

A Simple Test to Determine the Propensity of a Sample of Leather to the Formation of Chromium(VI)

by

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Abstract

Since the EU Commission Regulation of chromium(VI) in leather articles, there is a huge demand of analyses and controls in the leather sector for this parameter.

However, for many tanners and leather dealers, the necessary cost to have a laboratory capable to carry out the analyses according to an ISO method is not affordable.

An easy test has been developed to carry out a screening of a leather sample in order to check out its compliance with the Cr(VI) restriction. This test is able to distinguish leathers that contain chromium(VI) or show signs of tendency to develop it, from leathers that even after thermal ageing exposure remain free of it.

The test is based on the scientist principle of the ISO 17075-1 method. Some operations of this Standard have been adapted with the aim of saving costs and simplifying and shortening the workload of the test. The essential criterion of this adaptation has been that the developed test does not lead to false negatives.

The only required devices are a laboratory oven, a balance of 0.01g of resolution, and a shaker. Neither a spectrophotometer nor a colorimeter is necessary.

The method has four main steps. The first one is an ageing process at 80°C during 24 hours. After cooling down for 30 minutes, the sample is extracted for one hour, using an overhead rotatory shaker or a magnetic stirrer. The third step is the discoloration of the extract, to remove the dyes of the colored solution so as to eliminate interferences. Finally, the extract is assessed by visual colorimetry. The workload per sample is about 40 minutes.

So far, more than 300 samples of leather have been tested. The kit performed very well and only gave 5% of false positives. The kit did not commit any false negative.

Introduction

According to the EU Commission Regulation No 301/2014, leather articles coming into contact with the skin shall not be placed on the market when they contain chromium(VI) in concentrations equal to or greater than 3 mg/kg.¹ This amendment on the REACH regulation has resulted in a huge increase in the demand for analyses of determination of hexavalent chromium in leather.

In fact, to produce leather free from hexavalent chromium is a more complex task than the production of leather that accomplishes the limits of other restricted substances, like formaldehyde or banned arylamines.

Chromium(VI) compounds are no longer used in the leather industry. However, chromium(VI) may be formed within the leather by oxidation of free chromium(III) arising from chromium used for the tanning or retanning of the leather.⁵⁻¹⁰

Thus, different from aforementioned examples of formaldehyde and arylamines, in the case of hexavalent chromium for reaching compliance with general regulations is not sufficient to ensure that all raw materials used are free from the restricted substance.

There are various studies explaining the mechanisms of this oxidation process and giving efficient prevention measures to avoid chromium(VI) formation. Some of them are reviewed in several *Good Manufacturing Practices* reports.⁵⁻¹¹

Due to the complexity of the origin of chromium(VI) and due to the fact that a classic control of products used in the manufacturing of leather does not provide enough safety, it is highly desirable to perform in house analyses of chromium(VI) in the tanneries.

There are two Standards which determine hexavalent chromium in leather: ISO 17075-1 and ISO 17075-2. The second one, available since 2017, is a new method that employs HPLC chromatography fitted with an ion exchange column and with photodiode array

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detection. This Standard diminishes the workload of the former colorimetric ISO 17075-1.² Thus, it presents a large improvement in the reliability of the detection of hexavalent chromium and reduces the amount of laboratory wastes and its results are much more precise.^{3,4}

However, for many tanners and leather dealers the cost in terms of investment in equipment and qualified laboratory personnel to carry out the analyses by this ISO method is too high. For this reason, a rapid and very economic analytical test to detect the propensity of leather to the formation of chromium(VI) has been developed. This test, which is presented in this paper, has been called LeatherKit_Cr6.

This test is capable to detect leathers that contain chromium(VI) or show signs of risk to develop it under stress conditions.

Notably, there are leathers in which hexavalent chromium is not detected when analyzed directly after production. But, with time, often under the influence of heat and/or light, chromium(VI) is formed.⁵⁻⁸

The aim of the LeatherKit_Cr6 is to more easily detect leathers which contain or have a propensity to develop chromium(VI), already in the tannery. There are numerous advantages of such a testing. First of all, general product and consumer safety increases because possibly affected leathers can be removed from the supply chain at the earliest possible stage. The risk of any failure during the controls of the leathers or final articles, which is related with important economic losses, is furthermore drastically reduced.

