. J. Solid State Electrochem. 19 (2015) 1887–1903.  
9

10  
11 [83] A. Doménech-Carbó, M.T. Doménech-Carbó, F. López, F.M. Valle-Algarra, L.  
12 Osete-Cortina, E. Arcos, Electrochemical characterization of Egyptian blue pigment in  
13 wall paintings using the voltammetry of microparticles methodology. Electroanalysis 25  
14 (2013) 2621–2630.  
15  
16

17  
18 [84] A. Doménech-Carbó, M.T. Doménech-Carbó, L. Osete-Cortina, Electrochemistry of  
19 archaeological metals: an approach from the voltammetry of microparticles, en "Trends in  
20 electrochemistry and corrosion at the beginning of the 21st century (dedicated to Professor  
21 Dr. Josep M. Costa on the occasion of his 70<sup>th</sup> birthday); Brillas, E. Cabot, P.-L. Edits.  
22 Universitat de Barcelona, Barcelona (2004).  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

## Figures

**Figure 1.** a) Main menu of the web site ELCHER; b) Main menu of the ELCHER database with the description of the ELCHER voltammogram database initiative, terms of use and legal conditions.

**Figure 2.** a) Main menu of the ELCHER database; b) Record card of azurite pigment with the voltammogram, IR spectrum, UV-vis spectrum, backscattered electron image and x-ray spectrum as seen on the online ELCHER database.

**Figure 3.** CV of a malachite (K10300) deposit on graphite bar (Staedtler) immersed into 0.25 M HAc/NaAc, pH 4.75. Potential scan initiated at +0.75 V in the negative direction. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz.

**Figure 4.** SWV of malachite (K10300) deposits on a) Alpino, b) Staedtler, c) Disnak and d) Hoc-i-Noor graphite bars immersed into 0.25 M HAc/NaAc, pH 4.75. Potential scan initiated at +0.85 V in the negative direction. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz.

**Figure 5.** SWV of: Bohemian green (K17800); b) Umber (K40610); c) Sienna (K40451); d) French ochre (K40090) on Alpino lead in contact with 0.10 M HCl. Potential scan initiated at +0.85 V in the negative direction. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz.

**Figure 6.** a) “*La degollación de los Inocentes*” painted by the Valencian painter Miguel March (17th-18th century, belongs to the Basílica de la Virgen de los Desamparados canvas collection (Valencia, Spain)). b) Cross-section of the sample blue-greenish taken in the point marked with a spot: (1) paint layer, (2) ground.

**Figure 7.** a) “*Desposorios místicos de Santa Margarita*” painted by the Italian painter Girolano Francesco Maria Mazzola (Il Parmigianino) (1503-1540) exhibited in the Hall town of Malaga, b) Cross-section of the sample red R: (1) paint layer, (2) ground.

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
**Figure 8.** SWVs of sample S1 from “*La degollación de los Inocentes*” on graphite lead (Staedtler) in contact with 0.25 M HAc/NaAc, pH 4.75. Potential scan initiated at a) +1.05 V in the negative direction; b) –1.05 V in the positive direction. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz. (Tly: tin lead yellow; Az: azurite).

11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
**Figure 9.** Detail of two potential regions in the SWVs on graphite lead (Staedtler) in contact with 0.25 M HAc/NaAc, pH 4.75 for: a) sample S1; b) lead-tin yellow; a) sample S1; b) azurite. Potential scan initiated at +1.05 V in the negative direction. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz.

21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
**Figure 10.** Detail of the SWVs on sample S2 from “*Desposorios místicos de Santa Margarita*” attached to graphite lead (Staedtler) in contact with 0.25 M HAc/NaAc, pH 4.75 for: a) sample S2; b) lead white; c) sample S2; d) vermilion. Potential scan initiated at –1.05 V in the positive direction. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz.

