NEW DEVELOPMENTS IN APPLICATION OF HPLC IN ARCHAEOLOGY OF TEXTILES

I. Surowiec 1), W. Nowik 2), A. Quye 3), B. Lendi 3), M. Trojanowicz 3)
1) Department of Chemistry, Warsaw University, ul. Pasteura 1, 02-093, Warsaw, Poland (isuwchem@wp.pl)
2) Department of Chromatography, Laboratory for the Investigations of Historical Objects, 29 rue de Paris, 77420 Champs-sur-Marne, France,
3) Department of Conservation and Analytical Research, National Museums of Scotland, Chambers Street, Edinburgh EH1 1JF, Scotland, Great Britain,
4) Institute for Chemical Technologies and Analytics, Vienna University of Technology, Getreidemarkt 9-16, A-1090 Vienna, Austria

INTRODUCTION

Various aspects of social and cultural history can be revealed through the dyes used for the textiles. The identification of dyes in historical and archaeological textiles is usually based on comparison with known references, quite often however the chemical profile obtained for the sample extract does not match the references available. This can be caused due a number of reasons, including degradation of dyes by light, oxidation or reaction, which might be helpful in identification of unknowns in extracts from historical samples.

EXPERIMENTAL CONDITIONS

The work was done on a triple quadrupole mass spectrometer Quattro LC equipped with a CHROMEQ column (124.5 cm x 0.25 mm i.d., 5 µm particle size). The mass spectrometer with the selected ion monitoring in electrospray negative ion mode proved to be the most sensitive and selective from all the detectors tested for HPLC analysis of natural dyes in extracts from archaeological threads.

Structure elucidation based on UV/Vis spectra from DAD

Fluorescence detection (FLD) was applied in HPLC analysis of extracts from historical objects. The application of a piezo-actuated flow-through microdispenser as a solvent elimination multidetector was found to be a useful technique for on-line monitoring of evaporation of HPLC effluents. The developed method is easy to handle, fast, does not require complex instrumentation and allows simultaneous identification of classes of dyes through their IR and Raman spectra e.g. for degradation products of flavonoids.

CONCLUSIONS

The best extraction method for flavonoids, anthraquinoids, and lignoids proved to be one based on acidic hydrolysis followed by SBFMeOH extraction. Determination of these three classes of dyes with HPLC method could be then performed in the same run. Observation of double band in visible absorption region after post-column deposition was characteristic for 1,4-dihydroxyanthraquinones. Shifts of visible absorption maxima after post-column modification with anionic chloride for flavonoids were in good agreement with literature data, enabling the same primary structure elucidation of this class of dyes, identification of minor hydroxy groups in anthraquinoids was obtained with post column complexation with zircononyl ion.

Optimization of extraction procedure

To 100 µl of conc. H2SO4/H2O/H2O (0.1:0.1:0.1) solution 1 mg of the sample thread was added, heated in a water bath for 10 min, and then treated in a vuvanizer. The extracted thread after that was dissolved to 20 µl of 0.1M SBFMeOH (1:1:1) solution and left for extraction in room temperature for 50 min. Decanted using glass syringe (glycerine filter 0.2 µm) and 0.5 µl of obtained extract was injected into the chromatographic column.

CONSIDERED DYES - CHEMICAL STRUCTURES

BLUE DYES - MONOCHROMATIC CONTAMINANTS

CHROMATOGRAPIC CONDITIONS

In the conditions tested zirconyl ion proved to be much better complexating reagent enhancing fluorescence detection than most often cited in literature aluminum and gallium ones, giving values of signal to noise ratios (S/N) for the analyte compounds identified in the method presented here. The use of stationary phase with silanized surface improved retention of the analyzed compounds.

LIMITS OF DETECTION

The development of efficient dyes extraction method is possible by development of optimized post-column modifications, additional post-column enhancements for separation of classes of dyes with HPLC method could be then performed in the same run.