This method does not pretend to be an alternative to the ISO methods. It is a simple, economic, and easy to perform test for the screening of a set of samples. It is developed in such a way that if hexavalent chromium is not detected in a given sample, there is practically no risk that chromium(VI) would be detected in future analysis. Thus, the sample tested negative on chromium(VI) does not need to be sent to an external laboratory for analysis. The LeatherKit_Cr6 wants to be an on-site resource to confirm the absence of chromium(VI) in those leathers that have been processed under the aforementioned good manufacturing protocols.

All samples that do not pass the test of the LeatherKit_Cr6 will have to be sent to an accredited laboratory. Not all of them will actually contain or form hexavalent chromium in quantities higher than 3 mg/kg. Notably, the kit is designed in order to avoid false negatives results. However, because of this design and due to certain simplifications of the method, there is a possibility of false positive result of chromium(VI).

The LeatherKit_Cr6 is based on the scientific principle of the ISO 17075-1 method, and thus gives the best possible correlation with the results of the official standard. Given that the cost of an ionic

chromatograph would exceed the budget of a simple test laboratory, the basis to develop the LeatherKit_Cr6 was the colorimetric method.

This procedure could have the drawback that the leather extracts contain colored substances co-extracted from leather. However, since 2002, solid phase extraction is effectively employed in the discoloration of the extracts removing dyes and other interfering matter.¹³ This procedure has been successfully adapted and simplified in the LeatherKit_Cr6.

The process of development of the LeatherKit_Cr6 has consisted in the identification and adjustment of the operations of the ISO Standard with the idea to simplify and accelerate the test, but always in accordance with the essential basis of the method.

Materials and Methods

Samples

More than 200 samples of chromium tanned skins and hides were used in the tasks of development and verification of the test. Most of them were commercial leather for footwear, for clothing and for leather goods kindly supplied from local tanneries. Other samples were high chromium(VI) risk leather prepared in pilot plant using deliberately bad manufacturing practices⁵⁻¹².

Reagents and Instruments for the LeatherKit_Cr6 Method

1. Balance, capable of weighing 200 grams to the nearest 0.01 g.
2. Laboratory oven, capable of maintaining a stable temperature of $80 \pm 2^\circ\text{C}$ during 24 hours, with an interior made of inert materials.
3. Overhead rotary shaker Reax 2 (Heidolph, Germany). As an alternative option, magnetic stirrers without heating are also appropriated.
4. Deionized water.
5. Dipotassium hydrogen phosphate trihydrate analytical grade (Sigma-Aldrich, USA).
6. Orto-phosphoric acid 10% analytical grade (PanReac, Spain).
7. Extraction solution: Dissolve 22.8 g of dipotassium hydrogen phosphate trihydrate in some deionized water, add 4.55 g of orto-phosphoric acid 10% and make up to 1 liter. The pH of this solution is 8.0 ± 0.1 .
8. Methanol analytical grade (Sigma-Aldrich, USA).
9. Kit VisoColor ECO Chromium(VI) (Ref. 931020, Macherey Nagel, Germany)
10. Laboratory glass bottles with screw-cap GL32 with a capacity of 50mL (Duran, Germany).
11. Glass syringes of 10 mL, luer lock.
12. Cartridges for discoloration. Sep-Pak C18 Plus Short Cartridge, 360 mg Sorbent per Cartridge are suitable for most samples, but Sep-Pak C18 Long Cartridges, 820 mg Sorbent, are necessary for very colored extracts (both from Waters, USA)
13. Glass Petri dishes.
14. General glass and labware equipment.

