



Papanastasiou, M., N.S. Allen, A. McMahon, L.C.A. Naegel, M. Edge & S. Protopappas (2012). Analysis of indigo-type compounds in natural dyes by negative ion atmospheric pressure photoionization mass spectrometry. *Dyes and Pigments*, 92(3): 1192-1198. DOI: 10.1016/j.dyepig.2011.08.007

Analysis of indigo-type compounds in natural dyes by negative ion atmospheric pressure photoionization mass spectrometry

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Atmospheric Pressure Photoionization (APPI) in Mass Spectrometry (MS) has been utilized for a number of indigo-related compounds and was found to exhibit an excellent response. All structures were ionized in negative ion mode yielding almost exclusively deprotonated molecules. Their product ion mass spectra were also recorded and showed characteristic losses mainly of small neutrals such as CO, HBr and CONH₂. APPI-MS was applied further to the analysis of indigo dyestuffs of historical importance. HPLC with single ion monitoring (SIM) was employed for the separation and detection of the compounds. A simple HPLC gradient that separated the components in less than 10 min was developed. MS/MS spectra of the colouring components were also recorded and compared to that of the reference substances. The composition of Tyrian purple originating from *Murex trunculus* (*Hexaplex trunculus*), was by far the most complex, whereas some of the structures were also detected in *Purpura haemastoma* (*Stramonita haemastoma*) and *Plicopurpura pansa* (*Plicopurpura patula* subs. *pansa*). Further, a number of synthetic indigo dyes, produced at different times of the 19th century by different manufacturers, were analyzed; similar spectra were obtained suggesting that these were highly pure. Overall, the developed analytical procedure was very efficient offering high sensitivity and selectivity. APPI was proved suitable for ionizing the species under investigation producing clear mass spectra with characteristic fragment ions and may be used successfully in the future for the characterization of similar structures in historical art objects.

Palabras clave: Molluscs, Atmospheric pressure photoionization, Mass spectrometry, Indigo dyes, Tyrian purple

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