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Analysis of commercial Acid Black 194 and related dyes by micellar electrokinetic chromatography

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ABSTRACT

The commercial dye C.I. Acid Black 194 was analyzed by reversed-phase HPLC, Capillary Zone Electrophoresis and Micellar ElectroKinetic Chromatography under different operative conditions, with the scope to detect the impurity distribution typical of any production processes and synthetic batch. The three chrome(III) complexes deriving from the industrial synthesis of C.I. Acid Black 194, and one of the main impurities were isolated by silica flash chromatography and identified by mass spectrometry and NMR. More than twelve compounds present in the commercial mixture, but undetectable by the analytical protocols known in literature, were fully separated by the MECK mode capillary electrophoresis with low % Relative Standard Deviation of the main electrophoretic parameters. Two of them were identified by isolation from the commercial mixture. As additional examples two other commercial metal-based dyes, C.I. Acid Brown 432 and C.I. Acid Brown 434, were analyzed by the same protocol with very good results.

1. Introduction

The total worldwide consumption of dyes in several industries such as textile, leather, paper, pulp, plastics is estimated will grow to 2.3 million metric tons in 2013 [1]. Approximately 10,000 different dyes and pigments are produced annually worldwide and used extensively in the dye and printing industries [2]. Unfortunately, it is estimated to grow to 10–15% of unexhausted dyes, after the colouring process, are discharged into the waste streams irrespective of the substrate involved (e.g., leather, plastic) [3]. The complex chemical formulae of dyes, along with the presence of heavy-metal ions, has the potential of inducing chronic toxicity, for instance through mutagenic and carcinogenic effects. This is particularly true with azo dyes, which alone constitute about 50% of all industrial colourants produced worldwide [4]. These can be transformed into carcinogenic compounds under anaerobic conditions [5].

The main analytical methods applied to the characterization of metal dyes are HPLC and capillary zone electrophoresis (CZE). After a timid approach [6,7], the CZE analysis, has gained momentum and has been applied to a variety of cases. Perhaps the first report appeared in 1998, when Pérez-Ruiz et al. [6] described the CZE separation of fluorescein dyes by exploiting host-guest complexation with β-cyclodextrin. Subsequently, Borrós et al. [7] adopted CZE for studying the formation of carcinogenic aryl amines in azo dyes. There has been a significant increase in the use of CZE for analyzing dyes, especially artificial colourants added to foodstuff, such as brilliant blue and azorubine in red wines [8] and a variety of azo dyes in alcoholic beverages [9], not to mention synthetic dyes in ice creams [10] and milk beverages [11]. The list could continue with reports on CZE analyses of a variety of food colourants [12], including red food colourants [13]. The work done up to the year 2000 has been nicely reviewed by Boyce [14] and not only includes colourants in foodstuff, but also a variety of additives as well, such as preservatives, antioxidants, sweeteners and other modifiers.

Among the commercial dyes, Acid Black 194 is one of the most popular in both leather and wool, polyamide, silk and wool blended fabric dyeing [1], direct printing in wool, silk fabric fibre and nylon non-woven microfabric dyeing [15,16]. In the last case, hydrophobic interactions between dye and fibre and ion–ion electrostatic interactions between the dye anion and the protonated amino groups of the fibre are thought to contribute to the dye-substrate strong affinity [17]. ORISAN Black M-RL is a 1:2 symmetrical metal complex dye constituted by a mixture of three geometrical isomers [18], where the chrome(III) central atom is coordinated to two molecules of a tridentate organic ligand, according to an octahedral *mer*-distorting geometry. The chemical structure of one of the three N-α,β isomers [19] of the unsymmetrical azo ligands, is shown in Fig. 1A. The organic ligands are multi functional azo dyes

