

# Leather Dyes – Properties and Analysis

*Campbell Page<sup>1,\*</sup>, Jens Fennen<sup>1</sup>, Daniel Gagliardino<sup>2</sup>*

<sup>1</sup> TFL Leather Technology Ltd, Postfach 264, CH-4019 Basel, SWITZERLAND

<sup>2</sup> TFL Argentina S.A., Camino de la Costa Brava Km 6.5, Zarate, RA-2800 ARGENTINA

**Abstract:** The use of synthetic dyes to colour leather has a long tradition. Typically anionic acid dyes are used and this category consists of a number of chromophores which provide us with a wide range of colours and performance properties. For the tanner the chemistry and evaluation of dyes is often like a black box. But problems can arise when what appears to be commercially the same dye is found to perform differently on the leather. These variations are not well understood. With the introduction of the REACH Regulation in Europe there will be a need for the dye manufacturers to look more closely at the composition and structures of the dye molecules. Traditional methods of analysing dyes will be challenged and new techniques will be required. While HPLC now has come into routine use for dye analysis, one interesting relatively new development is the use of HPLC – MS. This can prove to be a very useful tool for determining the structural components present in a dye. The advantages and limitations of the analytical techniques used for typical leather dyes will be presented and explained.

**Key words:** leather; acid dyes; analysis; HPLC

## 1 Introduction

The synthetic dyes used to colour leather in the wet-end are traditionally the anionic, water-soluble, acid dyes. Other dye types such as direct, soluble sulfur and reactive are used but to a much lesser extent and mainly to achieve special colours or fastness properties<sup>1</sup>. To colour the substrate the dye molecule must have a chromophore that absorbs energy in the visible wavelengths (400 – 700 nm). The most important chromophore for organic colouring agents, including leather dyes, is the azo chromophore. That azo dyes are by far the largest group of leather dyes is important as the EU Regulation 1907/2006, commonly called REACH, contains restrictions forbidding the use of certain azo dyes which can split under reductive conditions to release aryl amines with carcinogenic or suspected carcinogenic properties. Although the number of azo dyes restricted is a very small number there is still a perception through misinformation that azo dyes are generally not allowed. Various publications azo leather dyes<sup>2,3</sup> and on this aspect of forbidden aryl amines<sup>4</sup>, including risk analyses of leather dyes have been published<sup>5</sup>.

By 2018 all leather dye substances manufactured or imported into the European Union (EU) will need to have completed a REACH registration process involving a lot of expensive analytical and toxicological testing. The traditional way to define dye composition is by using the Colour Index (C.I.) number system<sup>6</sup>. It is still a widely practised classification system in the leather dye houses and especially by those involved in purchasing, but colour experts know the strengths and weaknesses of this system. The generalisations in the C.I. numbering will come under more scrutiny now that new regulations such as REACH start to undertake rigorous testing of the chemical composition.

However, for the tannery the key elements required from wet-end dyes are:

- Consistence for reproducible production batches;
- Quality to meet the required colour specification;
- Flexibility to apply to various types of leather;
- Economical cost of dyes.

---

\* Corresponding author. E-mail: [campbell.page@tfl.com](mailto:campbell.page@tfl.com)

How can the dye supplier bring together the properties of the tanner's requirements and the manufacture of dyes that comply with the REACH restrictions?

There will be a need for the dye manufacturers to look closer at the composition and structure of the dye molecules. The traditional methods used to analyse dyes will be challenged and the use of new techniques required. Presented here are some of the developments and their relevance for the tannery dyehouse.

## 2 Consistency and quality in the manufacturing process of an azo dye

To better understand which challenges a chemist manufacturing leather dyes is facing, it is worth taking a short look at some of the critical steps in the manufacturing process.

In Fig. 1, a schematic overview is presented when resorcinol (IUPAC name: benzene-1,3-diol) reacts with the active diazonium salt to form an azo chromophore. This is a typical step in the production of many of the large volume brown dyes used for leather.

