Dyes and Pigments 94 (2012) 258–265

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

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

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ARTICLE INFO

Article history:
Received 12 September 2011
Received in revised form
23 December 2011
Accepted 28 December 2011
Available online 20 January 2012

Keywords:
Textile dyes
Metal complexes
Micellar capillary electrophoresis
REACH legislation
Acid Black analysis
Acid Brown analysis

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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doi:10.1016/j.dyepig.2011.12.014

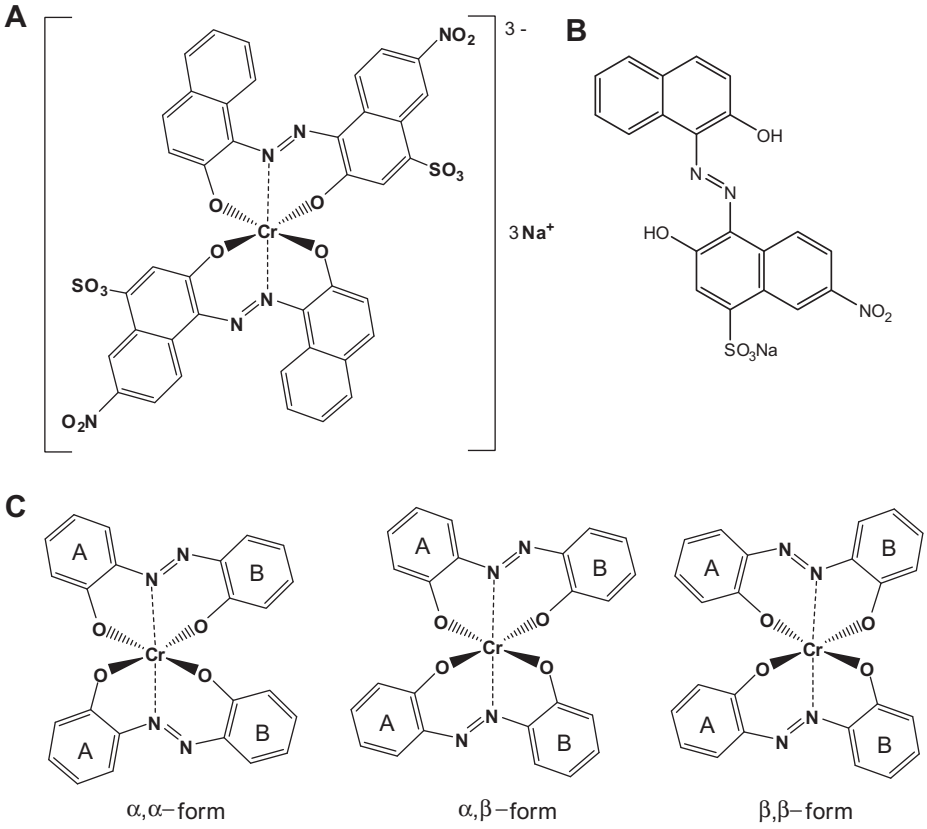

Fig. 1. Acid Black 194: A) one of the chemical structure of the three metal complex positional isomers. B) Chemical structure of the organic ligand in the mono sodic form. C) The three forms of the positional isomers.

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.

Then we directed our attention to Micellar Electrokinetic Chromatography [23–25] from which we obtained optimal results since it was possible to separate more than twelve compounds with high repeatability in about 8 min of analysis. The MECK mode was also the best applied for the analysis of other two metal dyes of the same family: the Acid Brown 432 and Acid Brown 434.

2. Materials and methods

2.1. Chemicals and materials

All the aqueous solutions were prepared with Sigma–Aldrich (St. Louis – MO – USA) HPLC grade water (Chromasolv Plus). Isopropyl alcohol, hexafluoroisopropanol (HFIP), formic acid, acetic acid, sodium tetraborate, sodium dodecyl sulphate (SDS), were from Sigma–Aldrich (St. Louis – MO – USA). Sodium hydroxide 1.0 M, CE commercial buffer solution at pH 7.4 (89 mM Tris, 332 mM boric acid) and pH 8.3 (89 mM Tris, 89 mM Boric Acid) were from Hewlett Packard GmbH (Waldbronn, Germany).

The commercial acid dyes Acid Brown 432, Acid Brown 434, Acid Black 194 and its organic ligand, 3-hydroxy-4-[(E)–(2-hydroxynaphthalen-1-yl)diazenyl]-7-nitronaphtalene-1-sulfonate sodium salt, were supplied from Origo Sas, Milano, Italy.

The main pigments, isolated by flash chromatography from the dye Black 194, are the Cr(III) complexes Trisodium,bis[(E)-7-nitro-3-oxido-4-((2-oxidonaphthalen-1-yl)diazenyl)naphtha-lene-1-sulfonate] chromate(3-), in the forms reported in Fig. 1(A and C).