31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65  
**Figure 11.** SWVs of: a) sample from a golden sculpture; b) gold electrode; c,d) silver bracelet from the *Camí de la Bola* archaeological site recorded using a portable equipment. a,c,d) samples taken using the ‘one-touch’ procedure at Staedtler graphite bars. Electrolytes, aqueous a,b) 0.10 M HCl; c,d) 0.25 M HAc/NaAc, pH 4.75, solutions. a, b, d) Positive-going scans; c) negative-going scan. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz.

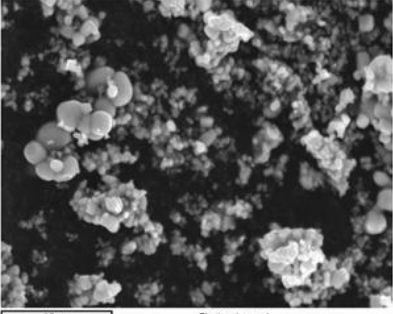
Figure 1.

a) b)




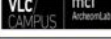

## ElcHer

ELECTROCHEMISTRY FOR HERITAGE GROUP

HOME	ABOUT	RESEARCH	DATABASE	WEBREPORTS	NEWS & EVENTS	LINKS	CONTACT
	Background Organization chart Facilities and equipments	R+D Projects R+D Contracts Papers Communications Books	About ElcHer Database Search		<u>Conferences and meetings</u> Lectures Workshops ElcHer in the news Other events		



10µm Electron Image 1

© 2014 Universitat Politècnica de València - © 2014 Universitat de València

102216 ELCHER - Electrochemistry Heritage Group

## ElcHer

ELECTROCHEMISTRY FOR HERITAGE GROUP

HOME	ABOUT	RESEARCH	DATABASE	WEBREPORTS	NEWS & EVENTS	LINKS	CONTACT
Background Organization chart Facilities and equipments Books	R+D Projects R+D Contracts Papers Communications	About ElcHer Database Search			Conferences and meetings Lectures Workshops ElcHer in the news Other events		

### Database / About ElcHer Database

**About Search:**

By searching the ElcHer Database you accept our Terms of use and Legal Conditions

Usage rules and search Terms of use and Legal Conditions

**ABOUT THE ELCHER VOLTAMMOGRAM DATABASE INITIATIVE**

The ElcHer Voltammogram Database is a online compilation of reference voltammograms of Cultural Heritage materials contributed by the members of the Group Electrochemistry for Heritage. This database currently contains over 100 voltammograms of various origins and origins groups, including well established materials in a number of cases the voltammograms is accompanied of all quantum, ultraviolet spectra, IR, Raman, X-ray fluorescence, XPS/ESCA and electron microscopy photographs.

Voltammograms are formatted with a consistent format to incorporate graph. Each file is an independent record.

Voltammograms are publicly available, however identification and copyright. Digital file exports of all contents are available to most of our members and interested.

**ELCHER COMMITTEE**

Chair

Prof. Dr. Andrés Domínguez-Carrión, ICPA, Química Analítica, Universidad de Valencia, Burjassot, Spain

Prof. Dr. María Teresa Domínguez-Carrión, Instituto Universitario de Restauración del Patrimonio, Universidad Politécnica de Valencia, Valencia, Spain

Current members

Dr. Lucía García-Cortés, Instituto Universitario de Restauración del Patrimonio, Universidad Politécnica de Valencia, Valencia, Spain

**INSTRUMENT AND ANALYSIS DETAILS**

Voltammetry of microelectrodes

Electrochemical experiments were performed at 295 K in three electrode cell after 10-15 min-bubbling of Ar. Square wave voltammograms (SWV) and conventional cyclic voltammograms (CV) were obtained with a CH 660B equipped. For the characterization of active working electrodes were obtained after the electrochemical cell is that only the counter and of the electrode was in contact with the electrolyte solution. This procedure provides an almost constant electrode area and reproducible background current. A 0.01 M HNO<sub>3</sub> solution reference electrode was used as a standard were used for electrode coupled the conventional three electrode arrangement. 0.50 M acetic acid as buffer solution was used for pH 3.75 and 5.0 (pH=3.75) were used as electrolytes.