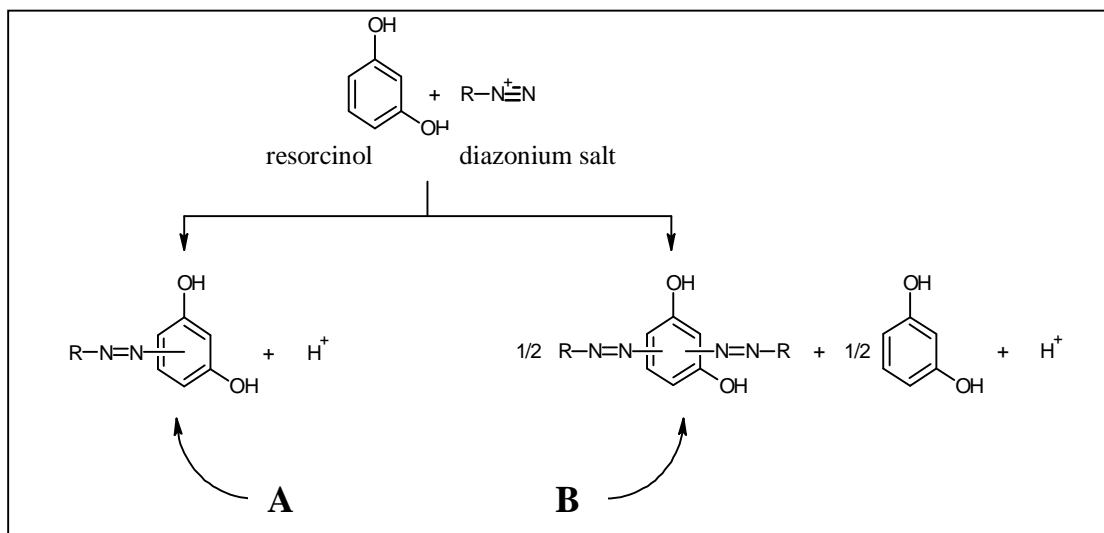


Fig. 1 Schematic overview of the reaction of the formation of azo dyes from resorcinol

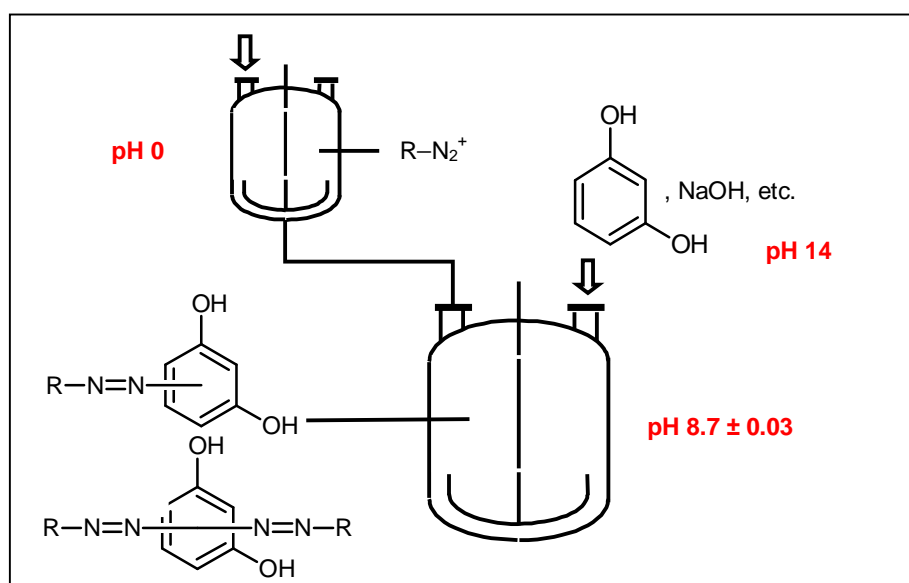
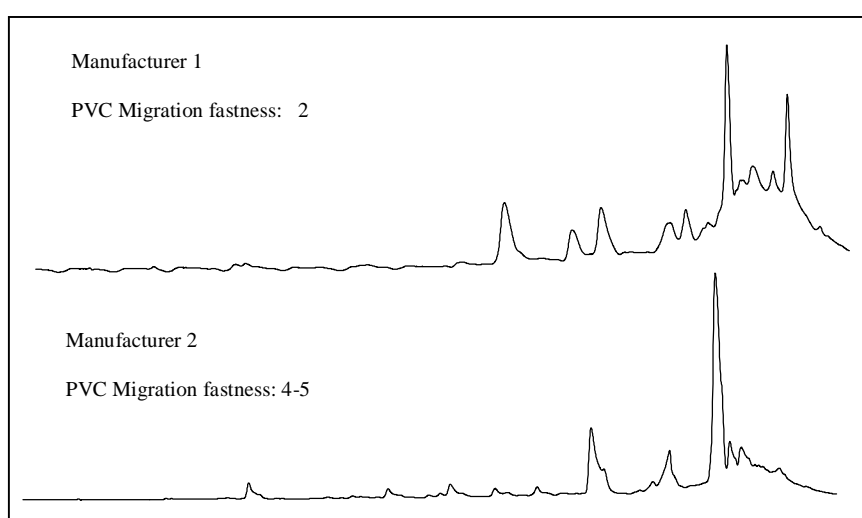


