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Analysis of anionic metallized azo and formazan dyes by capillary electrophoresis–mass spectrometry

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Abstract

Capillary electrophoresis–mass spectrometry was applied to the separation of several anionic dyes containing copper(II), chromium(III), or cobalt(III) as part of the dye molecule. The dyes were separated using a 110 cm×50 μm uncoated fused-silica capillary and a 5 m*M* ammonium acetate buffer (pH 9) containing 40% acetonitrile. Excellent separation efficiencies ($N = 500\,000$ plates/column) and low detection limits of 20–50 pg (selected ion monitoring, $S/N = 10$) were achieved. Mass spectra were acquired at different cone voltages. At low cone voltages (low collision energies), sensitivity was maximized and the mass spectra contained only signals of the (multiply charged) molecular ions and low levels of sodium ion and proton adducts. At higher cone voltages, the 2:1 (ligand:metal) chromium and cobalt dyes showed losses of one of the two dye ligands, accompanied by a reduction of the metal. The copper dyes showed signals due to loss of SO_2 and SO_3^-, but no release of metal. Azo cleavage, otherwise typical of azo dyes, was not observed with the metallized dyes.

Keywords: Dyes; Metal complexes

1. Introduction

Metal complex dyes are widely used in the textile industry because of their excellent light fastness. Metals used in metallized dyes include mainly chromium, cobalt, and copper. Metal complexes can be found in acid, direct, and reactive dyes, as well as in pigments [1,2].

A significant fraction of textile dyes are discharged with dyehouse effluents [3]. Environmental concerns arise from the carcinogenic properties of some dyes and from amines formed by reductive cleavage of azo groups [4]. In addition to these concerns, release of metals from metallized dyes may affect their ecotoxicity. The textile industry is currently under increased regulatory pressure to meet effluent standards for metals [5]. However, no data are available to predict the environmental fate of metals in metallized dyes.

Acid, direct, and reactive dyes exhibit low volatility and are not amenable to gas chromatographic separation or conventional electron-impact mass spectrometry. Anionic dyes can be separated by high-performance liquid chromatography (HPLC)

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[6–10] and capillary electrophoresis (CE) [11–15]. Mass spectral analysis of anionic dyes has been performed by fast atom bombardment (FAB) [16–18] and liquid secondary ion mass spectrometry (LSI-MS) [19–21]. Anionic dyes have also been analyzed by HPLC and CE coupled to MS and MS–MS [22–27].

Whereas many different dyes in different chemical classes have been extensively studied by various MS techniques, most metallized dyes have not been studied by MS. One study [27] focused on a mordant dye and its chromium complex. However, no mass spectra were given. Although existing separation methods based on CE and HPLC are potentially suitable for the separation of metallized dyes, mass spectra of metallized dyes may be notably different from the spectra of other azo dyes. The scope of this work was to optimize conditions for CE–MS of anionic metallized dyes using a selection of typical reactive, direct, and acid dyes with up to four negative charges containing chromium, cobalt, or copper. Characteristic features of the mass spectra of these metallized dyes were compared with those of non-metallized dyes.

2. Experimental

2.1. Materials

Dyes were obtained from the manufacturers and were used without further purification. In all cases, dye structures were provided on condition that structures could not be used with commercial names. Dye structures are thus given without names (Fig. 1). Water was purified by reversed osmosis; acetonitrile and isopropanol were HPLC grade (Aldrich, Milwaukee, WI, USA), and ammonium acetate and ammonium hydroxide were ACS reagent grade (Fisher, Pittsburgh, PA, USA).

2.2. Capillary electrophoresis

All analyses were performed on a Beckman P/ACE 5500 capillary electrophoresis system (Beckman, Fullerton, CA, USA) with a diode-array detection (DAD) system. Untreated fused-silica capillaries were obtained from Supelco (Bellefonte, PA, USA). Capillaries with 110 cm×50 μm I.D. (20 cm to the diode-array detector) were used for CE–MS experiments, whereas 57 cm×50 μm I.D. capillaries (50 cm to detector) were used for CE alone. New capillaries were rinsed with buffer for 20 min. Between runs, capillaries were rinsed with buffer for 5 min. Acid and base rinses usually employed in CE were not used in CE–MS experiments because it took in excess of 20 min to completely remove any residues of the rinses. A buffer stock solution was prepared at a concentration of 0.1 *M* by titrating ammonium acetate solution with ammonium hydroxide to pH 9. The separation buffer was prepared by dilution with water and acetonitrile to yield a buffer with 40% acetonitrile and 5 m*M* ammonium acetate. Samples were introduced by pressure injection (0.5 p.s.i.; 1 p.s.i. = 6894.76 Pa) for 2 s (CE alone) and 15 s (CE–MS). The separation voltage was 30 kV. Diode-array detection was performed at 500 nm with a wide bandwidth of ±100 nm. Separation efficiencies were calculated as theoretical plates per column, *N*, as:

$$N = 5.54(t_R / w_{1/2})^2$$

where t_R is the migration time of a peak and $w_{1/2}$ is its width at half-height.

2.3. Mass spectrometry

A Fisons Platform II (Micromass, Manchester, UK) quadrupole mass spectrometer, fitted with an electrospray source and a CE probe, was operated in the negative ion mode. The CE probe consisted of a triaxial arrangement with the CE capillary surrounded by a stainless steel capillary supplying the sheath liquid, and another stainless steel capillary supplying the sheath gas. The sheath liquid (isopropanol–water, 80:20) was supplied by an Isco 100D syringe pump (Lincoln, NE, USA) at a flow-rate of 2 μL/min. Sheath and drying gases were both industrial grade nitrogen at flow-rates of 20 and 50 L/h. The source temperature was maintained at 80°C.

