

In the studies of paintings the identification of the materials plays an important role. Organic dyestuffs are natural components of many objects of cultural heritage. Identification of colouring substances present in historical artistic paints provides relevant information for a wide range of specialists dealing with works of art. Analysis of natural dyes in historical objects is fundamental for the development of effective and appropriate conservation strategies, to determine the origin of an artefact, as well as to obtain historical information necessary for the purposes of documenting an artwork and a work's authenticity. Identification of a particular dyestuff is usually based on the presence of its main components, while minor components are important for differentiating between dyes originating from closely related sources. Knowledge of the composition of the historical paints helps not only in determining the period of a paintings' creation or its origin, but also to verify the authenticity and finally the development of adequate and effective procedures for its conservation. Knowledge of painting materials is an essential tool for art conservators, and getting to know the precise chemical composition of colouring substances allows identification of the dyestuffs (dye's raw) used by the artist. Knowledge of the exact composition of the dyes in artistic paints allows, as much as possible, for their precise reconstruction, and thus carrying out the renovation works according to the ideological and aesthetic decisions taken by its creator. Determining the chemical composition of colouring substances enables a better evaluation of their resistance on chemicals used for cleaning and removing the varnish from paintings during conservation works. The isolation and identification of dyestuffs from paints used by artists is complicated and time-consuming. Paints in its composition contain not only dyes, but also painting binder and other additives which hinder the full identification of colouring substances. In addition, the procedure of taking samples of paint from a picture is more controversial than that of collecting of single fibres from historical textiles. Natural organic dyes extracted from plants, insects or shellfish, due to their natural origin, are often found in the form of glycosides (linked with sugar units). It is important to note that the colour of a dye can correspond to several substances with very similar or very different physicochemical properties. Aim of the research project is to develop a universal method of the dyestuffs' isolation from paints and the identification of organic dyes used in the 19th-century paintings using high performance liquid chromatography coupled with UV-Vis spectroscopy and mass spectrometry (HPLC-DAD-MS). As a result, a database of natural organic dyes and possibly synthetic ones will be created, used during this period. Isolation of colouring substances from such complex matrices like artistic paints is a difficult task. Natural organic dyestuffs exist in paints in the form of so called lakes, which are complexes of colouring substances with a metal, bonded on inorganic supports. In order to identify the dyestuffs, first they must be isolated from the lakes and paint binders, in such a way as not to cause changes in their original chemical structure. Most of the natural dyestuffs are bound to a mordant, thus forming a dye lake through co-precipitation with an inorganic substrate by strong chelate bonds. The process of dyes extraction is yet more complicated because of the presence of aged binding media, varnishes, and other constituents of the samples. The conventional methods of extracting dyes from lake paints are based on utilization of strong inorganic acids, such as sulphuric and hydrochloric acids, at elevated temperatures in order to facilitate hydrolysis of metal-dye complexes, which are very stable and difficult to decompose. These conditions should facilitate the hydrolysis of metal-dye complex. Unfortunately, the strong mineral acids hydrolyse not only the metal-dye complex which is desired reaction, but they also cause structural changes within the dye molecule. Therefore, the identification of the exact composition of the dyes is impossible. For this reason, there is an ongoing search for effective and mild reagents enabling the isolation of colouring substances from paint matrix. The aim of the study is therefore to try to use milder reagents enabling the isolation of dyestuffs. Conditions of extraction processes will be optimized, including the influence of a temperature changes, process time, the type and amount of extractant (chemical reagent supporting isolation of colouring substances from lakes and paint binders) on the efficiency of extraction and the state of preservation of dyes. As a result, a universal and most effective method of isolation of dyes from the binder painting will be developed. After the effective isolation of colouring matter, the next step in the process of identifying them will rely on the optimization of chromatographic parameters of the apparatus, enabling the separation of dye components into its individual components. Analytical techniques using for identifying colouring substances must ensure their complete separation into individual components, and then detection of these compounds. Therefore, the separation of the dyestuffs will be carried out using reversed phase high performance liquid chromatography (RP-HPLC). Chromatographic conditions will be optimized for the separation process, including the type of chromatography column, mobile phase composition, process temperature, type of additives to the mobile phase to increase the resolution of the system. In order to identify the separated colouring matters the UV-VIS detection will be applied, coupled with mass spectrometry (MS). By means of LC-DAD-MS a full identification of organic colouring substances used by nineteenth-century Polish artists will be carried out. Thanks to our close cooperation with the National Museum in Krakow, Poznan, Bydgoszcz and Katowice, as well as the Department of Conservation and Restoration of Modern Art of the Nicolaus Copernicus University in Torun, we received microsamples of paints from the workshops of: Jan Matejko, Jacek Malczewski, Leon Wyczółkowski, Julian Fałat, and Józef Pankiewicz. Several samples were collected by restorers from specific paintings during conservation works. Some samples, originating from the individual paintings, were collected in the past by restorers during conservation works.

Based on the obtained results, a detailed database of organic dyes used at that time by Polish painters will be set up. It will include a library of spectrochromatograms, mass spectra and UV-Vis spectra of natural and synthetic organic dyes identified during the analysis. **Until now, a comprehensive database containing complete data in the form of UV-Vis and mass spectra of natural organic dyestuffs has not been created.**

The next stage of research will be to prepare paints from natural organic dyestuffs. In most cases it will be necessary to precipitate lakes from the extracts of raw materials. The lakes will be precisely produced from plant extracts (e.g.: madder, brazilwood, weld, etc.) according to the recipes found in the historical sources. For this purpose, the dye extracts offered by Kremer Pigmente will be used. The obtained samples of paint will be artificially aged via UV irradiation in the accelerated aging chamber. The exposed paint will be sampled at specified time periods in order to establish a relationship between the exposure time, degradation rate, and the formed products of photodegradation. The subsequent stage of the project will consist of a comparison of the UV-aged samples and reference samples in order to establish any significant changes occurring in the chemical structure of colouring substances. These UV-induced changes will be analysed by means of LC-DAD-MS. Based on the obtained results, the possible photodegradation pathways for organic dyestuffs, which cause the fading and colour change of a given paint, will be established. The knowledge about these reactions, collected in a short time but dealing with the processes that in reality take years or even centuries, will enable us to determine the optimal conditions for storage and presentation of paintings considered as cultural

heritage. **Until now, the chemical changes of dyestuffs due to light exposure have not been investigated in a systematic way, thus the undertaken research will have innovative character.**

Developed results will allow for better understanding of the painter's workshop and for more reliable dating and authentication of works created by the 19th-century Polish artists. This information will be significant to the art history professionals, as well as the art auction market, and the museums making their new purchases. The conducted research will become a compendium of knowledge for art historians, museum curators and art experts specializing in art authentication. It will also supply valuable information to other scientific fields, including conservation chemistry, chemistry of natural compounds, and materials engineering.