Fig. 2 pH differences of the reaction components when making azo dyes from resorcinol

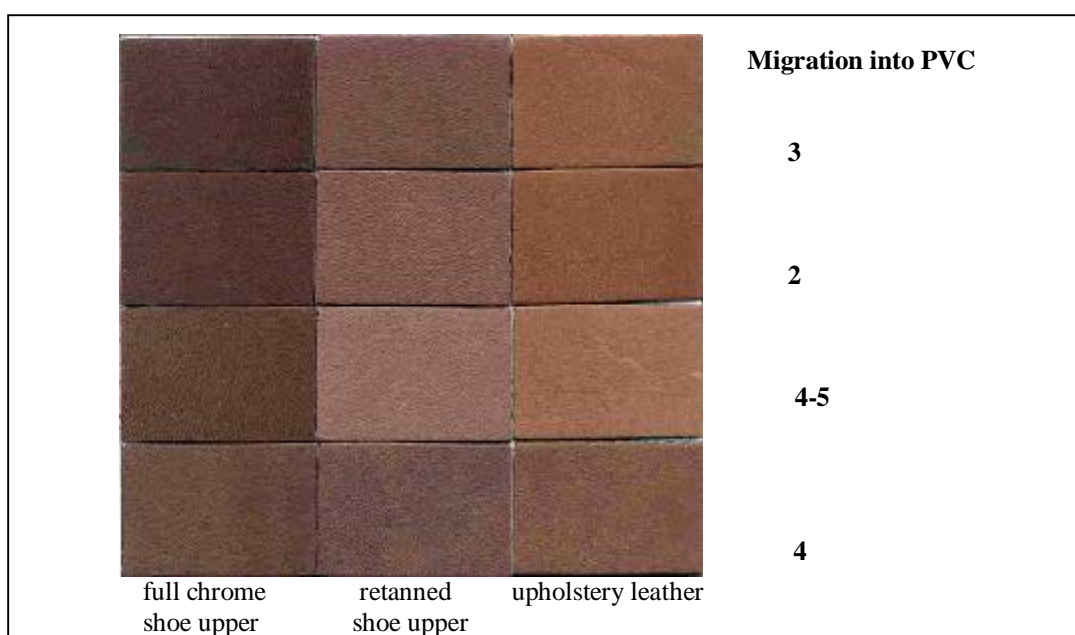
The two possible reaction pathways, A or B, shown in Fig. 1, depend on many factors, such as temperature, pH, concentration, reaction vessel geometry, stirring speed, etc., so it is obvious that it will be difficult for 2 manufacturers to produce exactly the same dyestuff. Consider, for example, just the pH aspect; Fig. 2 shows the pH comparison between the 2 reaction components (diazonium salt at pH 0 and resorcinol at pH 14) and how precise the pH of the end reaction mass (pH 8.7) must be maintained.

Considering one is combining the reaction components at the extreme pH values of pH 0 and pH 14, it is clear that at a manufacturing scale to maintain this level of precision of pH ( $8,7 \pm 0.03$  pH units) is very difficult. For many manufacturers this means the result is a variation in the composition and colour from one production batch to the next batch.

How does this variation show up? We can take an example of Acid Brown 75, a large volume brown azo dye based on resorcinol. If we run the HPLC chromatogram, it shows the clear variation in the components in the dye composition, see Fig. 3.