The electrospray voltage optimized between −3 and −3.5 kV, resulting in an overall separation voltage of −33 to −33.5 kV, the HV lens was set to 0.1 kV, the skimmer lens offset was 5 V, and the

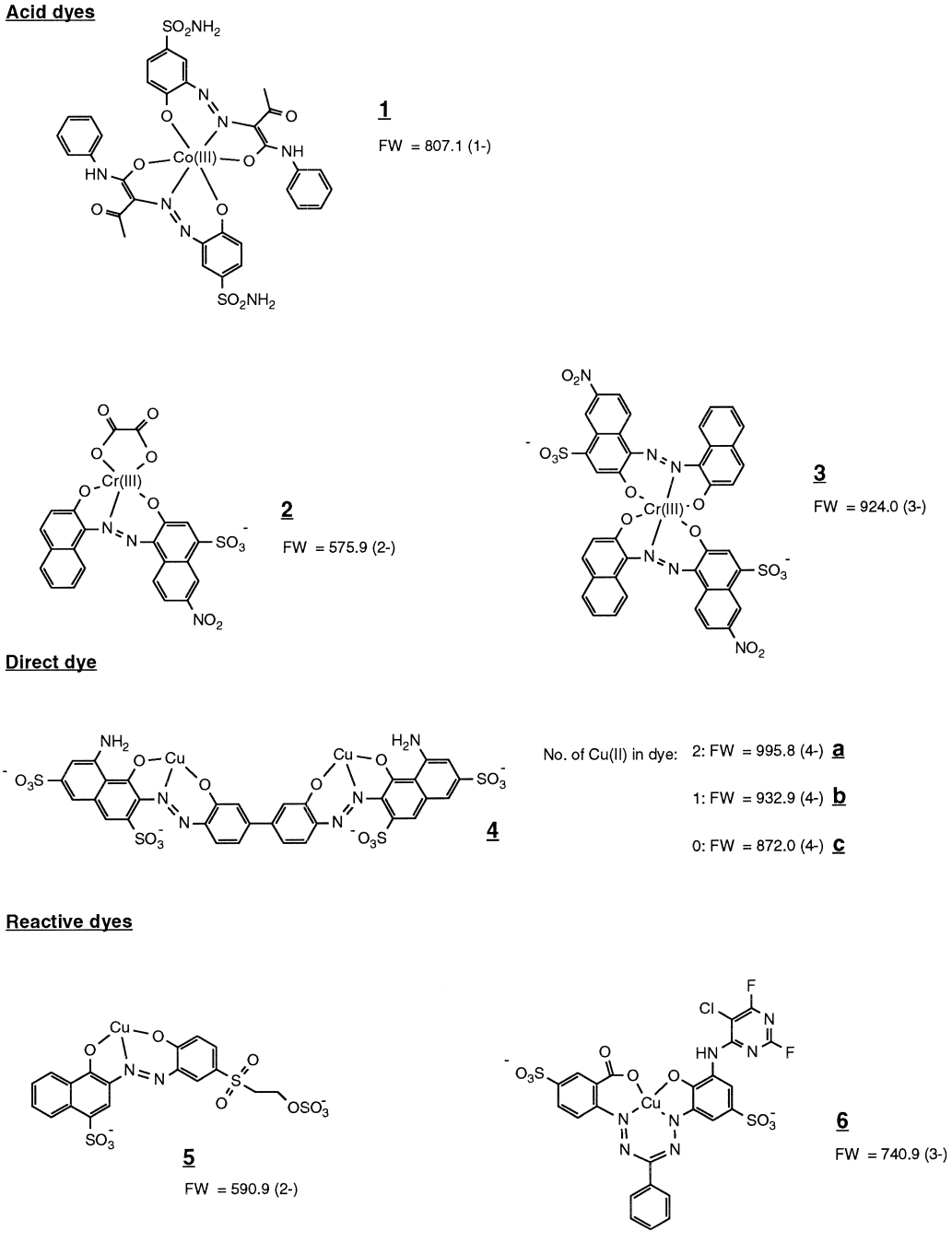

Fig. 1. Structures of anionic dyes used in this study. Monoisotopic molecular masses (Fw) and charge in neutral solution (in parentheses) are listed for each dye.

Table 1
Cone voltage settings used for the different dyes

Dye[a]	Cone voltage for little to no fragmentation (V)	Cone voltage range for moderate fragmentation (V)
1	15–60	60–120
2	15–20	20–60
3	15–60	–[b]
4	15–20	20–30
5	15–20	20–40
6	15–20	20–40

[a] Numbers refer to dye numbers in Fig. 1.
[b] No fragments observed at any voltage.

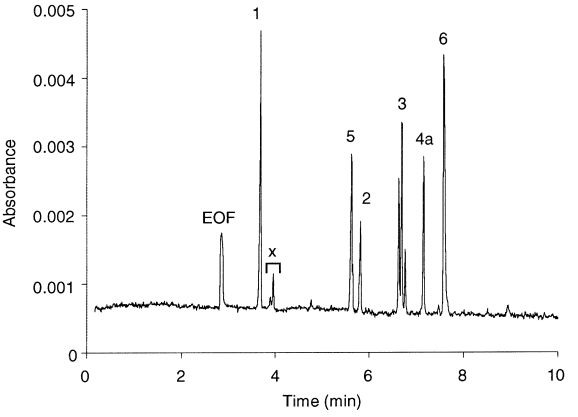

Fig. 2. Separation of a dye mixture by CE with diode-array detection. 100 pg of each dye was injected. Peak numbers refer to dye numbers in Fig. 1, x refers to impurities in dye **5**.

multiplier was set to 650 V. High and low mass resolutions were set to 14.5, and the ion energy was set to 1, which provided approximately unit mass resolution. The cone voltage, which influences the fragmentation of analyte ions in the source, was set so that either sensitivity was maximized (very little fragmentation) or that moderate fragmentation was obtained (Table 1). During injection, the electrospray voltage was set to 0 kV to avoid discrimination of ions entering the capillary. The mass spectrometer was calibrated in the negative ion mode using sodium iodide in 80% isopropanol.