The main pigment present in the Acid Brown 432 dye is the Trisodium, bis [2-((E)-(4-hydroxy-2-oxido-3-((E)-(5-sulfonatonaphthalen-1-yl)diazenyl)-phenyl)diazenyl)benzoate] chromate(3-). The ma-in pigment present in theAcid Brown 434 dye is the (Trisodium bis [5-((E)-(4-((E)-(3,5-dinitro-2-oxidophenyl)diazenyl)-2-hydroxy-3-oxidophenyl)diazenyl)-naphthalene-2-sulfonate]ferrate(–) (see Fig. 7A and B).

2.2. Thin layer chromatography and flash chromatography

Thin layer chromatography (TLC) was performed by TLC precoated glass plates of Silica Gel 60 F_{254}, purchased from Merck. An AcOEt: MeOH: AcOH = 8:1:1 mixture was utilized as eluent. The isolation of the three metal complex dyes and of a yellow impurity present in the commercial sample, was performed by flash chromatography using direct-phase silica gel 35–70 μm, purchased from Merck, and the same eluent described above. For 0.5 g of dye mixture, a 5 cm diameter chromatographic column filled up to 20 cm with silica gel was utilized. The mobile phase flow was set to 2.5 cm/min and 20 mL fractions of eluent were collected.

2.3. HPLC analysis

The HPLC analyses were performed by a Merck-Hitachi instrument, equipped with two pumps (L-6200A and L-6000 intelligent Pumps), auto sampler AS 200A and UV–VIS detector L-4250. A Hypersil BDS-C18, 5 μm, 125 × 4 mm column by Merck was utilized as column. The best analytical results were obtained with the following conditions: column temperature 30 °C, eluent flow 0.5 mL/min, wavelength 254 nm, injection 10 μL, programmed gradient mode eluting as reported: time,%MeCN,%H_2O = 0,10,0; 5,10,0; 10,8,2; 15,8,2; 20,7,3.

2.4. Capillary electrophoresis

The analyses were performed with a Hewlett–Packard $3D^{CE}$ instrument, equipped with a UV–Vis diode array detector. Fused silica capillaries (I.D. 50 μm) were purchased from Composite Metal Services LTD (UK). Typical capillary pre-treatment: a new silica capillary (50 cm total length) is washed for 10 min with a 1 M sodium hydroxide solution then, for 5 min water and 5 min with the background electrolyte (BGE) solution. After which it is ready for use. Typical preconditioning step (between analyses): flushing for 1–2 min with the BGE solution. All the capillary flushings were performed at high pressure (4.5 bar). Typical electrophoretic conditions: voltage 25 or 29 kV, cassette temperature 20 °C, working wavelength 233 nm. A 1 mg/mL of aqueous mother solution of any sample was diluted 2–5 times before injecting. Injection: diluted sample 30–50 mbar × 3 s followed by BGE 10 mbar × 5 s (specific conditions are reported in the legends).

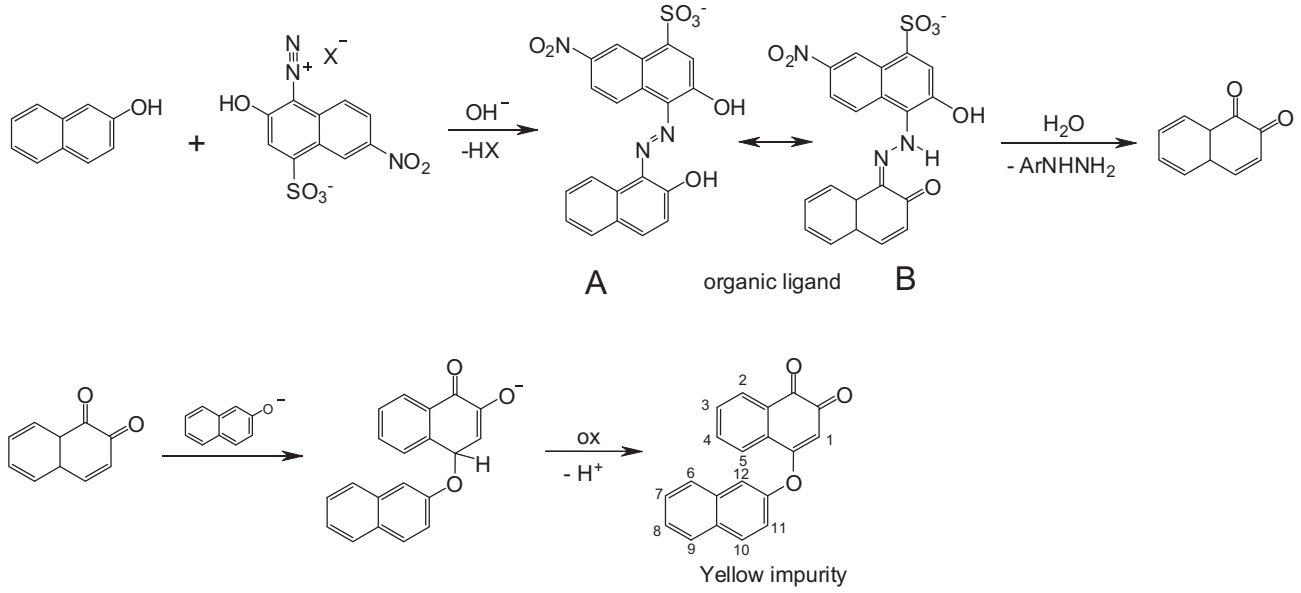

Fig. 2. Possible synthetic pathway of the yellow impurity isolated from a commercial sample of the Acid Black 194 dye. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

