Applications of the ion chromatography in the leather sector. Part1

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1. Abstract

Chromatographic methods of ion exchange, with direct and indirect ultraviolet detection, have been developed for the determination of the main anions (chloride, nitrate, sulphate, formate, phosphate…) which are of interest in the leather industry. The direct UV detection does not allow the analysis of analytes that do not absorb in the ultraviolet, as in the case of chloride and sulphate. For this reason, the indirect detection (suitable for all the anions) has been also used. The used mobile phases are potassium biphthalate (indirect detection) and sodium sulphate (direct detection).
The methods have been successfully applied to the analysis of different samples of chemicals and leathers. Anionic impurities in dyes, tannins extracts and naphthalenesulfonic dispersants have been determined. Likewise, commercial formic acids have been quantified and the anionic content of twelve hide samples has been analyzed.
The efficiency of the extraction process of anions from the leather in accordance with the UNE-EN ISO 4098: 2006 (IUC6) Standard was checked. It was confirmed that the shaking rate must be increased up to 170 ± 10 rpm. It was also concluded that a single extraction is not enough to quantify the total anion content in leather, and in some cases, multiple extractions are recommended. It has been observed that, in some complex samples of leather, the formate anion is difficult to quantify. This is due to that formate and phosphate anions have similar retention times in the chromatography with indirect detection. A method that solves this problem is proposed.

Keywords: chromatography, ultraviolet detection, leather dyeing, naphtalenesulfonic products.

1-Introducction

Quality control in leather manufacture needs appropriate analytical methods to examine the raw materials, to verify production processes, to check emissions and their treatments, and ultimately, to ensure the quality of the final product [1].
A part of the chemicals used in the different processes of leather manufacture are absorbed by the hides, while the remainder passes to wastewater. Many of these chemicals have an anionic component.
The laboratories of the leather sector need to analyze anionic species in different samples such as wastewater, residual baths of different manufacturing processes, tanned hides and chemicals. In addition, the high salinity of tannery discharges is one of the main environmental problems in this industry.
Currently, the ion chromatography is the best technique for the analysis of ions since it allows us to detect and quantify ions simultaneously in an effective, fast and reproducible manner [2-5]. However, up to now, the anions of interest in the leather industry have been analyzed by classical analytical methods or by instrumental methods, which determine individual ions and are different from the chromatographic methods. Traditional methods have certain disadvantages: they are slower and less accurate, they involve a higher consumption of reagents, they present more matrix interferences and they produce a higher amount of laboratory wastes. Although there are colorimetric or potentiometric methods, redox titrations, etc ... for determining anions in an individual manner, ion chromatography provides the ability to determine quickly, reliable, robust and simultaneously the different anions in a sample.
Other sectors use the ionic liquid chromatography with conductometric detector for ion analysis. Most laboratories in the leather sector also have liquid chromatograph, although with ultraviolet detector (UV), because of its high versatility. The liquid chromatograph with ultraviolet detector is a part of the standard equipment in an analysis laboratory of the leather sector (analysis of formaldehyde, fungicides as TCMTB [6, 7, 8]). But these laboratories do not use chromatography for analysis of ions because

the direct UV detection does not permit direct analysis of non-absorbent ions, such as chloride or sulphate. It would require a financial investment in the acquisition of a conductimetric detector.

This work presents ion chromatographic methodology with ultraviolet detector to analyze absorbent and non-adsorbent anions in the ultraviolet region. Anionic impurities in chemicals (dyes, naphthalenesulfonic, mimosa) are determined and the anionic content of hides is quantified. Two research lines, which differ in the detection system, direct UV detection and indirect UV detection, have been carried out.

a) Direct Ultraviolet Detection

UV detectors directly measure the absorbance of analytes having a chromophore group. The ion chromatography with direct ultraviolet detection allows determining absorbent anions (such as nitrate, nitrite and bromide) and slightly absorbents (formate). A non absorbent mobile phase is used and when the analyte elutes an increase in absorbance is produced, which is evidenced by a peak in the chomatogram. In this work, the photodiode array detector (PDA) is used. This detector provides three-dimensional information, i.e. values of absorbance, wavelength and time. This detector allows simultaneous measurement at all wavelengths and provides full spectra for each length. This enables to detect each analyte at the optimum wavelength since, in each case, the most suitable detection conditions can be selected [9,10].

The most important advantage of the direct detection is that the authenticity of an anion can be confirmed by comparing the UV-VIS spectrum of a standard with that of the sample.

b) Indirect Ultraviolet Detection

The indirect ultraviolet detection is suitable for anions that do not absorb in the UV-VIS region (chloride, sulphate, phosphate, fluoride) although also allows to analyze absorbent anions. It is based on the use of eluents having a constant and intense absorption in the ultraviolet region. In this way, during the chromatographic process, the UV detector measures the decrease in the background absorption caused by the non absorbent analytes. The indirect ultraviolet detection allows using the same equipment that the one employed for the direct detection, being the change of the mobile phase the only difference [11-15].