Square wave voltammograms at potential modified graphite bars (PMG) (Inherent rate 0.10 V/s) were obtained at 0.20 M NaOH solution and after at pH 4.75. Negative going scan. Potential step increment 4 mV, square wave amplitude 100 mV, frequency 1 Hz.

Square wave voltammograms at potential modified graphite bars (PMG) (Inherent rate 0.10 V/s) were obtained at 0.20 M NaOH solution. Potential step increment 4 mV, square wave amplitude 20 mV, frequency 1 Hz.

http://elc.her.uv.es/irp/database/about.php

Figure 2

a)

**ElcHer**  
ELECTROCHEMISTRY FOR HERITAGE GROUP

HOME ABOUT RESEARCH DATABASE WEBREPORTS NEWS & EVENTS LINKS CONTACT

Background R+D Projects About ElcHer Database  
Organization chart R+D Contracts Search  
Facilities and equipments Papers Workshops  
Communications ElcHer in the news  
Books Other events

**DataBase / Search**

Keyword(s) Search by: All

© 2014 Universitat Politècnica de València · © 2014 Universitat de València

b)

**ElcHer**  
ELECTROCHEMISTRY FOR HERITAGE GROUP

HOME ABOUT RESEARCH DATABASE WEBREPORTS NEWS & EVENTS LINKS CONTACT

Background R+D Projects About ElcHer Database  
Organization chart R+D Contracts Search  
Facilities and equipments Papers Workshops  
Communications ElcHer in the news  
Books Other events