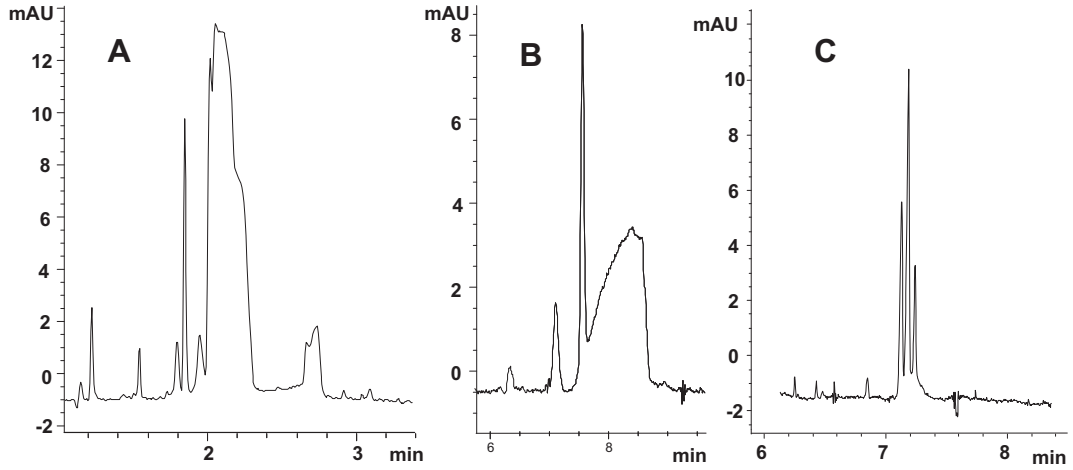

Fig. 3. CZE of commercial Acid Black 194 dye at different BGE compositions and pH. A: BGE 89 mM Tris, 89 mM boric acid, pH 8.3; 33.5-cm long capillary, voltage −25 kV. B: BGE 25 mM sodium tetraborate, pH 9.3; 50-cm long capillary, voltage +29 kV. C: BGE BGE 5 mM ammonium acetate pH 9–40% MeCN [20]; 33.5 cm long capillary, voltage +20 kV.