Instruments for the ISO 17075-2 Reference Method

It was used an Alliance 2695 HPLC system fitted with a 2998 PDA Detector and with an ion-exchange IC – Pak Anion HR column, 4.6 x 75mm (Waters, USA)

Operating Procedure for LeatherKit_Cr6 Method

The leather samples are cut into small pieces of 3 mm to 5 mm side length, using scissors with a sharp blade, according to ISO 4044.

Weigh 1.8–1.9 grams of the cut sample in a Petri dish and cover it.

Ageing

Place the Petri dish that contains the leather sample uncovered in the oven at $80 \pm 2^\circ\text{C}$ for 24 ± 1 hours. It is very important to check out that the pieces of leather are lying flat on the surface of the Petri dish, without piling up.

Cooling After ageing

Remove the Petri dish from the oven, cover it, and allow it to cool down for 30 ± 1 minutes at room temperature.

Extraction

Transfer 1.50 ± 0.01 grams of aged and cooled down sample pieces with the aid of a solids addition funnel to a glass bottle of 50 mL.

Add 50 mL of extraction solution to the sample's bottle.

Close the glass bottle, place it in the shaker and extract the sample for 60 ± 1 minutes. If using an overhead rotary shaker, set the frequency at 100 min^{-1} . In case of using a magnetic stirrer, adjust it to have an intense stirring, about $700\text{-}800 \text{ min}^{-1}$, but keeping the magnet in a stable rotation over time.

Discoloration Process

Take a clean and dry glass syringe. Attach a short cartridge for discoloration in the bottom part of the syringe.

Pre-treat the cartridges passing the following liquids.

1. Flush the cartridge first with 5mL methanol,
2. afterwards with 5mL distilled water,
3. directly afterwards with 10mL of extraction solution.

Open the box of the kit VisoColor ECO Chromium(VI). Take tubes A and B.

Attach the pre-treated discoloration cartridge in a clean and dry syringe. Transfer 10mL of the extract into the syringe. Place the plunger and press it in order to flush the extract through the cartridge and discolor it. Collect the first 5mL in tube A (reference tube) and the next 5mL in tube B (sample tube).

If the discoloration has not been effective, the process will be repeated using a long cartridge and, if it is still ineffective, the result of the test of the sample will be Inconclusive.

Measurement

Place tubes A and B in the comparator of the kit VisoColor ECO Chromium(VI).

Be sure to exactly follow the manufacturer's instructions: add 5 drops of reagent 1 and reagent 2 only in tube B, wait 3 minutes and slide the comparator until the colors match in the inspection hole on top. If the developed coloration is in-between two values of the scale, always the higher value should be written down. If it is not possible to make the reading because the extract is colored or it has excessive amount of suspended fibers, the result is inconclusive.

Multiply by 33 the value of the scale to have the concentration of hexavalent chromium in mg Cr (VI) / kg of leather.

Results and Discussion

Ageing

In regard to thermal ageing, there are three parameters to be fixed: the kind of oven, the temperature and the duration of the ageing.

There are ovens with fans and ovens with natural convection, without any air circulating system. With the aim to keep the investment cost as low as possible, both types of ovens are acceptable for the LeatherKit_Cr6. The idea behind is to make use of the available resources in the laboratory.

There is a consensus between the bibliography^{8,9,12}, the routine practice of the laboratories, and the critical conditions of the draft Standard ISO DIS 17075-3 to set the temperature at $80 \pm 2^\circ\text{C}$ for 24 hours.¹⁴

Relative humidity of the air is not an independent variable: it is function of the temperature. At 80°C it remains below 10% HR, if there are not other sources of humidity in the oven. It is not required using a tropical chamber because it would make the test much more expensive.

A series of trials to find out the influence of time of ageing in the amount of chromium(VI) developed has been carried out. An oven with natural convection, without a vent, has been employed. The temperature has been set to $80 \pm 2^\circ\text{C}$.

In our tests, three types of behavior of the leather have been identified. Most of the samples tested do not show a tendency to form hexavalent chromium. They are stable against thermal ageing. Another group of leather samples develop chromium(VI) during the first hours of heat exposure, showing an asymptotic behavior before the 24 hours of ageing. We could call them "rapidly aged leather". And finally, there are leathers that remain initially some hours without forming chromium(VI) but after that stage they rapidly start to develop it. These samples, called "retardedly aged leather", need considerable time to show chromium(VI) formation.