The indirect ultraviolet detection provides negative chromatographic peaks that are not integrated by the software. The chromatograph should be programmed in order to invert the detector response and present a graph with positive peaks. Otherwise, the obtained negative peaks would require a manual integration of the areas. The inversion is solved by the software of capture of 2D chromatograms. The detector response is multiplied by a factor of (-1) at the working wavelength. Figures 1 and 2 show chromatograms of a standard before and after the inversion, respectively.

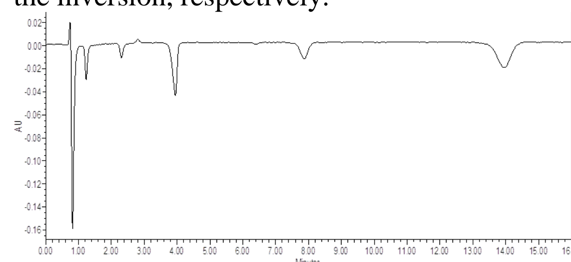

Figure 1. Chromatogram of a standard of inorganic anions (nitrite, nitrate and sulphate) before inverting the detector response

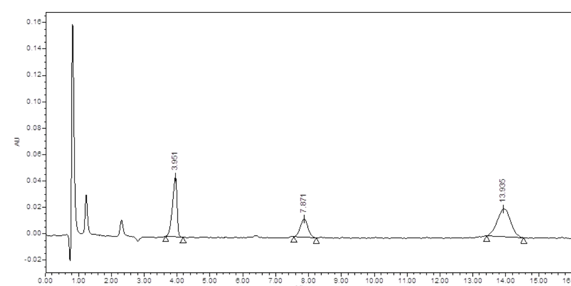

Figure 2. Chromatogram of a standard of inorganic anions (nitrite, nitrate and sulphate) after inverting the detector response

In conclusion, a new way towards the application of ion chromatography in salinity control and analysis of ions in the tanning industry is opened.

This will mean a progress in the analysis possibilities of a laboratory of the leather sector since salinity may be determined by chromatography in a single analysis without the need for an investment in a conductimetric detector. By only changing the column, a better performance will be obtained from the chromatographic technique since the necessary equipment in ion chromatography for the determination of anions is a normal liquid chromatograph with an anionic column.

2. Experimental

2.1. Materials

Samples
The following samples have been used in this work: two brown dyes for drumming (commercialized in the Spanish market); two naphthalensulfonic; two mimosa extracts; five commercial formic acids and twelve leather samples.
Equipment
High Performance Liquid Chromatograph (HPLC) equipped with automatic injector and UV detector (Waters ALLIANCE 2695 Module equipped with PhotoDiode Array (PDA) 2996 detector).
UV – VIS Spectrophotometer Lambda 25 (Perkin-Elmer Inc, EE.UU). (For the determination of phosphates in complex leather samples)

2.2. Methods

Ultrapure water (Milli-Q quality) must be used in all the methods.
Determination of anions in dyes and naphthalenesulfonics (indirect detection)

1 g of sample was accurately weighed , dissolved and made up with water in a volumetric flask of 1L.
An SPE (solid phase extraction) cartridge was activated by eluting slowly therethrough 5 mL of acetonitrile and then 15 mL of water.
An aliquot of 5 mL of product solution was passed through the activated SPE cartridge followed by 15 mL of water. The eluate was collected in a volumetric flask of 25 ml and made up with water for further chromatographic analysis
An aliquot of the extract was filtered through a 0,45 μm syringe filter and transferred to a sample vial and injected to the HPLC system.

The following chromatographic conditions were used:
-Flux: 0.9 mL/min Flux:
-Mobile phase: 1mM potassium biphthalate with 8% of acetonitrile, pH 6.19± 0.1
-Temperature: 30± 1 ° C
-Injection volume: 20 μL
-Detection: Indirect with PhotoDiode Array (PDA) detector and recovery of the chromatogram at 260 nm. Inversion of the negative peaks by multiplying by a factor of (-1)

The retention times (minutes) in the above conditions are shown in Table 1.

Los tiempos de retención (minutos) en las anteriores condiciones se muestran en la Tabla 1.

Anion	Retention times (minutes)
	Indirect detection
Formate	2.9-3.0
Phosphate	2.9-3.0
Chloride	3.8
Nitrate	7.9
Sulphate	14.0

Table 1. Retention times using 1mM potassium biphthalate with 8% of acetonitrile, pH 6.19± 0.1 as mobile phase. Temperature 30ºC, 260 nm and indirect detection

Determination of impurities in mimosa extracts (indirect detection)

1g of sample was accurately weighed, dissolved and made up with water in a volumetric flask of 1 L. An aliquot of 5 ml of this solution was transferred to a volumetric flask of 25 mL and made up with water. This dilution was filtered through a syringe filter of 0,45 μm and afterwards was subjected to ion chromatography. The chromatographic conditions were the same as those used for the analysis of anions in dyes and naphthalenesulfonics.

Determination of impurities in commercial formic acids (indirect detection)

0.5 g of formic acid were accurately weighed and made up with water in a volumetric flask of 500 mL. An aliquot of 25 mL of this solution was transferred to a volumetric flask of 100 mL and made up with water. An aliquot of this dilution was filtered through a syringe filter of 0,45 μm, transferred to a sample vial and injected to the HPLC system using the same chromatographic conditions as those employed for the determination of anions in dyes and naphthalenesulfonics.