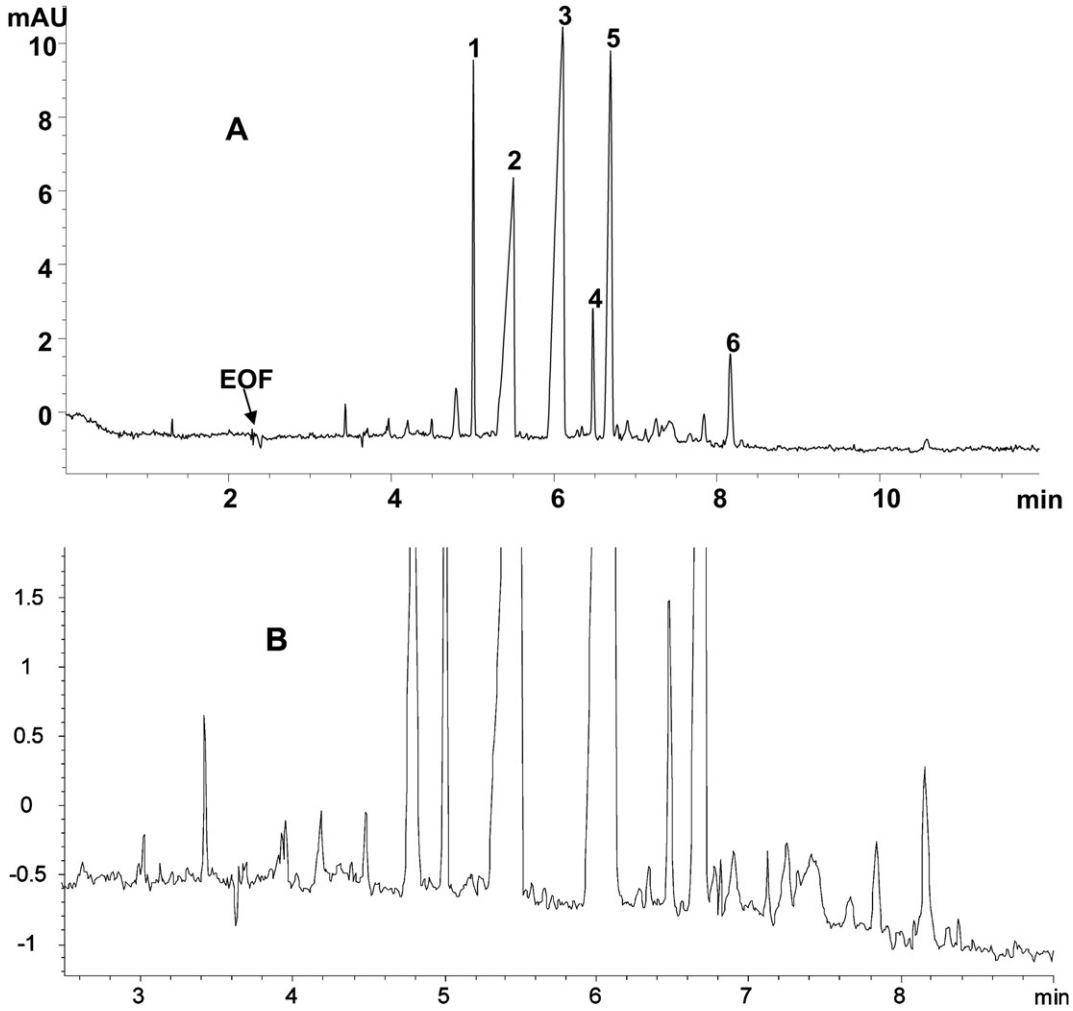

Fig. 4. A) Full scale electropherogram of commercial Acid Black 194 dye by MECK mode. Peak n.1 = yellow impurity; peaks *n*. 2, 3 and 5 = metal complex positional isomers, peak n.6 = free organic ligand. BGE: 10 mM SDS in 25 mM sodium tetraborate, pH9.3. Operative conditions: 50-cm long capillary, voltage +29 kV. B) Electropherogram magnification of commercial Acid Black 194 dye. To note the large number of impurities separable and detectable by UV–Vis CE MECK mode. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

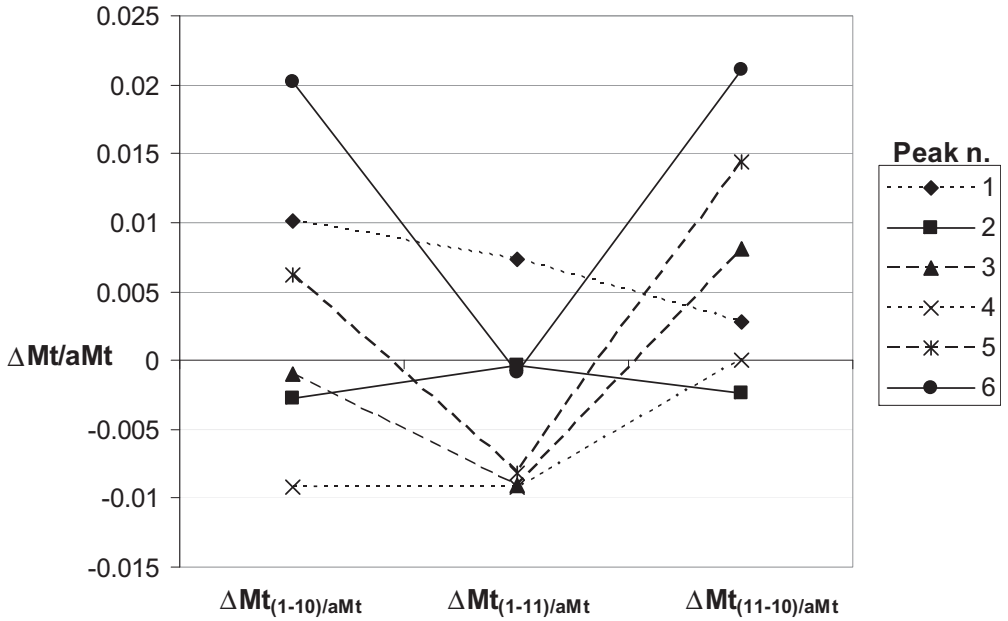

Fig. 5. Analysis of the commercial Acid Black 194 dye by the MECK mode. Trend of the migration time differences among several injections with and without replacing the working BGE: ΔMt(1–10)/aMt, ΔMt(1–11)/aMt, ΔMt(11–10)/aMt = migration time difference (ΔMt) on the average migration time (aMt) among, respectively, the first and the tenth injections without working BGE replacement, the first and the eleventh injection (this last with BGE replacement), the eleventh and tenth injection.

2.5. 4-(naphthalen-2-yloxy)naphthalene-1,2-dione): ^{1}H NMR and MS-ESI characterization

^{1}H NMR spectra were recorded in DMSO-D_6 at 300 K on a Brucker Avance 400 MHz: δ ppm 8.18(dd, $J = 7.39$, 1.39, 1H, H_9), 7.84(dd, 1H, H_6), 7.56(d, $J = 7.3$, 1H, H_{10}), 7.74(dt, $J = 7.47$, 1.23, 1H, H_4), 7.36 (M, 4H, $H_{3,5,7,8}$), 7.30 (s, 1H, H_{12}), 7.28 (d,d, $J = 7.14$, 1.05, 1H, H_2), 6.88(dd, 7.74, 1.15, H_{11}) 6.53 (s, 1H, H_1).

MS-ESI spectra were recorded by a Bruker Esquire 3000 Plus: 301 (M+1, 23.1), 283(15.4), 273(100), 255(38.5), 254(92.3), 231(30.8).