The relative position of the three coaxial capillaries at the probe tip was critical for obtaining a stable signal. Optimal conditions were achieved with the fused-silica capillary protruding 0.2 mm and the liquid sheath capillary protruding 0.5 mm. The fused-silica capillary was tapered at the tip before installation according to the procedure described by Kirby et al. [28] by subsequently sanding with 1200, 3600, and 6000 mesh sanding paper. Progress of the procedure and symmetry of the tapered tip were frequently checked under a microscope.

3. Results and discussion

3.1. CE separation

In previous studies, acidic dyes were successfully separated using buffers at pH between 8 and 10 containing up to 50% acetonitrile [13,14,29,30]. In this study, using an ammonium acetate buffer (pH 9) with 40% acetonitrile, excellent separation efficiencies were achieved for all dyes with up to 360 000 theoretical plates per column (peak 4a, Fig. 2). All six dyes were baseline separated within 8 min. Sharp peaks for all dyes and the absence of peaks for the metal-free dyes (ligands) indicate that negligible metal exchange occurs over the course of the separation. The peak marked EOF (electroosmotic flow) originates from the elution of neutral dye impurities; no neutral marker was added to the samples.

The copper azo dye **5** is a vinylsulfone reactive dye. In a dyebath, under alkaline conditions, the sulfato group is readily released to yield the vinylsulfone. The small peaks marked by *x* (Fig. 2) correspond to the vinylsulfone and to a water adduct of the vinylsulfone, that is both precursor of the sulfato-form of the dye and a side-product that is formed in the dyebath at high pH and temperature [31,32]. Both compounds were present in the commercial dye formulation in small amounts. As is evident from Fig. 2, the peak for dye **5** has a small shoulder that is also visible when the copper-free form is analyzed (data not shown). This indicates that the dye contains an impurity that is structurally very similar to (possibly an isomer of) the dye, which is supported by the fact that both exhibit the same molecular mass and both form a copper complex.

The 2:1 (ligand:metal) chromium dye **3** (Fig. 2) shows three peaks with a relative abundance of roughly 2:3:1. This is likely due to three isomeric

forms where the chromium is bound to either one of the two nitrogens of the azo group. This isomerism, also referred to as N_α:N_β isomerism, was previously described for chromium dyes [33]. Isomerization between the three forms is apparently slow enough to allow for a separation into three sharp peaks by CE.

Separation of copper-free (0:1), half copperized (1:1), and fully copperized (2:1) dye **4** can be performed using the same conditions (Fig. 3). Copper exchange between copperized and copper-free dye in aqueous solution at pH ~6 was used to form the half copperized dye. Because the dye is symmetric with respect to the two binding sites for copper, the half copperized dye only shows one peak. At neutral pH, Cu exchange is relatively fast ($t_{1/2} \approx 60$ min, data not shown). However, at the higher pH of the separation buffer (pH 9), copper exchange is slow enough to allow for an efficient separation of the different species by CE.

3.2. Optimization of the CE–MS coupling

Several parameters were crucial to achieving good signal stability and sensitivity in CE–MS, including the shape of the CE capillary in the interface, the relative position of the three capillaries in the coaxial arrangement, the flow-rate and type of liquid sheath, and the flow-rates of sheath and drying gas. The optimization of most of these parameters followed the guidelines given by Kirby et al. [28].

Tapering the tip of the fused-silica capillary strongly improved signal stability. Tapering was done with sanding paper of different mesh size and typically required less than 15 min for completion. The tapered tip was not particularly fragile, allowing the capillary to be handled in the same way a normal capillary would be handled during installation. The relative position of the three coaxial capillaries at the CE probe tip was also very critical for stable spray, although, with tapered capillaries, stable conditions were found much more easily than with non-tapered capillaries. Optimal conditions were usually obtained with the fused-silica capillary protruding 0.2 mm from the liquid sheath (LS) capillary and the LS capillary protruding 0.5 mm from the sheath gas capillary.

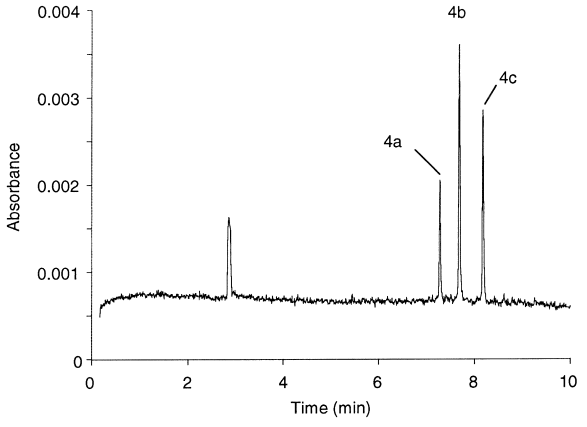

Fig. 3. Separation of a mixture of copperized, half copperized and uncopperized dye **4**. Total amount (a+b+c) injected: 400 pg.

The following sheath liquids were tested for this study: acetonitrile–water, methanol–water, and isopropanol–water. Acetonitrile–water mixtures tended to yield the strongest signals for the dyes. However, acetonitrile caused release of the polyimide coating from the fused-silica tubing, causing problems such as unstable spray and contamination of the source. As a result, when acetonitrile–water was used, the polyimide had to be stripped from the fused silica prior to installing the capillary, which made the capillary very sensitive and easy to break. In addition, the larger spacing between the fused-silica and the LS capillary resulting from the smaller outer diameter of the stripped fused silica caused the signal to become very unstable. Release of polyimide was not observed with methanol–water mixtures, which gave better signal stability, but produced much weaker signals for the dyes than acetonitrile–water mixtures. Isopropanol–water (80:20) provided the best compromise with excellent signal stability and good sensitivity. A LS flow-rate of 2 μL/min was sufficient to obtain a stable spray at minimal dilution highest sensitivity.