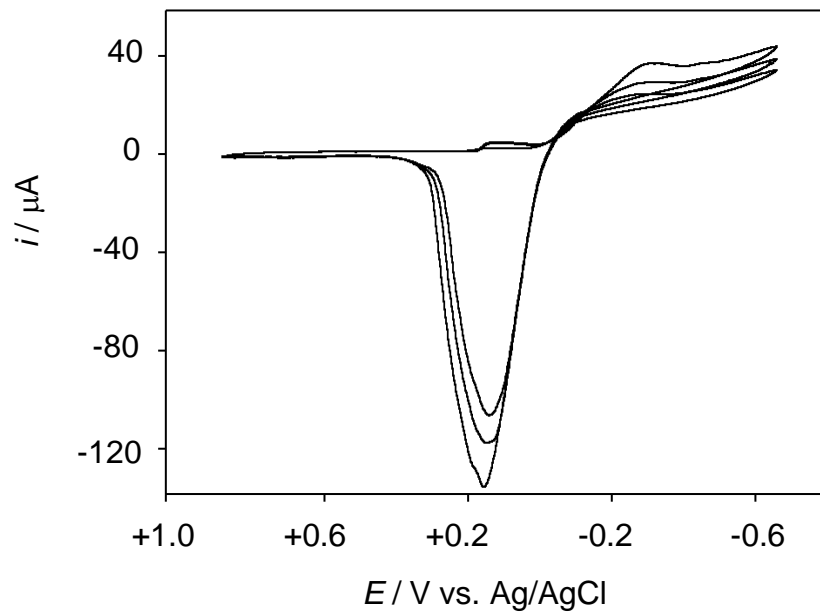
**Database / azurite 01**

Current I/cA vs Potential V/Li

© 2014 Universitat Politècnica de València · © 2014 Universitat de València

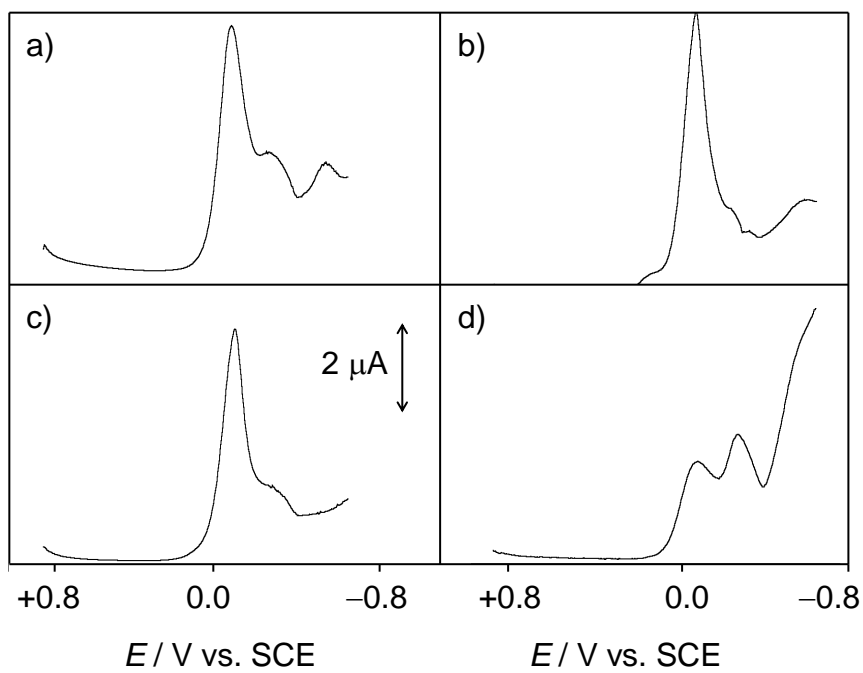


Figure 3



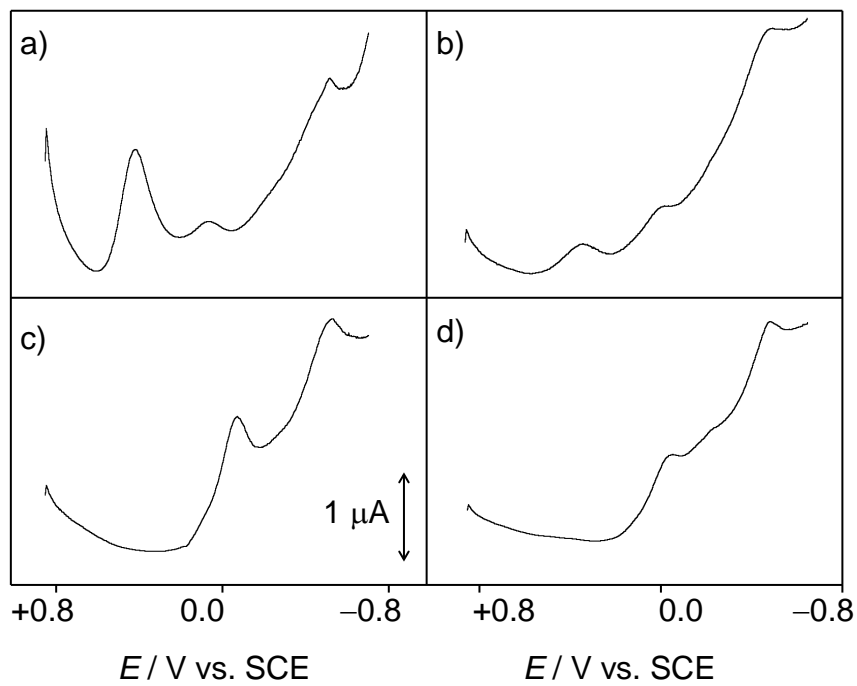
1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

Figure 4.



1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

Figure 5.