3. Results and discussion

Normal phase TLC analysis of the dye Black 194, allowed the separation of the three positional isomers as black spots with $R_f = 0.17$, 0.13, 0.09, respectively. Due to the strong polarity of the metal complexes, the three compounds can be not separated as clean spots but as lightly streaked stains. The same problem was encountered during the flash chromatography separation of the complexes but, due to an over-dimensioned chromatographic column, it was possible to isolate the three isomers with very small

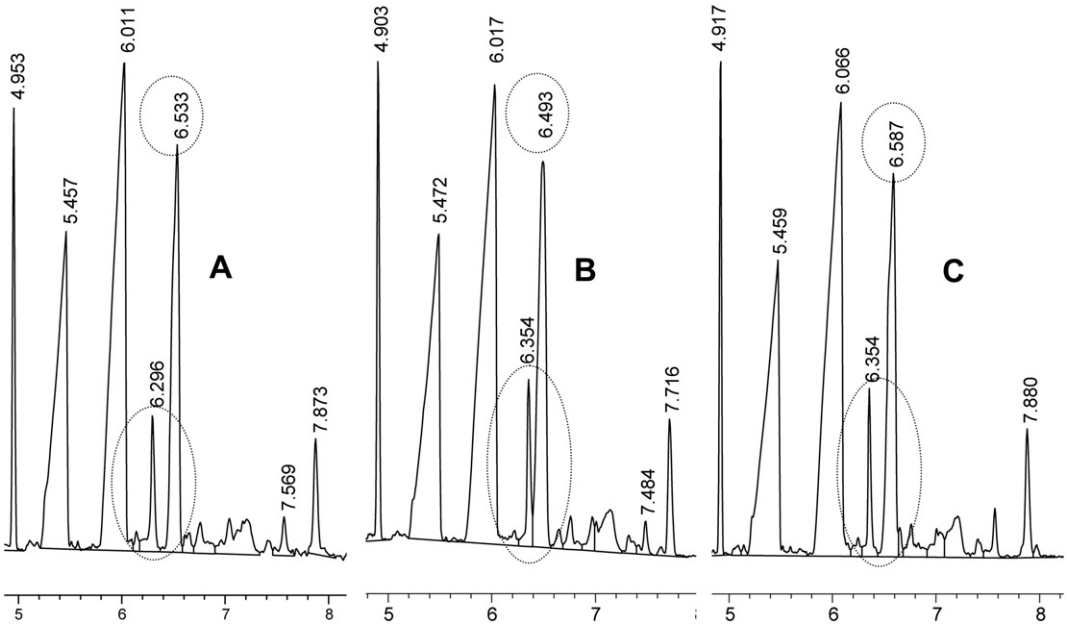

Fig. 6. Analysis of the commercial Acid Black 194 dye by the MECK mode. Importance of the working BGE solutions replacement (inlet and outlet) between the runs on the migration time reproducibility and resolution. A: first injection with fresh working BGE solutions; B: tenth injection with the same working BGE solutions; C: eleventh injection with fresh working BGE solutions. BGE: 10 mM SDS in 25 mM sodium tetraborate, pH 9.3. Operative conditions: 50-cm long capillary, voltage +29 kV.