Sheath and drying gas flows were kept as low as possible to avoid problems with aspirating liquid through the CE capillary or pressurizing the source region [34]. Stable spray was achieved at a sheath gas flow-rate of 20 L/h and a drying gas flow-rate of 50 L/h. During injection, a pronounced suppression of highly charged dyes **3**, **4**, and **6** was observed with the electrospray voltage on, i.e. less negatively charged ions were injected preferentially, whereas highly charged ions were injected much less, if at all.

This kind of suppression is also observed with electrokinetic injection. Thus, to avoid preferential loss of highly charged dyes during and after injection, the electrospray voltage was always turned off during injection and buffer was injected for 2 s after injection of the sample, prior to switching on the electrospray and separation voltages.

Total ion current CE–MS chromatograms in the scan range m/z 200–600 did not usually give good signals for the dyes, due to intense background ions at m/z 227, 241, 253, and 255. Using reconstructed ion chromatograms (RIC), such as the example shown in Fig. 4, gave much better signals. The CE–MS chromatogram (Fig. 4) looks very similar to the offline CE–DAD chromatogram (Fig. 2). The separation efficiency is maintained, as is the relative order of migration. The migration times of the dyes are longer due to the longer capillary used for CE–MS. Good sensitivity ($S/N > 10$) for all dyes in scanning mode was obtained with 100 pg dye injected. Using single ion recording, 20 pg of all dyes except **4** were detected with $S/N > 10$ (Fig. 5). At such low dye concentrations, electrodispersion is virtually eliminated, so that very sharp peaks are obtained. Separation efficiencies of up to 500 000 plates/column could be achieved (peak 1, Fig. 5). The fact that no signals could be obtained with DAD using the same low dye concentrations indicates that

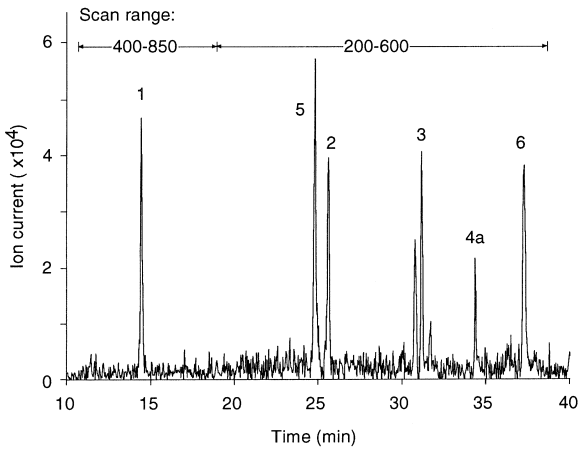

Fig. 4. Reconstructed ion current electropherogram of the same dye mixture as in Fig. 2 (100 pg of each dye injected). The scan range in the first 20 min was m/z 400–850 (m/z 807 extracted), in the last 20 min m/z 200–600 (m/z 295.5, 288, 308, 249, and 371 extracted); the background was subtracted.

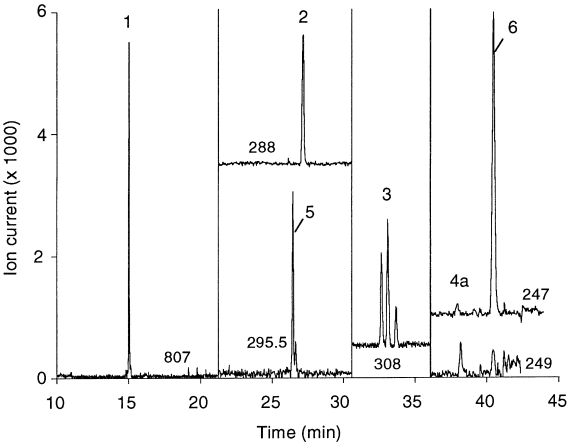

Fig. 5. Timed single ion recording of a diluted dye mixture (20 pg of each dye injected).

the sensitivity achieved by single ion recording MS greatly surpasses that of DAD. However, considering the small volumes of sample injected (~12 nL), the few picograms required for detection still correspond to rather high concentrations of several milligrams of dye per liter. Therefore, to be able to detect these dyes in environmental samples, an effective method for the preconcentration of dyes is required [30,35].

3.3. Mass spectra of individual dyes

The cobalt dye **1** (Fig. 1) has a calculated monoisotopic molecular mass of 807.1. The structure contains no ionizable groups. However, the dye has a nominal charge of -1 due to the four deprotonated hydroxy groups that form the complex with cobalt (III). The mass spectrum of this dye is shown in Fig. 6. The observed isotope distribution of 4:2:1 of the molecular ion corresponds well with the calculated distribution. Cobalt has only one natural isotope (M_r 58.9). When the voltage at the sampling cone is increased to >60 V, in-source fragmentation occurs, producing two fragments at m/z 432 and 433 (Fig. 6). The fragment at m/z 433 corresponds to the loss of one of the two ligands making up the dye complex. The fragment at 432 corresponds to the loss of a ligand and a hydrogen atom. When the cone voltage is increased further, only the fragment at m/z 432 is observed. It is worth noting that the fragmentation occurs without change of charge of the