Figure 1 Shows the performance of these three types of leather subjected to thermal ageing.

According to the results obtained, it was concluded that it is not reasonable to shorten the length of the ageing step of the method. Leathers of retarded ageing behavior have not yet shown their tendency of developing Cr(VI) in the first hours of the process. Therefore, carrying out the determination after an ageing exposure of less than 24 hours could very likely give rise to false negatives in the detection of propensity to Cr(VI) formation.

Furthermore, an ageing time of 24 hours is useful for the day-to-day work organization.

Thus, the ageing conditions of the LeatherKit_Cr6 are set the same as in the Standard ISO DIS 17075-3.

Cooling Down Time

The current version of the draft Standard ISO DIS 17075-3 fixes a cooling time of 2 hours. As the aim of the LeatherKit_Cr6 is being a rapid test, the time required to cool the aged samples has been studied.

Experiments have been carried out at two different room temperatures, 23°C and 29°C, respectively. Figure 2 shows the results obtained.

From the results, it is clear that 30 minutes is enough time to cool down the aged samples, even at a room temperature of 29°C.

To study the influence of cooling down time in the results, four different leathers that it is known that contain hexavalent chromium after ageing were selected. Once aged, they were cooled down during 30, 60 and 120 minutes at 23 °C and analyzed by ISO 17075-2, in duplicate. The average of the results at 120 minutes of cooling down time differed 1.5% in comparison with the results obtained at 30 minutes. Given that the average of Relative Standard Deviation (RSD) of the duplicates of all the analyses carried out has been found to be $\pm 1.6\%$, we concluded that the

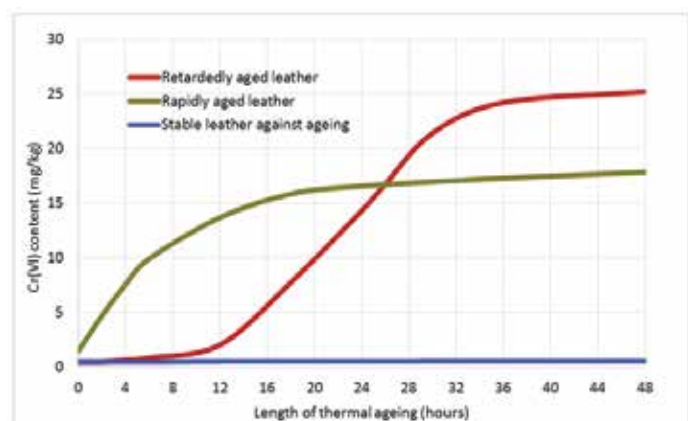


Figure 1. Performance of three types of leather subjected to heat ageing.

cooling down time has not substantial effect in the results in the range 30-120 minutes.

In conclusion, it is not necessary to cool down the samples for two hours; 30 minutes is enough.

Degasification of Samples and Extraction Solution

To carry out the degasification process, either argon or nitrogen is required. Furthermore, pressure reducers, aeration tubes, and flow meter regulation instruments are also necessary.

On the one hand, our research shows that to skip the displacement of the oxygen of the extraction solution does not give qualitative differences in the assessment of the results. In other words, the result of the test remains unchanged for the large majority of the samples that are free of chromium(VI). Besides, this implies an important saving in terms of equipment, consumables and workload.

On the other hand, when the samples and extraction solution are not degasified, the measured concentration of Cr(VI) could slightly be increased in those leathers that anyway they contain more than 3 mg/kg.

The impact of not degasifying the test solution gives rise to a small increase of false positive results, and an important saving in terms of equipment, consumables and workload.

Therefore, unlike both ISO Standards, samples and extraction solution of the LeatherKit_Cr6 should not be degassed.