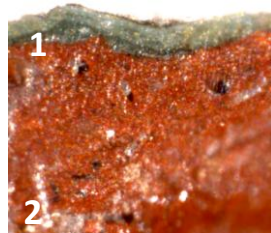


**Figure 6.**

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65



200  $\mu\text{m}$  **b)**

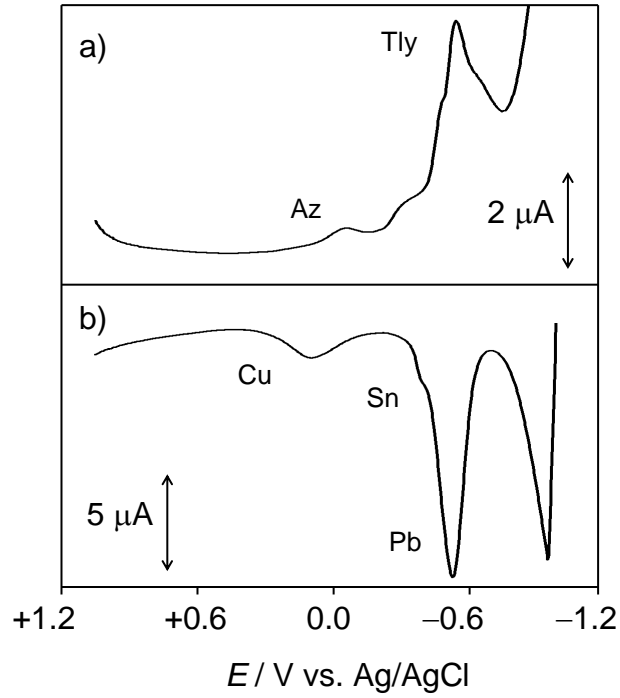


**Figure 7**



1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

Figure 8.



1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

Figure 9.

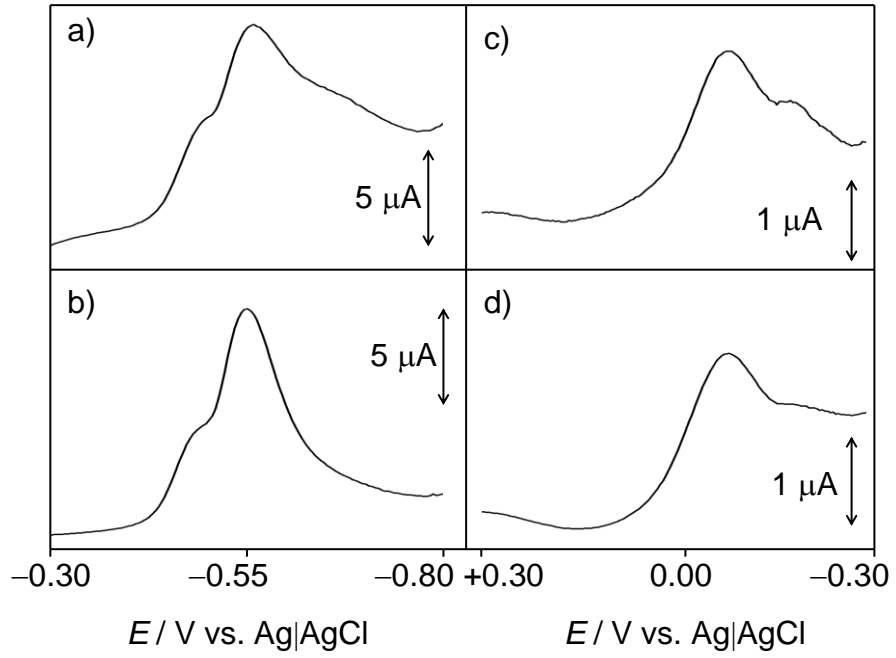


Figure 10.