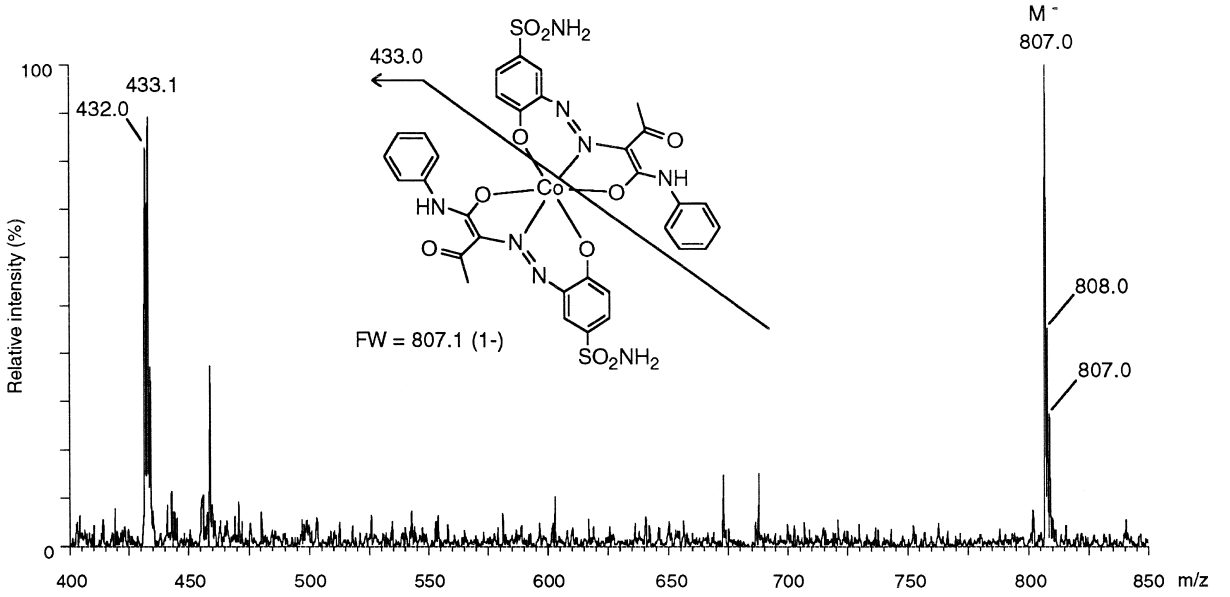

Fig. 6. Mass spectrum of dye **1** at a cone voltage of 90 V.

remaining complex, indicating that the ligand exchange reaction is accompanied by a reduction of Co(III) to Co(I).

The 1:1 chromium dye **2** has a monoisotopic molecular mass of 575.9. Two negative charges from the oxalate ligand and three negative charges from the azo dye ligand compensate the +3 oxidation state of chromium to yield an overall charge of −2. The mass spectrum of this dye is shown in Fig. 7. Only one ion at m/z 288 (m/z 576/2) is observed at

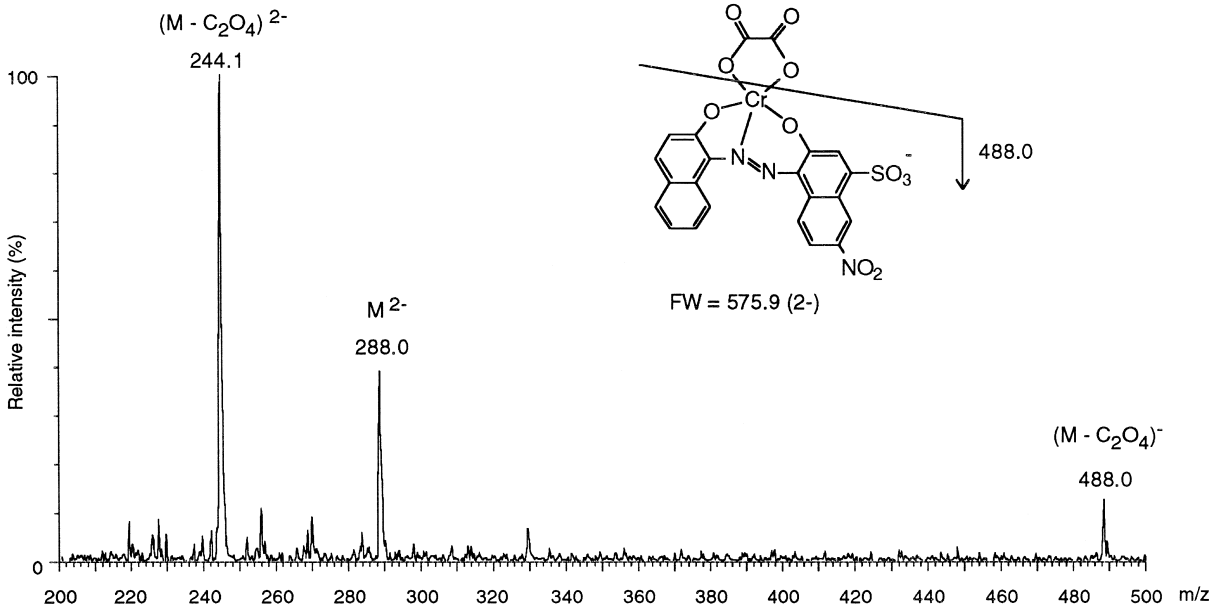

Fig. 7. Mass spectrum of dye **2** at a cone voltage of 30 V.

low cone voltage (data not shown). With increased cone voltage, fragment ions at m/z 244 and 488 are observed (Fig. 7). The ions correspond to $(M-C_2O_4)^{2-}$ and $(M-C_2O_4^-)^-$, or to loss of oxalate (or $2CO_2$) with an apparent reduction of Cr(III) to Cr(II) and Cr(I), respectively.