**Fig. 3 HPLC chromatograms of 2 different samples of Acid Brown 75**

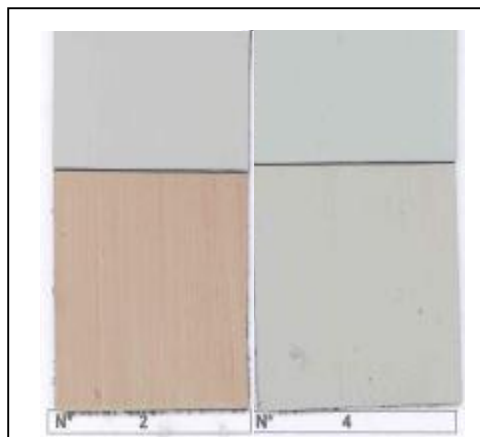


**Fig. 4 Leather dyeings with Acid Brown 75 from 4 different sources**

But if the colour on the leather is the same then this difference does not matter? The extra components in the reaction mix do have an influence on the leather colour and the migration fastness of the colour.

In Fig. 4, the variation in colour is clear and corresponds to the amount of side products from the reaction process. Interestingly, one finds that the fuller, nicer brown colours are those with the additional components but with a poorer migration into PVC. By contrast, the manufacturing process optimised to minimise the side products, results in an empty, redder colour. Since the side products are typically yellowish in colour this is to be expected.

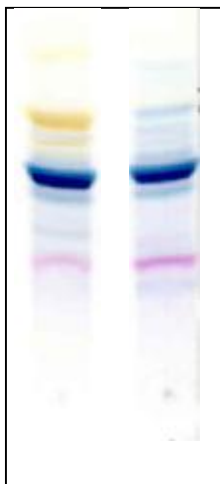
An additional colour migration technique introduced in the last years is the propensity of the dye to migrate into the finish coat. The introduction of water-based finish coats containing low volatility solvents and the resultant slower drying process has lead to a re-evaluation of some of the dyes used in automotive leathers. To check the tendency of a colour to migrate, the leather is dyed and afterwards a light grey finish coat is applied on top. Part of the coated leather is exposed to 90% relative humidity and 70°C for 16h and the resultant colour change is compared with the original unexposed piece<sup>7</sup>. As shown in Fig. 5 some dyes with side products from the reaction show a considerable discoloration and are not suitable for automotive use.



**Fig. 5 Results of a test for colour migration into a finish coat**

### **3 Analytical techniques for leather dyes**

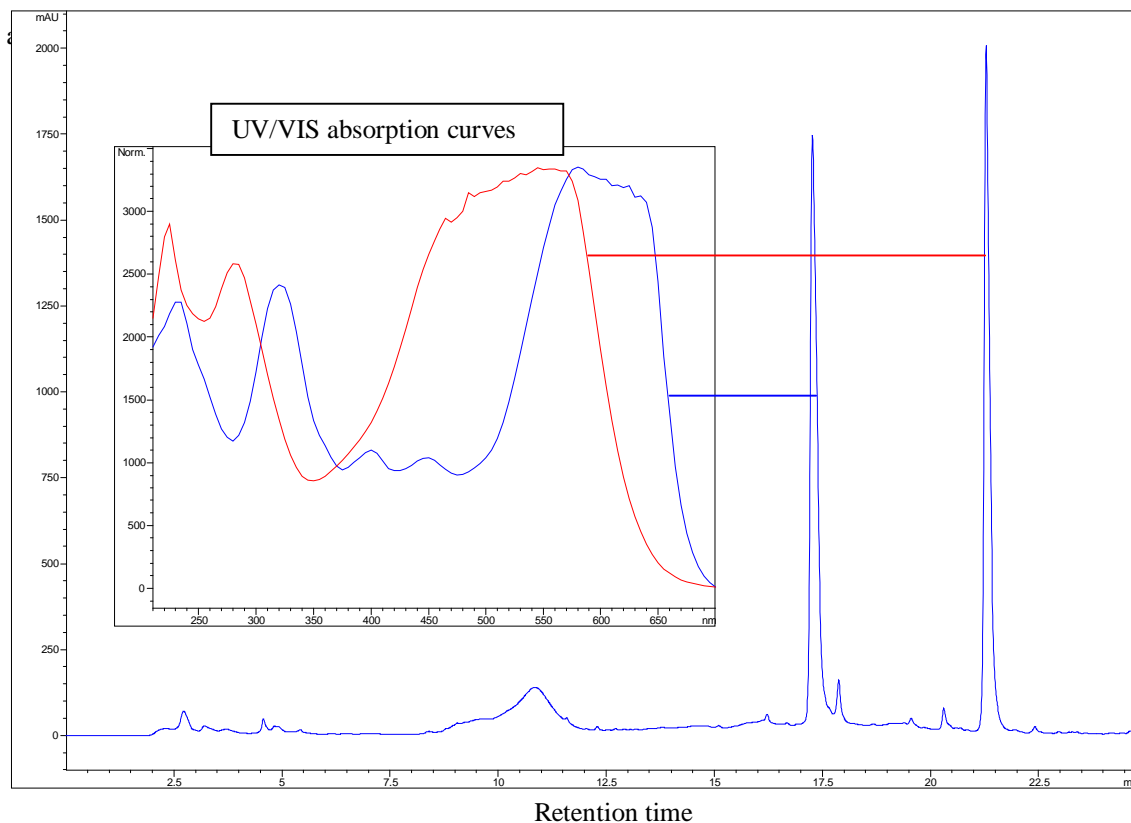
REACH will require those involved in manufacturing dyes to have even a better knowledge of the dyes and side products, so there will be an increased need to use the best available analytical techniques for leather dyes. Many analyses are carried out using thin layer chromatography (TLC) to separate and analyse dyes, see Fig. 6 for an example. It is a simple, relatively quick and economical method. It gives qualitative information and for identification of the dye component it requires a known reference, but the visual colour bands often help in identifying dyes in mixtures.