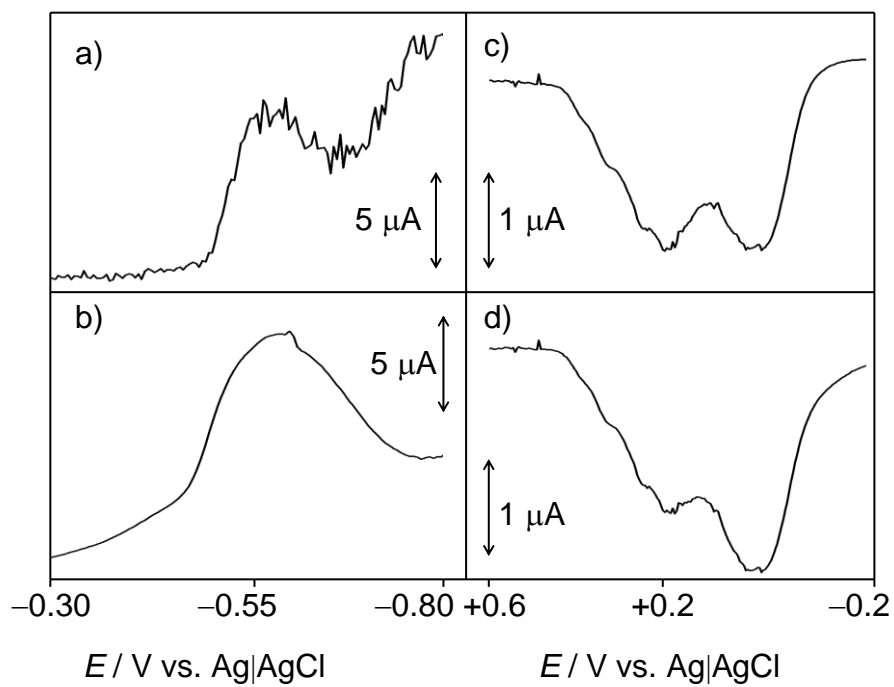
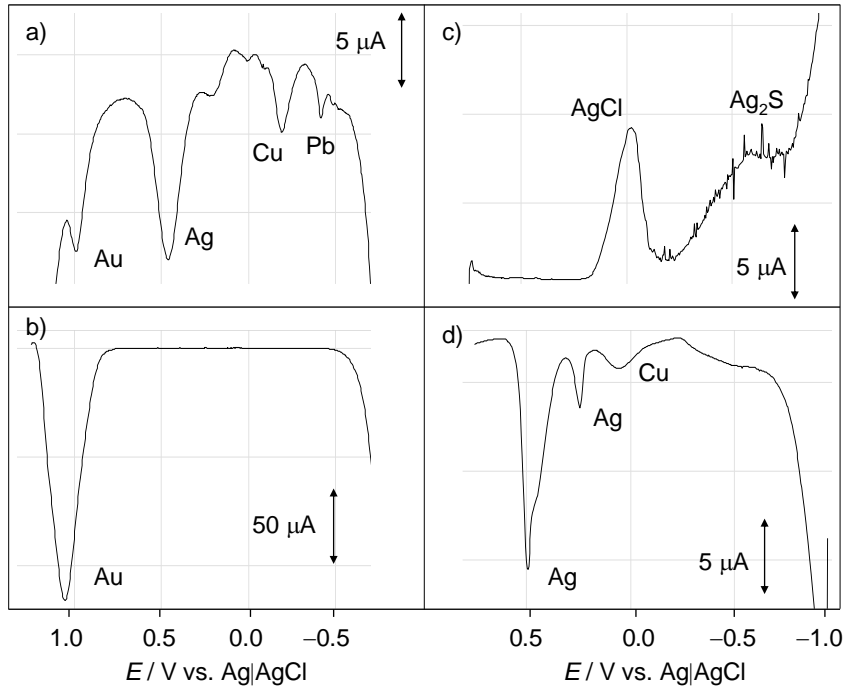




Figure 11.



**Electronic Supplementary Material (online publication only)**

**[Click here to download Electronic Supplementary Material \(online publication only\): ELCHERSupplementaryelectronic material.](#)**