The 2:1 chromium dye **3** with a calculated monoisotopic molecular mass of 924 has a nominal charge of −3. The corresponding ion was evident in the mass spectrum at m/z 308 (Fig. 8). All three isomers (see above) exhibit the same mass spectrum. Some proton and sodium ion adducts $(M+H)^{2-}$ and $(M+Na)^{2-}$ were observed at m/z 462.5 and 473.5, respectively. No fragments in the M_r range of 50–500 were observed upon increase of the cone voltage up to 60 V. However, the intensity of the ions at m/z 308, 462.4, and 473.6 decreased steadily upon increase of cone voltage.

The doubly copperized diazo dye **4a** has a molecular mass of 995.8. The corresponding dyes containing only one copper or no copper have molecular masses of 932.9 and 872.0, respectively. All three compounds have a nominal charge of −4, yielding molecular ions at m/z 248.9, 233.2, and 218.0, respectively (Fig. 9). The mass spectra of all dyes also contain proton and sodium ion adducts of relatively low abundance. The abundance of these adducts is higher with lower copper content. The spectrum of the uncopperized dye even contains a small amount of $(M+2H^+)^{2-}$. In-source fragmentation of the fully copperized dye at a cone voltage of >20 V only resulted in the formation of a fragment ion due to loss of SO_3^- at m/z 305.3. The half copperized and the uncopperized dyes show the azo cleavage typical of azo dyes [18,19]. Azo cleavage leads to a fragment ion at m/z 164.9 for both dyes. Due to the symmetry of the molecule, cleavage of either azo group in the *uncopperized* dye leads to the same fragments. Thus, the abundance of the fragment ion at m/z 164.9 for the uncopperized dye is roughly twice that of the half copperized dye. The larger fragments from azo cleavage of the half copperized and the uncopperized dyes are m/z 301.8 and 271.2, respectively. No ions resulting from loss of copper were observed for either the half or fully copperized dye.

The copper azo dye **5** is a vinylsulfone reactive dye. The dye has a molecular mass of 590.9 Da and a nominal charge of −2 resulting from the sulfonate and sulfate groups, respectively. At low cone voltage

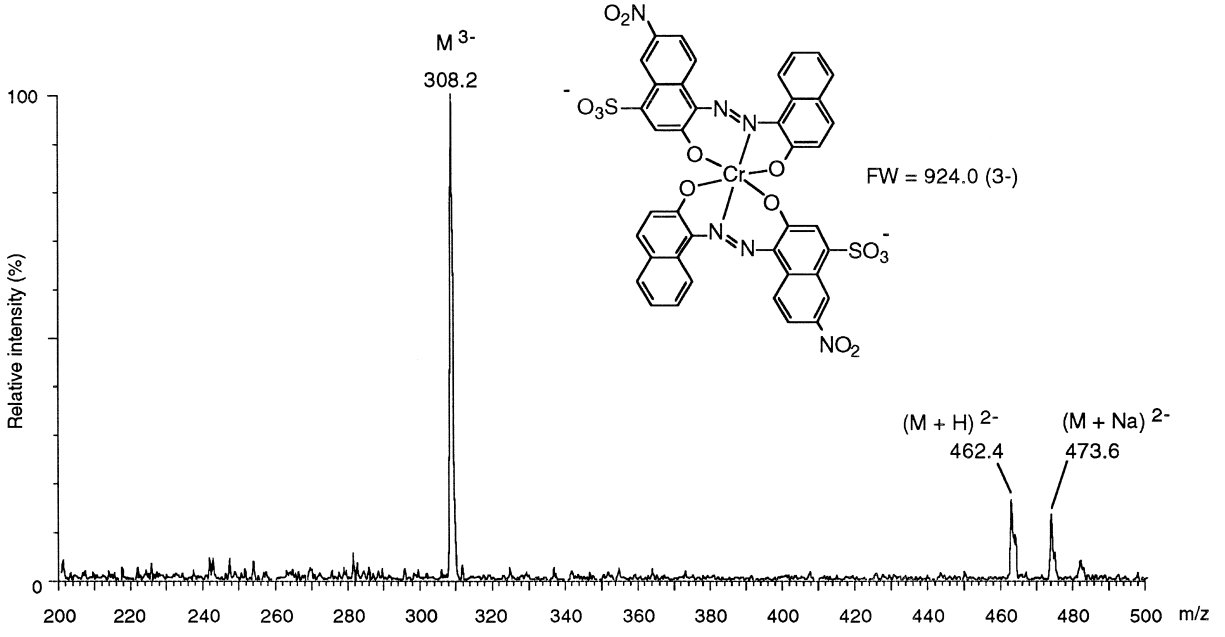

Fig. 8. Mass spectrum of dye **3** at a cone voltage of 30 V.