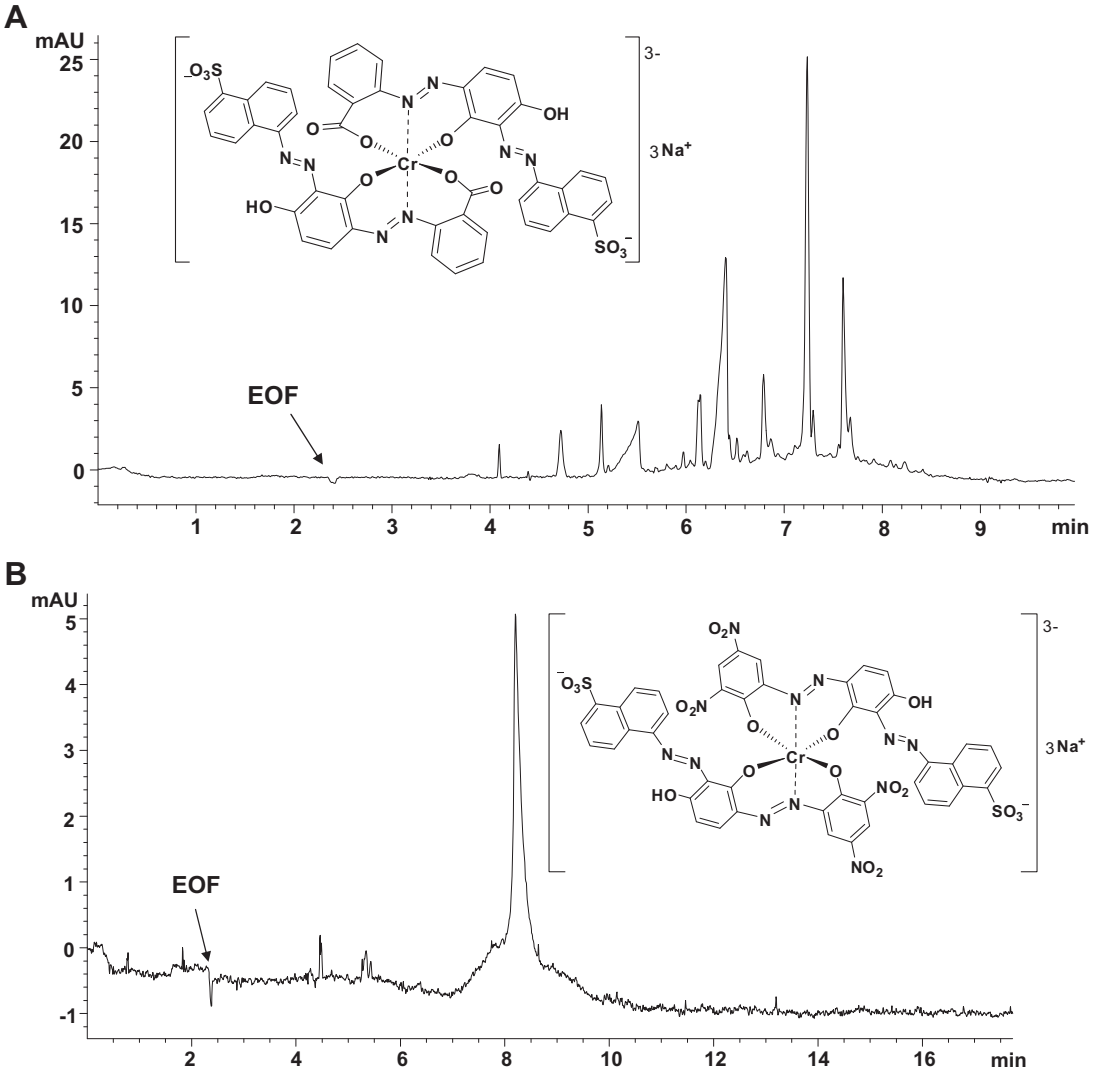

Fig. 7. A: analysis of the commercial Acid Brown 432. B: analysis of Acid Brown 434 BGE: 10 mM SDS in 25 mM sodium tetraborate, pH 9.3. Operative conditions: 50-cm long capillary, voltage +29 kV.

reciprocal contamination, and confirm them by mass spectrometry (MS-ESI) (data not shown). The TLC analysis of the mixture also showed the presence of a yellow, low-polarity compound with $R_f = 0.75$, which was also isolated by flash chromatography and identified by ^{1}H NMR and MS as the 4-(naphthalen-2-yloxy) naphthalene-1,2-dione (see Section 2.5). The presence of this compound in the dye is connected to the typical synthesis of mordant azo dyes performed at alkaline pH. In this case the coupling process is between the6-nitro-1,2,4-acid and 2-naphthol, as reported in Fig. 2. The tautomeric form B of the ligand [26], can be hydrolyzed to the 1,2 naphthoquinone which can react with the 2-naphthol to give the yellow impurity isolated.

The classical chromatographic approach to the analysis of commercial samples of the Acid Black 194 dye appeared quite difficult. Direct and reversed-phase HPLC experiments were performed with several eluents, in all cases, however, with poor resolution among the three main compounds and a low sensitivity on the detection of other impurities. The ability of these metal derivatives to establish multiple interactions with the silica surface was clearly confirmed also by preliminary experiments performed via CZE: the classical, MS-compatible, background electrolyteat acidic pH, based on HCOOH/HCOO$^-$ or AcOH/AcO$^-$ pairings, as the typical neutral or basic running buffers resulted thoroughly inappropriate. Also the use of hydro-organic buffers did not give satisfactory results in particular in the detections of the dye contaminants: in Fig. 3 some examples of electropherograms obtained with these types of BGE are reported.

Excellent results were instead obtained by the Micellar ElectroKinetic Chromatography (MECK), based on the use of SDS in tetraborate buffer. Under these conditions, optimal separations of more than twelve compounds, present in the commercial sample, were achieved in about 8 min of analysis. The three positional metal complex isomers were fully separated, together with the impurities described above, and the presence of free ligand was also detected. Fig. 4 displays the electropherogram obtained by MECK mode in a BGE composed by 10 mM sodium dodecyl sulphate (SDS) in 25 mM sodium tetraborate. For evaluating the robustness of the method, three sets of eleven analyses of the same sample were performed. The quantitative data obtained are reported in Table 1: as evidenced, the % Relative Standard Deviation (%RDS) of the main parameters is very low, which confirms the validity of the technique, applicable also for developing validated methods for analyzing this type of mixtures.

As a last observation, it is interesting to note the relative migration time sensitivity of the different compounds due to the chemical composition modification of the working BGE (inlet and

Table 1
%RDS of the main electrochromatographic parameters collected during the analysis of the commercial Acid Black 194 dye by MECK mode.