Extraction Procedure

There is no method of analyses available today to detect Cr(VI) accurately directly in the sample of leather. All the detection methods applied or proposed up to now act on aqueous extracts obtained from the analyzed leather sample.

It has been decided to carry out the extraction using an aqueous solution with the same composition and pH as the ISO standards,

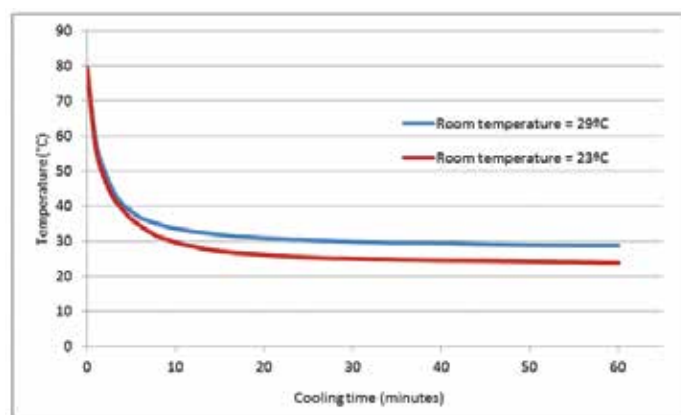


Figure 2. Variation of the temperature of aged leather samples contained in a Petri dish during the cooling process.

in order to get the best correlation possible. The pH should be maintained because it is known that at lower pH values, very different results could be obtained.¹⁵

The effect of the extraction time using an overhead rotary shaker has been studied. The results are presented in the Figure 3.

As can be seen in Figure 3, the overhead rotary shaking at 100 min⁻¹ allows similar results than the ISO method with only 1 hour of extraction. It shows that with a slower shaking movement more time would be required for achieving stable values of chromium(VI). Similar results have been obtained with other samples.

Unlike the ultrasound assisted extraction, which has also been tested, this shaking system does not increase the temperature of the sample during the extraction.

The performance of overhead rotary shaking at 75 and 100 min⁻¹ and magnetic stirring, at 700-800 min⁻¹ was compared in the analyses of nine different samples of leather (figure 4). Other extraction systems (orbital, ultrasonic) were discarded after preliminary testing.

As can be seen in Figure 4, no significant differences were observed using rotary shaking at 100 min⁻¹ compared with magnetic stirring. On the other hand, in samples 2 and 9 significant differences were found between rotary shaking at 75 min⁻¹ and the other two tested extraction conditions. This is in good agreement with behavior showed in Figure 3.

Keeping in mind that compliance with the shaking speed is very important, it was concluded that both instruments are appropriated for the extraction process. It is a decision that is left to be made by the different users that will apply the kit.

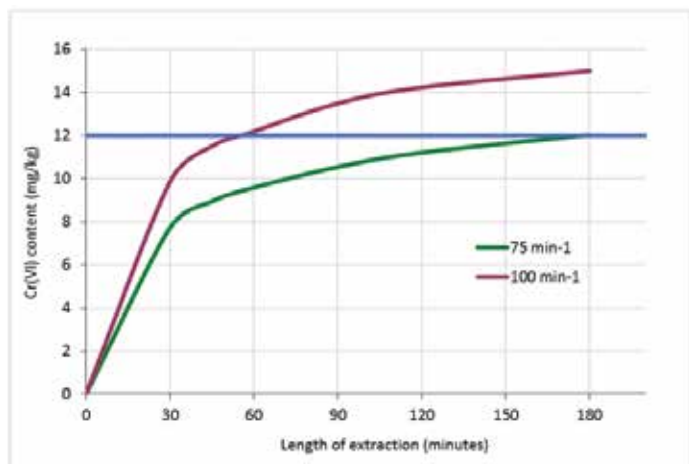


Figure 3. Cr(VI) content obtained as a function of the duration of the extraction process at shaking frequencies of 75 and 100 min⁻¹ (green and purple curves, respectively). The analysis of this sample by the ISO 17075-2:2017 gave a result of 12.0 mg/kg (blue line).

The basis for the selection of the types of shaking devices are more related to practical considerations like making use of instruments already available that technical ones.