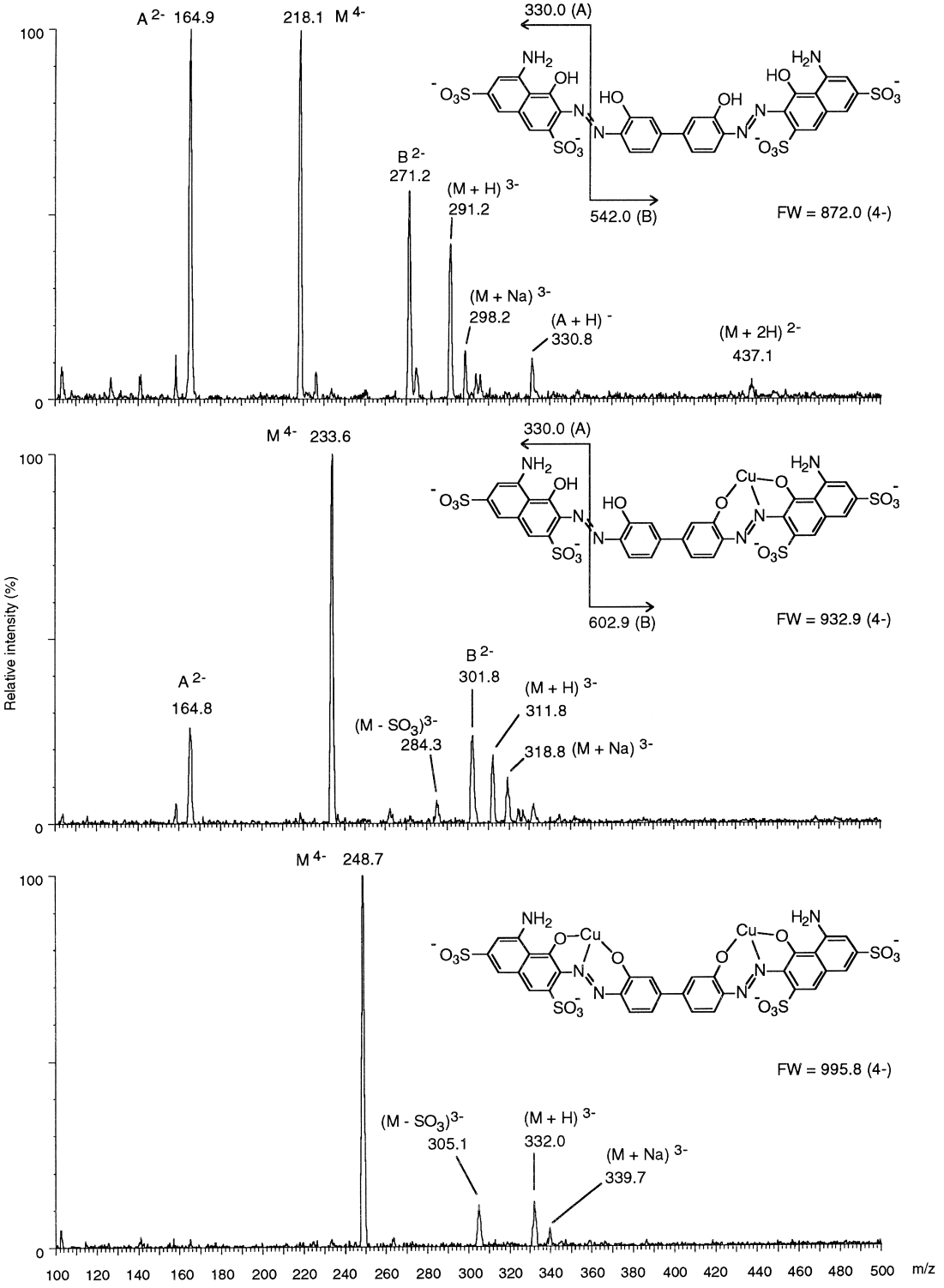

Fig. 9. Mass spectra of copperized, half copperized and uncopperized dye **4** at a cone voltage of 25 V.

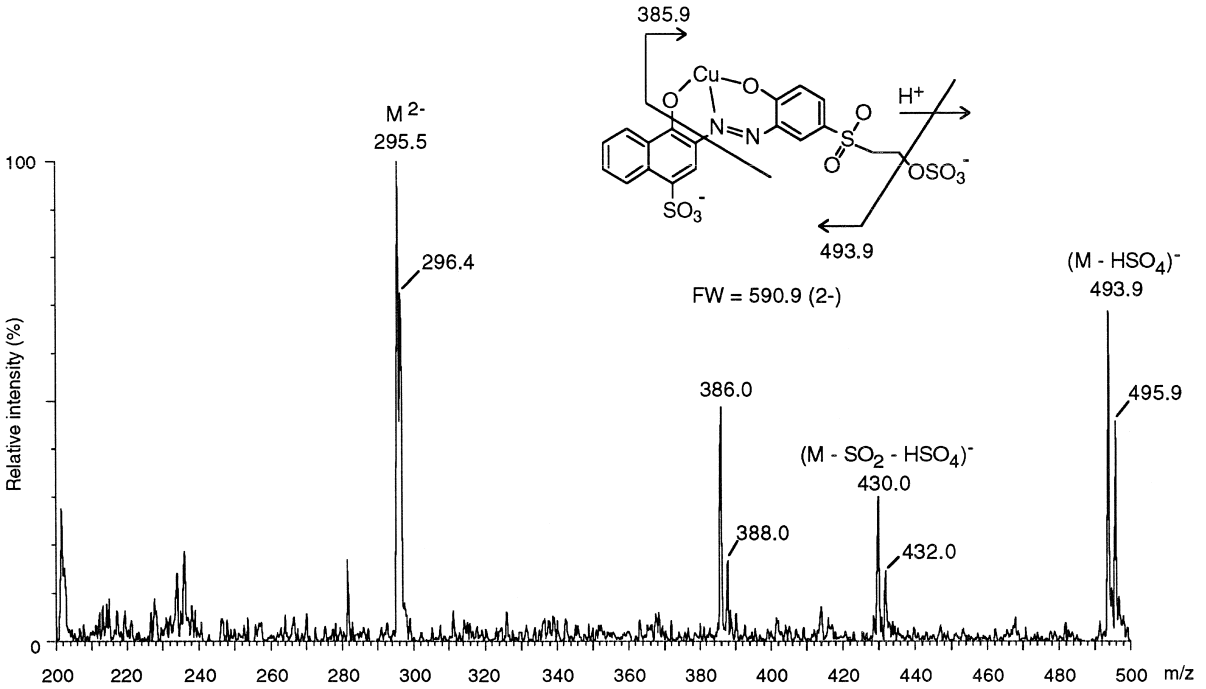

Fig. 10. Mass spectrum of dye **5** at a cone voltage of 40 V.

the molecular ion is observed at m/z 295.5 (Fig. 10). Copper has an isotopic distribution similar to chlorine with an isotope at M+2 with 44.5% relative abundance. This isotopic pattern can be easily resolved for doubly charged ions (Fig. 10). At higher cone voltage (40 V) several fragment ions are observed. Loss of HSO_4^- leads to m/z 494. The corresponding signal for hydrogen sulfate can be observed at m/z 97 (data not shown). Further loss of SO_2 leads to m/z 430. Both fragmentations have previously been reported for dyes in LSI-MS [21]. Another fragment at m/z 386 may be explained by loss of naphthalene sulfonate (Fig. 10). Loss of copper was not observed. However, at cone voltages >60 V a number of fragments were observed, the interpretation of which would probably require more systematic investigations using MS–MS.