**Fig. 6 TLC results of 2 dye mixtures with the same main component**

In the last 20 years the liquid chromatographic procedure using HPLC equipment with a UV/VIS detector has taken over as the preferred method of analysis for dyes, see Fig. 7. Today the HPLC is used extensively world-wide and a lot of experience in analysing leather dyes has been built-up using this technique. It can deliver results fast and the equipment is available at a reasonable cost. Again, to identify a dye component a known reference is required for comparison.

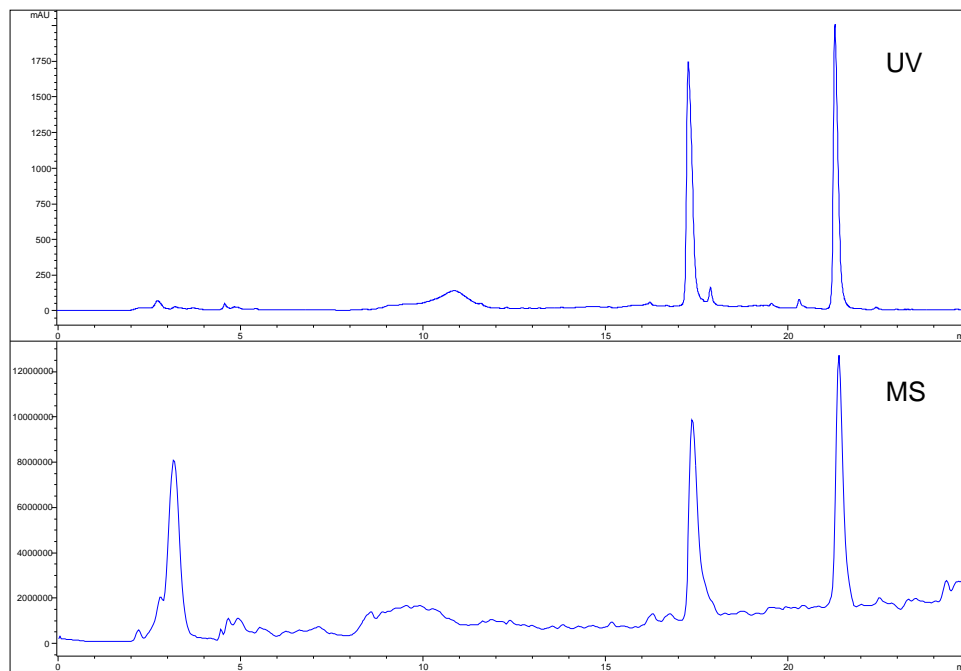
With an appropriate detector it is possible to measure and save a UV/VIS spectrum for each peak of the chromatogram during elution. This spectrum can be used to identify the substance by comparison with a database of pre-recorded UV/VIS spectra for reference dyes.