Nevertheless, the speed control is more reliable for overhead rotary shakers than for magnetic stirrers and for that reason the first ones are preferred.

It was decided that the extraction step in the LeatherKit_Cr6 shall last one hour instead of the three hours of the ISO methods.

Color Removal

A survey analyzing some commercial leathers underlined the need of removing the dyes co-extracted before carrying out the colorimetric determination. It has been decided to adapt the discoloration procedure of the Standard ISO 17075-1, modified in order to avoid the dilution of the solution.

The discoloration is based in the Solid Phase Extraction (SPE), which uses single use cartridges filled with a C₁₈ reversed phase. This stationary phase retain non-polar components such as dyes while ionic substances, like chromate, elute through the cartridges without retention.

When 10 mL of sample extract flush through a SPE cartridge, the elution profile (Figure 5) shows that the first fraction of 5 mL (from 1st to 5th mL) do not contain the real amount of Cr(VI) of the sample. For this reason, it is transferred to the tube used as a blank reference. On the other hand, Figure 5 reveals that the second fraction of 5mL (from 6th to 10th mL) eluted from the cartridge has the same concentration as the extract has without discoloration. This 5 mL aliquot goes to the sample's tube and it will be reacted with the diphenylcarbazide reagent in the last step of the method.

In our test, the concentration of chromium(VI) in the discolored solution remains the same as before the process. Consequently, there is no loss in sensitivity.

Determination

The method of determination is based in the reaction of diphenylcarbazide with chromium(VI) at acid pH to form a red-

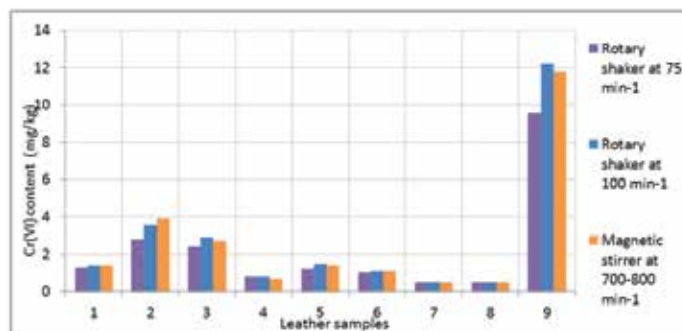


Figure 4. Comparison of results obtained extracting nine different leathers for one hour at three different experimental conditions.

violet dye. There are in the market ready-to-use kits that contain all the reagents needed. These kits are obtainable both for photometric and for visual evaluation. We found that the visual colorimetry has similar or even better sensitivity, avoids the need of filtrating the extracts, and has lower costs and ease of use.

Thus, we selected the visual determination as the best measuring method. The scale of the color chart of the recommended Kit VisoColor ECO Chromium(VI) ranges from 0.02 to 0.5 mg/L, which in the conditions of the proposed method means 0.7 to 17 mg/kg of Cr(VI). Each box of this kit contains sufficient reagent for 140 determinations. It is commercially available from Macherey Nagel (Germany) and primarily it is used for performing tests on Cr(VI) in surface water and sewage.

Notably, there are also pocket photometers for water testing that can be supplied already calibrated for chromium(VI). After testing different commercially available options, we did not find advantages for such photometers.

Evaluation of the Results

In a first stage, the evaluation of the results of the test has been carried out in our laboratory. Once passed this evaluation, the LeatherKit_Cr6 has been implemented in a local tannery where more than 300 different samples of leather have been tested up to now.

In our laboratory, 36 different samples of leather have been analyzed by the LeatherKit_Cr6 and simultaneously by the Standard ISO 17075-2, with and without thermal ageing.

75% of samples were high quality commercial leathers, free from Cr(VI). 14% were selected from the market because they tested positively by ISO method, some of them even without ageing. And the remaining 11% were leathers retanned and fatliquored in pilot plant using some type of bad manufacturing practices to obtain leather with propensity to generate chromium(VI).