Quantification of commercial formic acids (direct detection)

Two dilutions with final concentrations of 10 and 25 mg/L were prepared from each sample.
0,25 g of sample were accurately weighed and made up with water in a volumetric flask of

500 mL (solution A). Solution A was diluted 1:20 to have a final concentration of 25 mg/L. Likewise, solution A was diluted 1:50 (final concentration of approximately 10 mg/L).
The diluted samples were injected in duplicate and using the following chromatographic conditions:
-Mobile phase: 1mM sodium sulphate, 8% (V/V) of acetonitrile and final pH 6.80± 0.1
-Detection: Direct with PDA and recovery of the chromatogram at 202 nm (to quantify formate).
-Temperature, flux and injection volume as those used in the indirect detection

The areas obtained were interpolated on the calibration curve.
Table 2 shows the approximate retention times of the different anions that may appear with direct detection when the chromatograms are recovered at 202 nm and 210 nm.

Analyte	Wavelengtth of the recovered chromatogram (nm)	Retention time in min (direct detection)
Nitrate	210	14.33
Bromide	210	11.32
Nitrite	210	8.323
Formate	202	4.049
Acetate	202	3.144

Table 2.Approximate retention times (in min) for different anions chromatographed with the mobile phase: 1mM sodium sulphate, 8% of acetonitrile and final pH 6.8

Determination of anions in leather

- Extraction
1 g of air dried and ground leather was weighed in a round bottom flask. 50 mL of water was added and the round bottom flask was stoppered. The flask and its content were mechanically shaken at 170±10 rpm for 2 hours at a temperature between 20 – 25 ºC. Finally, it was vacuum filtered. The filtered extract was subjected to ion chromatography and the extracted leather was stored for consecutive extractions.
An aliquot of the extract was filtered through a 0.45 µm syringe filter and was transferred to a sample vial for chromatographic analysis.

- Chromatographic analysis.
For the indirect detection, the following conditions were used:
-Flux: 0.9 mL/min Flux:
-Mobile phase: 1mM potassium biphthalate with 8% of acetonitrile, pH 6.19± 0.1
-Temperature: 30± 1 º C
-Injection volume: 20 µL
-Detection: Indirect with PhotoDiode Array (PDA) detector and recovery of the chromatogram at 260 nm. Inversion of the negative peaks by multiplying by a factor of (-1)

The direct detection was carried out under the following conditions:

-Mobile phase: 1mM sodium sulphate, 8% (V/V) of acetonitrile and final pH 6.80± 0.1
-Detection: Direct with PDA and recovery of the chromatogram at 202 nm (to quantify formate) and 210 nm for the other anions.
-Temperature, flux and injection volume as those used in the indirect detection

The retention times with indirect and direct detection are those shown in Tables 1 and 2, respectively.

In some leathers, the determination of formate was difficult because, as observed in Table 1, the formate and phsophate anions have the same retention times when the indirect detection system was used. Photocolorimetry was used as a complementary technique for the determination of phosphate in complex samples in which the presence of formate by the UV-VIS spectrum provided by the detector could not be confirmed.
Formate was always determined by direct detection. Formate presence was confirmed by comparing the peak obtained with that of a standard. When both peaks did not coincide, quantification of formate was carried out by combining the chromatographic technique of direct detection and the photocolorimetric analysis
The following protocol was followed:
- The extract was injected using the indirect detection. If there was no peak at 2.9 - 3 minutes, the leather did not contain formate or phosphate and the areas of the other peaks were interpolated on the corresponding calibration curves.
- In those cases in which the analysis by indirect detection revealed the presence of a peak at 2.9 – 3 minutes, the extract was also chromatographed by direct detection. The spectrum of this peak was compared with that of a formate standard. If both spectra were

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coincident, the identity of the formate peak was confirmed.

The area of the formate peak obtained by direct detection was interpolated on the calibration curve and the concentration of the formate anion was obtained. The concentration was also calculated, from the peak area obtained at 2.9-3 minutes by indirect detection, assuming that there was only formate. The coincidence in formate concentrations obtained by the two detection systems also indicated the absence of phosphate in the leather sample. If both concentrations were not coincident, it meant that the peak obtained by indirect detection corresponded to formate and phosphate. To determine the peak area corresponding to phosphate, the area corresponding to the concentration of formate obtained by direct detection was calculated in the peak of indirect detection and this area was subtracted from the total peak area. The difference corresponded to the area of phosphate, which was interpolated on the corresponding calibration curve in order to obtain phosphate concentration.

When the direct detection did not allow confirming formate identity by comparison of spectra, the phosphate content was determined by photocolorimetry. With the calibration curves of phosphate for chromatography with indirect detection and the phosphate concentration obtained by photocolorimetry, the area corresponding to this peak was calculated in order to subtract it to the total area of the peak detected at 3 minutes (phosphate plus formate). In such a way, the area corresponding to formate was estimated and interpolated on the calibration curve in order to determine its concentration.

Continued in Part 2