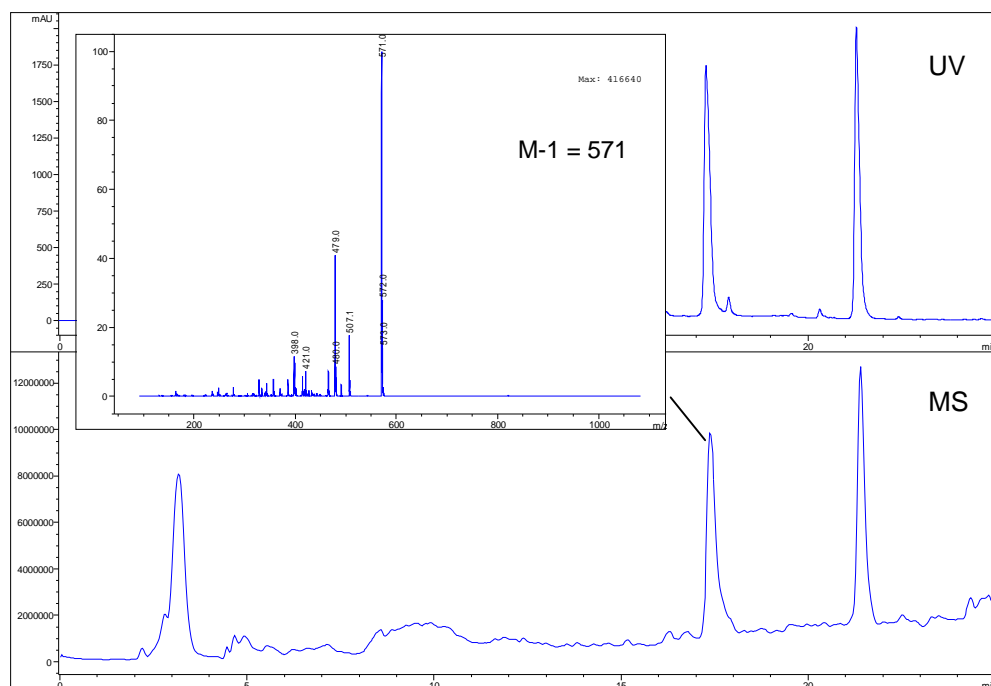
**Fig. 7 HPLC chromatogram of 2 dyes, with UV detection at 254nm  
As insert, the UV/VIS curves of the 2 peaks.**

A more recent extension of the HPLC technique has been to use mass spectrometry as the detector, see Fig. 8. This is a more expensive analytical technique and requires experienced operators to get the full benefit of the results. However, it does allow the possibility of the identification of substances without having to directly compare it with a known reference.

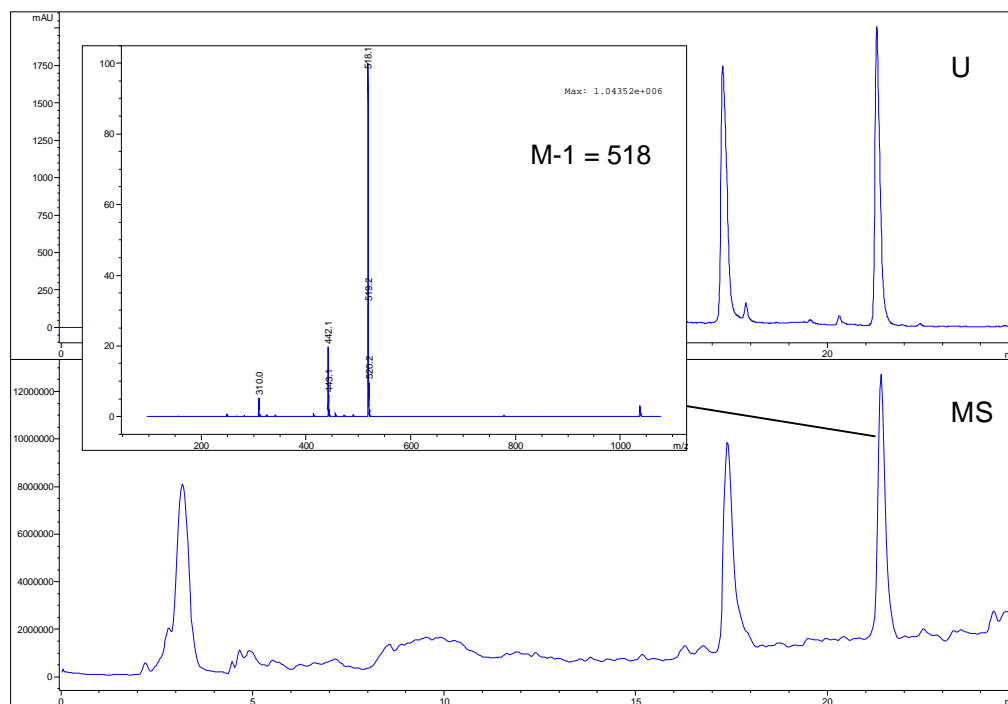
As shown in Fig. 8, provided the same eluent solvents can be used, the HPLC chromatogram obtained with a MS detector can be similar to that obtained with the UV/VIS detector, especially for those substances which absorb in the UV/VIS region.