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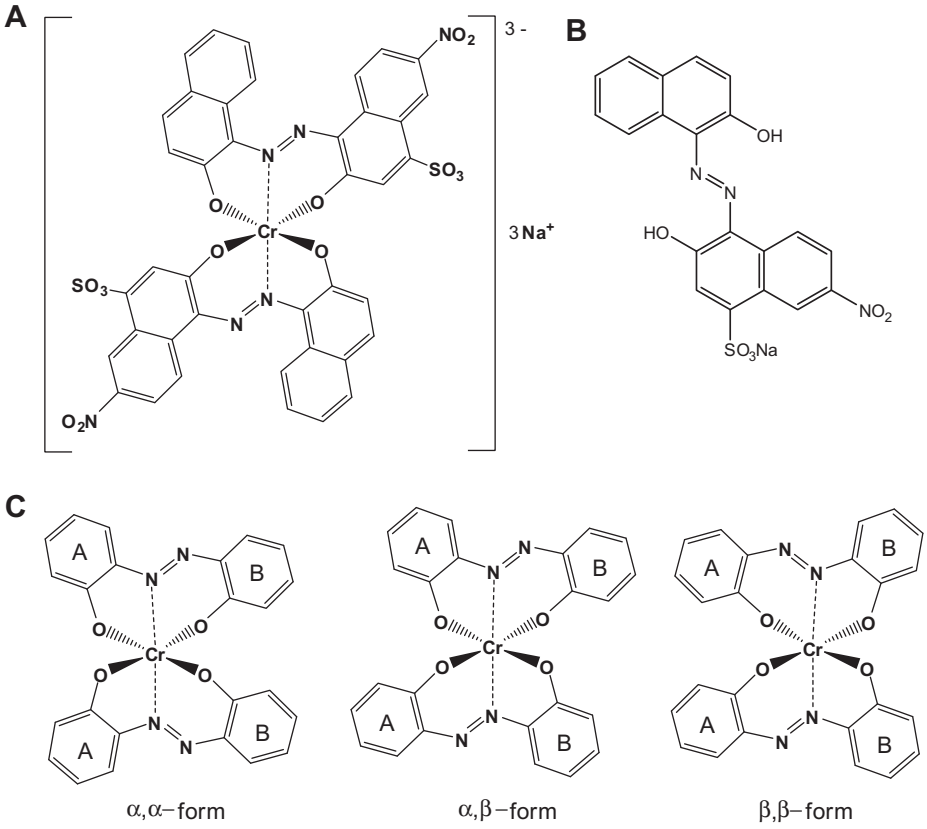

Fig. 1. Acid Black 194: A) one of the chemical structure of the three metal complex positional isomers. B) Chemical structure of the organic ligand in the mono sodic form. C) The three forms of the positional isomers.

of the family called Mordant Black, characterized by the presence of one azo group, one strong and two middle acidic functions in appropriated positions that allow multiple coordination to the metal ion and give to the complexes a multiple negative charge (at least 3^-) necessary to ensure a good solubility of the dye in water. In Fig. 1B a chemical structure of the organic ligand, in the mono sodium salt form, is shown, whereas in Fig. 1C the three α,α-, α,β- and β,β- forms of the three N-α,β isomers ring A and B being differently substituted, are reported [19].

Considering the toxicity towards the environment of the metal complex dyes and in particular that of C.I. Acid Black 194, that is at least one order of magnitude higher than in the case of other dyes (DL50 for fish of the order of 10 mg/L, as compared with Acid Violet 90 with >100 mg/L), analytical protocols based on CE-MS able to screen its presence in waste waters were proposed [20]. The same analytical method were applied with good results in forensic analysis too [21] however, the protocols suggested were focused on the separation of the complexes of the metal isomers only.

In relation to the European legislation known as REACH (Registration, Evaluation, Authorization of Chemical), the problem has occurred to develop simple, fast and stable analytical methods for the analysis of the metal complex dyes able to highlight the main impurity present in the commercial products so to give, at least, a "finger print" to the batches produced and marketed. Within the European Union, 2000–2500 different dyes and organic pigments are produced and marketed and an even wider number of substances must be considered when their synthetic intermediates are taken into account. These substances are subjected to REACH registration requirements and can not be produced or sold within the EU marketplace without the requisite data. For this area the REACH compliance activities are complex and challenging owing to the serious amount of work to provide deep toxicological, ecotoxicological, chemical and physical–chemical properties which are not often available. There are fears that some of these products could be categorized as being very persistent and very bioaccumulative and therefore registration can be more expensive than expected without suitable safer replacements available. To harmonize and provide consistent registration dossiers, in 2010 seven consortia for phase 1 substances and five for phase 2 substances were formed. The complex and sometimes huge mix of ingredients within a given product exacerbates the difficulty of providing information but development of scientific data to increase understanding of the possible health and environmental effects of dyes, contaminants, impurities, by products and residues remain unavoidable. The starting point for this information flow is a quantitative and accurate fingerprint distribution of organic compounds present in the dye mixtures provided by organic analysis and of the various techniques available, capillary electrophoresis can play a relevant role for its versatility, selectivity and accuracy.

So, with the purpose of identifying a more practical analytical method able to detect the largest possible number of compounds, with high efficiency and reproducibility, the analysis of the dye mixtures were handled by chromatographic and electromigration approaches in accordance with the analytical protocols applied in literature. After testing two methods HPLC and CE, under different analytical conditions identified in the scientific data [20–22] available and focussing on protocols, at the beginning, compatible with MS detectors, no satisfactory results were achieved.