The copper formazan dye **6** is a reactive dye of the chlorodifluoropyrimidine type. It has a molecular mass of 740.9 Da and a formal charge of −3, resulting from the displacement of three protons by Cu(II) in the ligand. A molecular ion at m/z 247.3 and proton and sodium ion adducts at m/z 371 and 382 were observed in the mass spectra (Fig. 11). The unusual isotopic distribution for the m/z 371 ion is caused by the combination of isotopes from chlorine, copper and sulfur, and it matches the calculated distribution. In-source fragmentation produced fragment ions due to loss of SO_3^- (m/z 331.1) and loss of chloride (m/z 353.1). Loss of copper could not be observed even at high cone voltage. However, as in the case of the other copper dyes, a number of small fragments were observed that could not easily be linked to the dye structure.

4. Conclusions

Coupling of CE and negative ion electrospray MS is a sensitive and selective method for the identification and characterization of negatively charged metallized dyes. Multiply charged dyes produced molecular ions with m/z equal to the mass divided by the number of charges. Proton and, to some extent, sodium ion adducts were also observed for dyes with more than two charges. Sodium ion

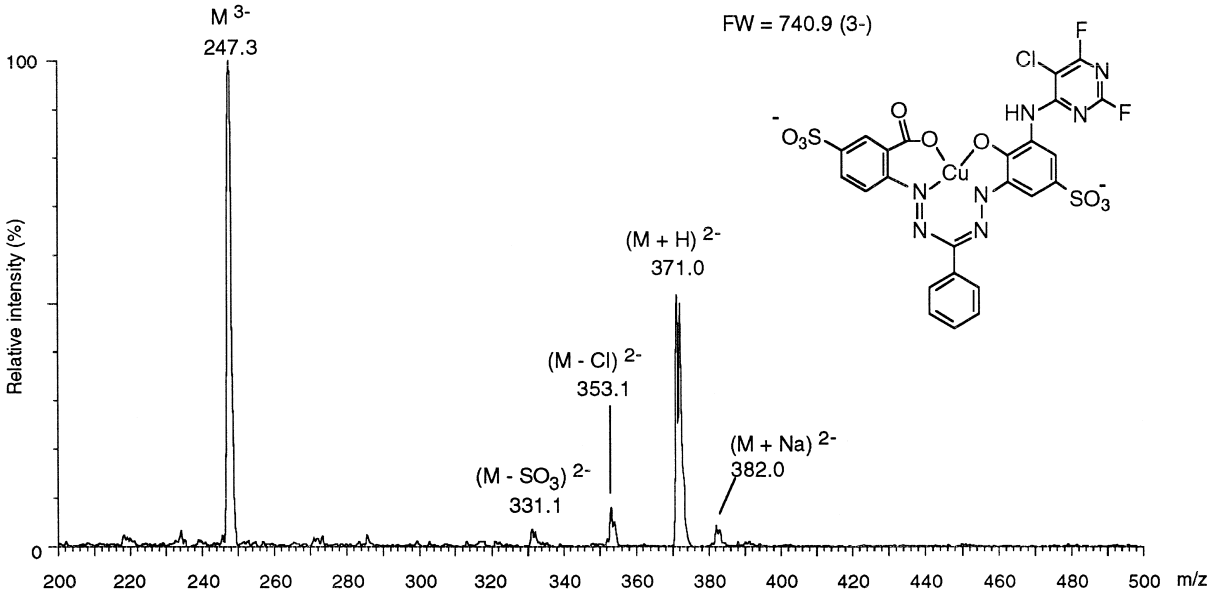

Fig. 11. Mass spectrum of dye **6** at a cone voltage of 30 V.

adducts were, however, less important than in FAB-MS or in direct infusion of dyes to electrospray MS, where the salt content of the solutions is typically rather high. Using low cone voltages (15–20 V), little or no fragmentation was observed and the molecular ion and small amounts of proton and sodium ion adducts were the only signals observed. These conditions provided the most sensitive detection.

In-source fragmentation of metallized dyes using cone voltages of 25–60 V, with one exception, was found to be similar to the fragmentation of non-metallized dyes. Loss of SO_3^- or SO_2 was observed for some sulfonated dyes. Loss of HSO_4^- was observed with the sulfato-form of a vinylsulfone dye. However, no cleavage of azo groups, as is otherwise very typical of azo dyes, was found in metallized azo dyes. Most likely the complexation with metals has a stabilizing effect on the azo groups. Loss of metal was not observed with any of the dyes. Only at very high cone voltages (high collision energies) did the molecules appear to break up completely.

The characteristic isotopic distribution of copper was found to be a very useful diagnostic tool both for the identification of the parent copperized dyes and for their fragments. For highly charged copperized dyes, the resolution of the quadrupole mass spectrometer was not adequate to resolve the isotopic distribution without sacrificing the sensitivity necessary for detection.

Despite the excellent sensitivity of CE–MS for negatively charged dyes, identification of these dyes in environmental samples requires rigorous sample preconcentration methods. In combination with solid-phase extraction, CE–MS is well suited for the identification of anionic dyes in textile wastewater [30]. Although demonstrated only for anionic metallized dyes, the analytical system presented here is also potentially suited for other aromatic anionic compounds used in the textile and paper industry.

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