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Tutorial

On-line database of voltammetric data of immobilized particles for identifying pigments and minerals in archaeometry, conservation and restoration (ELCHER database)

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HIGHLIGHTS

- A web-based database of voltammograms is presented.
- The voltammetry of immobilized particles is used.
- Artist's pigments and corrosion products of ceramic, stone and metal objects are included.
- Examples of application on works of art are discussed.

GRAPHICAL ABSTRACT

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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 studies involving identification of pigments and a case study describing deterioration of an archaeological metallic object are presented.

Contents

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1. Introduction

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

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

The special requirements of the analytical procedures when they are applied to works of art and archaeological artifacts makes VIMP particularly useful because of its inherently high sensitivity, requirement of minimal amounts of sample, no need of sample pretreatment and partial sample recuperation and use for multiple analysis. Since its first application for identifying inorganic pigments [29], the VIMP methodology has been increasingly used in the analysis of pigments in works of art [30–38], their alteration products [36,38], as well as metals [39] and metal corrosion products [40–44]. The scope of this technique in the archaeometric field has been enhanced by the use of 'graphite pencil' sampling [45–48], local [49,50] and layer-by-layer analysis [51]. The analytical capabilities of VIMP have been expanded to provide relevant information for the authentication [52,53], tracing and dating [54–57] of archaeological metal. Hybrid inorganic-organic pigments of historical relevance such as Maya blue have also been studied by VIMP [58–64].

It is pertinent to note that the VIMP technique should be viewed as complementary to other existing techniques for studying pigment and alteration products. Generically, the VIMP can be considered as interesting by the low amount (at the nanogram order) of sample required, its versatility and inexpensive equipment (including portable options). Relative to commonly used atomic techniques such as X ray fluorescence, VIMP has the advantage of allowing for the identification of minerals and evaluating oxidation states. However, VIMP cannot offer information on several elements and in particular ultra-trace elements. Relative to molecular techniques like infrared and Raman spectroscopies, the VIMP offers as advantage the possibility of yielding information of minority components (pigments are usually highly diluted in paint layers) in the presence of substrates such as calcareous supports in frescoes displaying signals of considerably larger intensity (infrared spectroscopy) or significant fluorescence (Raman spectroscopy). The disadvantage of VIMP is the lack of specificity in cases such as in several copper pigments, where a detailed analysis of voltammetric curves (Tafel analysis, see Refs. [42,47,48]) is required for pigment identification.

The purpose of the current report is to present a web-based database "Electrochemistry for Heritage" (ELCHER) covering the VIMP response of artist's pigments and products of alteration of stone, ceramics, metals and pigments and illustrating the capabilities and constraints of the database by means of selected case studies. The voltammograms database is complemented with scanning electron microphotographs and X-ray spectra, IR absorption spectra obtained by ATR-FTIR and UV–vis diffuse reflectance spectra. A complementary set of data from SECM and AFM coupled to electrochemical measurements is presented. Such data are of interest for applying them in the conservation and restoration field where these analytical techniques have been recently applied for the localization of proteins in paint layers [65] and the identification of pigments and corrosion products at the nanoscopic scale [37,66].

2. The ELCHER database

The ELCHER database is available on the internet website: http://www.elcher.info. The website was developed using HTML 4.0, CSS 2.0, PHP 4.0 and JavaScript programming languages. The voltammograms as well as microphotographs, X-ray, IR and reflectance spectra are available online. The whole database has, at this moment, 100 voltammograms, 30 X-ray spectra, 50 ATR-FTIR spectra (spectral range: 600–4000 cm^{-1}) and 50 UV–vis spectra (spectral range: 200–800 nm) of 70 different materials specifically used by artists from prehistoric times until nowadays.

The home page contains a banner with graphs and photographs of a selection of pigments from the database. The web page is organized in seven areas (Fig. 1a). Tabs in the header allow the user to move from one major content area to another. The first area includes general information on the electrochemistry for heritage (ELCHER) research group (background, organization chart and facilities and equipments). The second area is a summary of the main results obtained by the ELCHER group in the last years (R+D projects, papers and books). The main results of a case study of