**Fig. 8** HPLC chromatogram of the same dye with a UV detector (above) and MS detector (below)



**Fig. 9a** HPLC chromatogram with MS identification of the first peak



**Fig. 9b HPLC chromatogram with MS identification of the second peak**

However, the real analytical impact of the technique comes when the molecular fragments of the MS information are interpreted. In Fig. 9a and 9b the molecular fragments of the MS detector enable the molecular mass of the 2 main peaks to be readily identified. With help of MS data bases the chemical formula of the fragments can be determined.

The HPLC-MS technique may look to be an ideal method for analysing leather dyes. However, in practise there are limitations and the HPLC-MS equipment requires a high amount of skilled maintenance to keep it operational. The ionisation and resultant fragmentation of the molecules requires relatively volatile chemicals otherwise the ions are not detected. It can be that the eluent system used with the traditional HPLC analysis may need to be modified for use with the HPLC-MS. This means the direct use existing HPLC data bases and peak retention times may not be possible as a starting point for analyses in the HPLC-MS mode.

If the dye molecule is relatively stable then a much higher fragmentation voltage is needed to form the ions. If the molecular mass is too high (more than 1000 g/mole), either from large molecules or from aggregation of acid dyes like Acid Black 210, then it is not possible to detect the fragments.

Other aspects that must be considered with HPLC-MS; for example, when solvent gradients use high concentrations of acetonitrile it is not possible to determine fragment masses as ions cannot be formed in pure acetonitrile. Also the pH of the solvent mix has a very considerable impact on the retention time and the ionisation of the peaks.

Despite the limitations, there is no doubt that the HPLC-MS technique will be developed further and used in the determination of the chemical components in dye substances for the REACH registration process.

#### 4 Conclusions

Many homogeneous leather dyes consist of several components due to side reactions during the manufacturing process. To be able to identify these components for the REACH registration process will require skilled analytical experts and techniques.

The commonly used analytical techniques to date have typically relied on comparing samples with those from known reference samples. To be able to identify components where no references are available will require the use of relatively new analytical techniques for dyes, such as HPLC-MS. Here through fragmentation of the dye molecule it is possible using the molecular masses of the individual fragments to determine the dye composition.

## References

- [1] C. T. Page; C. Gabagnou; A. Tidei. *Leather International*, 1997, 199(4664): 37-40.
- [2] A. Püntener. *J. Soc. Leath. Tech. Chem.*, 1991, 75: 48-51.
- [3] A. Püntener. "Leather Dyes" in *Industrial Dyes: Chemistry, Properties, Applications*, edited by K. Hunger, Wiley-VCH Verlag, 2003.
- [4] C. T. Page; J. Fennen. *J. Soc. Leath. Tech. Chem.*, 1998, 82: 75-7.
- [5] A. Püntener. *J. Soc. Leath. Tech. Chem.*, 1998, 82: 1-4.
- [6] *Colour Index International*, available On-line from the Society of Dyers and Colourists / American Association of Textile Chemists and Colorists.
- [7] Test procedure TFL/D-018. (TFL Leather Technology Ltd, Postfach 264, CH-4019 Basel, Switzerland.)