

18.12. Identification of degradation products and new colouring components in shellfish purple and indigo by UHPLC-MS/MS

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Degradation products of indigo [1] and shellfish purple and four colourants of shellfish purple which are not often detected [2] were identified (i) in standard solutions of indigotin and 6-monobromo-indigotin, (ii) pigments and (iii) aged textile samples using a UHPLC-MS/MS method. Chromatographic separation in UHPLC was carried out on ACQUITY UPLC BEH C18 (1.7 μ m, 2.1 x 1.8 mm) column thermostated at 40°C. The mobile phase consisted of solvent A: water – 0.1% (v/v) formic acid and solvent B: ACN – 0.1% (v/v) formic acid using a gradient elution program during a time course of 38 min. The flow rate was 300 μ L min⁻¹. MS was performed using an electrospray ionization (ESI) Ion Max source with a HESI-II probe. The ESI was operated in positive mode (ESI+) for the detection of the colouring components and in negative mode (ESI-) for isatin (IS) and the degradation products of indigotin and 6-monobromoindigotin. In order to achieve adequate ionization in ESI for direct infusion analysis of the standard compounds, a novel solution preparation approach had to be developed since DMSO, the solvent into which the compounds are readily diluted in, is not fully compatible with ESI direct infusion analysis due to its high viscosity and high boiling point. The primary solutions of the colouring components, indigotin and 6-monobromoindigotin, were prepared by diluting with NaOH aqueous solutions for optimisation of detection parameters. To sum up, the four colourants were identified in all shellfish purple samples in small quantities. These components belong to the same structural class with the mono-, di- and non-brominated indigoids and have one unit lower masses than indigotin and its mono- and di-brominated derivatives. Two degradation products, isatin and isatoic anhydrite (DP3) were detected in indigotin and 6-monobromoindigotin standard solutions. Isatin and some other indigoid degradation products were identified in both shellfish purple and indigo samples, as well as, in the standard solutions of indigotin and 6-monobromoindigotin.

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References

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