Peak n.	% RSD day by day (three days)					% RSD daily				
		Mt (min.)	Corrected area (mAU)	Plates	Resolution		Mt (min.)	Corrected area (mAU)	Plates	Resolution
1	Average	4.965	0.086	242,731.342	3.632	Average	4.917	0.083	249,452	3.600
	St. Dev.[a]	0.030	0.002	16,643.019	0.099	St. Dev.	0.031	0.002	15,912	0.116
	%RSD	0.61	2.10	6.86	2.73	%RSD	0.63	2.14	6.38	3.22
2	Average	5.539	0.283	9806.367	4.351	Average	5.471	0.278	10,070	4.300
	St. Dev.[a]	0.037	0.006	445.068	0.091	St. Dev.	0.038	0.006	445	0.090
	%RSD	0.68	2.02	4.54	2.08	%RSD	0.69	2.02	4.42	2.09
3	Average	6.135	0.410	8784.241	2.444	Average	6.078	0.394	9689	2.600
	St. Dev.[a]	0.029	0.008	212.658	0.063	St. Dev.	0.031	0.009	216	0.063
	%RSD	0.47	2.02	2.42	2.57	%RSD	0.51	2.16	2.23	2.41
4	Average	6.434	0.032	242,362.926	1.907	Average	6.354	0.031	280,547	1.870
	St. Dev.[a]	0.048	0.001	26,757.382	0.141	St. Dev.	0.047	0.001	27,596	0.143
	%RSD	0.74	3.24	11.04	7.42	%RSD	0.73	3.42	9.84	7.64
5	Average	6.646	0.177	33,585.407	2.094	Average	6.588	0.171	34,624	2.470
	St. Dev.[a]	0.028	0.004	2851.317	0.299	St. Dev.	0.026	0.004	2213	0.301
	%RSD	0.42	2.28	8.49	14.28	%RSD	0.39	2.35	6.39	12.20
6	Average	7.965	0.027	190,952.714	4.702	Average	7.880	0.027	196,719	4.820
	St. Dev.[a]	0.044	0.001	5702.605	0.033	St. Dev.	0.046	0.001	6129	0.038
	%RSD	0.55	3.06	2.99	0.69	%RSD	0.58	3.37	3.12	0.79

[a] Average of the St. Dev. calculated on the three days analysis.

outlet vials) subjected to protracted electrolysis. In Fig. 5 the trend of the migration time differences between several injections with and without replacing of the working BGE is reported. The peaks *n*. 2 and *n*. 6 follow respectively the almost perfect V and Λ shape expected; also the peaks 3 and 5 follow the expected trend but less rigorously, while the peaks 1 and 4 move clearly away from it.

The analytical result of this behaviour is particularly relevant for the peaks *n*. 4 and 5 (see Fig. 6), where the relative position of these two peaks change significantly during ten analyses performed without replenishing the working BGE, thus compromising their resolution. The appropriated relative positions are promptly re-established just by replacement of the two working solutions with fresh running buffer.

Just for evaluating the possible generality of this analytical method for the analysis of metal complex dyes, other two metal-based commercial dyes, Acid Brown 432 and Acid Brown 434, were analysed by MECK. The results are reported in the Fig. 7A and B. Also here, the Acid Brown 432 displays a complex mixture of at least eleven compounds, clearly visible by this technique. On the contrary, the MECK analysis of the Acid Brown 434 exhibited a single-peak electropherogram (Fig. 7B).

4. Conclusions

The analytical protocols reported in literature based on direct and reversed-phase HPLC techniques and CZE did not prove to be a convenient approach for the analysis of commercial metal-based dyes, such as Acid Black 194. On the contrary, the well-consolidated micellar electrokinetic chromatography constitutes an easy, fast and robust analytical method for this type of mixtures (that have proven much more complex than expected), thus being a good candidate for validation measurements. High efficiency and reproducibility can be guaranteed with the proviso of replacing the working BGE after every analysis (a simple golden rule in electrokinetic methodologies often underestimated). The danger of electrode polarization, i.e. cation and anion depletion due to their migration towards the respective electrodes, is maximized in CZE due to the small electrodic vessel volumes). The method was also shown to work successfully for the analysis of analogue mixtures of dyes without introducing relevant modifications to the protocol. If anything, the present data prove once again the tremendous power and versatility of the MECK technique, which, although invented by Shigeru Terabe in 1987 [25], is still alive and well in Anno Domini 2011. Infact, as known, the main limitation that have reduced the use of MECK in CE is its incompatibility with the MS detectors. But, as shown in a very recent work of Barbula et al. [27], this disadvantage will be hopefully removed in the near future, so that the immense potential of this technique in combination with a mass spectrometer detector will be fully expressed.

Acknowledgements

The authors thank Itaca Nova S.r.l. and Origo Sas for support. PGR is supported by a grant from PRIN-2008 (Rome, Italy).

References

[1] World dyes & organic pigments. Industry study with Forecasts for 2013 & 2018. Fridonia Group, www.freedoniagroup.com; 2009.
[2] Rodriguez E, Pickard MA, Vazquez-Duhalt R. Industrial dye decolorization by laccases from ligninolytic fungi. Curr Microbiol 1999;38:27–32.
[3] Brown DH, Hitz HR, Schafer L. The assessment of the possible inhibitory effect of dyestuffs on aerobic waste-water bacteria experience with a screening test. Chemosphere 1981;10:245–61.
[4] Kulkarni SV, Blackwell CD, Blackard AL, Stackhocese CW, Alexander MW. Textile dyes and dyeing equipment, classification, properties and environmental aspects. Research Triangle Park, NC: U.S. Environmental Protection Agency; 1985. EPA-600/2–85/010.
[5] Chung1 K-T, Stevens E. The reduction of azo dyes by the intestinal microflora. Crit Rev Microbiol 1992;18:175–90.
[6] Pérez-Ruiz T, Martinez-Lozano C, Sanz A, Bravo E. Separation of fluorescein dyes by capillary electrophoresis using β-cyclodextrin. Chromatographia 1998;48:263–7.
[7] Borrós S, Barberá G, Biada J, Agulló N. The use of capillary electrophoresis to study the formation of carcinogenic aryl amines in azo dyes. Dyes Pigm 1999; 43:189–96.
[8] De Villiers A, Alberts F, Lynen F, Crouch A, Sandra P. Evaluation of liquid chromatography and capillary electrophoresis for the elucidation of the artificial colorants brilliant blue and azorubine in red wines. Chromatographia 2003;58:393–7.
[9] Patsovskii AP, Rudometova NV, Kamentsev Ya S. Electrophoretic determination of synthetic dyes in alcoholic beverages. J Anal Chem 2004;59(2004): 150–4.
[10] Del Giovine L, Piccioli Bocca A. Determination of synthetic dyes in ice-cream by capillary electrophoresis. Food Control 2003;14:131–5.
[11] Huang HY, Shih YC, Chen YC. Determining eight colorants in milk beverages by capillary electrophoresis. J Chromatogr A 2002;959:317–25.
[12] Huang HY, Chiu CW, Sue SL, Cheng CF. Analysis of food colorants by capillary electrophoresis with large-volume sample stacking. J Chromatogr A 2003; 995:29–36.
[13] Ryvolová M, Táborský P, Vrábel P, Krásenský P, Preisler J. Sensitive determination of erythrosine and other red food colorants using capillary

electrophoresis with laser-induced fluorescence detection. J Chromatogr A 2007;1141:206–11.
[14] Boyce MC. Determination of additives in food by capillary electrophoresis. Electrophoresis 2001;22:1447–59.
[15] Burkinshaw SM, Lagonika K. Sulphur dyes on nylon 6,6. Part 3. Preliminary studies of the nature of dye–fibre interaction. Dye Pigm 2006;69:185–91.
[16] Koh JS, Kim YG, Kim JP. Dyebath reuse in dyeing of nylon microfiber non-woven fabric with 1:2 metal complex dyes. Fibers Polym 2001;2:35–40.
[17] Lewis DM. Wool dyeing. Soc Dyers Colour; 1992:219. Bradford.
[18] Szuster L, Niepsuj B, Grajkowski P. Black C.I. Acid Black 194-compositional analysis. Barwniki, Srodki Pomocnicze 2002;46(1/2):3–14.
[19] Lehmann U, Rihs G. In: Yoshida Z, Kitao T, editors. Chemistry of functional dyes. Tokyo: Mita Press; 1989. p. 215.
[20] Poiger T, Richardson SD, Baughman GL. Analysis of anionic metallized azo and formazan dyes by capillary electrophoresis–mass spectrometry. J Chromatogr A 2000;886:259–70.
[21] Stefan AR, Dockery CR, Nieuwland AA, Roberson SN, Baguley BM, Hendrix JE, et al. Forensic analysis of anthraquinone, azo, and metal complex acid dyes from nylon fibers by micro-extraction and capillary electrophoresis. Anal Bioanal Chem 2009;394:2077–85.
[22] Lemr K, Holčpek M, Jandera P, Lyčka A. Analysis of metal complex azo dyes by high-performance liquid chromatography/electrospray ionization mass spectrometry and multistage mass spectrometry. Rapid Commun Mass Spectrom 2000;14:1881–8.
[23] Terabe S. Peer reviewed: micellar electrokinetic chromatography. MEKC belongs to a mode of CE but also to micro-LC. Anal Chem 2004;76:241A–6A.
[24] Terabe S. Micellar electrokinetic chromatography for high-performance analytical separation. Chem Rec 2008;8:291–301.
[25] Cohen AS, Terabe S, Smith JA, Karger BL. High-performance capillary electrophoretic separation of bases, nucleosides, and oligonucleotides: retention manipulation via micellar solutions and metal additives. Anal Chem 1987;59:1021–7.
[26] For the tautomeric equilibrium of azo-naphthols see Fabian Walter MF, Antonov Liudmil, Nedeltcheva Daniela, Kamounah Fadhil S, Taylor Peter J. Tautomerism in hydroxynaphthaldehyde Anils and azo analogues: a combined experimental and computational study. J Phys Chem A 2004;108:7603–12.
[27] Barbula GK, Safi S, Chingin K, Perry RH, Zare RN. Interfacing capillary-based separations to mass spectrometry using desorption electrospray ionization. Anal Chem 2011;83(6):1955–9.