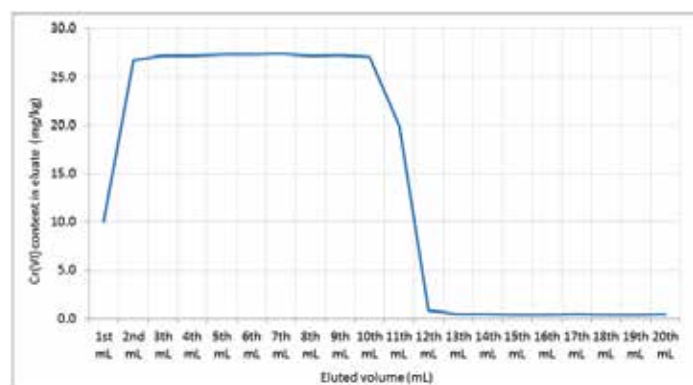


Figure 5. Elution profile of chromate after flushing a C_{18} cartridge with 10mL of a sample extract that contains 27 mg/kg of Cr(VI), and afterwards with 10mL of extraction solution.

Given that the LeatherKit_Cr6 is an internal test, and it works with more aggressive conditions than the ISO methods of analysis, each laboratory could decide which is the limit of decision to classify the samples of leather between the “Pass” group and the fraction of samples where the kit detected some risk to contain Cr(VI). These last samples will have to be sent to an accredited external laboratory to find out whether they really contain or show some tendency to develop Cr(VI), or whether it is false positives of the kit.

We consider that a suitable limit is the 3 mg/kg reference, and this is the limit we have used in this work to evaluate the results obtained.

From the 36 samples analyzed, nine were found to contain more than 3 mg/kg of Cr(VI) after ageing, including two which contained significant amounts of Cr(VI) even without ageing. All these 9 samples have been successfully detected by the kit, setting the threshold for “passed”/“not passed” at 3 mg/kg. For the 27 samples which were free from Cr(VI) (with and without ageing) measured according to ISO 17075-2, the result of the LeatherKit_Cr6 gave “passed” in 26 leathers. Therefore, only in one sample the result was a false positive.

In summary, the kit detected risk of chromium(VI) in the 100% of the tested samples that contained Cr(VI) or had propensity to develop it. The kit made 0% of false negatives. And finally, the LeatherKit_Cr6 was in good agreement with the ISO method in the 96.3% of leathers free of Cr(VI). In other words, it made 3.7% of false positives.

After this successful initial evaluation phase, the LeatherKit_Cr6 method overcame the internal validation. Although it is very encouraging that both methods have agreed on the qualitative assessment of all the risky samples, and in a very large percentage of the non-risky ones, more testing of real samples is required to evaluate its performance.

The next and definitive stage of the validation process was to ascertain whether the kit could be easily used in a tannery and if it could be capable to produce reliable results in this environment, especially in light of the fact that it would be operated by personnel that very likely does not have the skills and professional background of qualified analysts.

The LeatherKit_Cr6 was implemented in Curtidos Badia SA, a tannery located in Igualada, Spain.¹⁶ It is a prestigious company that produces fine calf leather for leather goods for luxury brands. The staff of this company did not find out difficulties in the utilization of the method, and after testing more than 170 samples, the kit performed very well. The measurements with the kit gave 5% of false positive and 0% of false negative results. This means that 95% of leather samples tested in this tannery passed the Cr(VI) internal quality control in a very quick and economic way thanks to the LeatherKit_Cr6.

In our opinion, the mentioned percentage of false positives could be explained by the fact that the kit, unlike the ISO Standards, does not remove the oxygen from the extraction solution. However, it is a minor inconvenience that undoubtedly can be assumed by the users of the kit given that it is a small percentage. Moreover, the correct determination of these particular samples can be carried out in accredited laboratories without major troubles.

Conclusions

A simple, quick and cost-effective test has been developed for tracking leathers which contain chromium(VI), or have the propensity to develop it with time. The LeatherKit_Cr6 is an on-site resource to confirm the absence of chromium(VI) directly in a tannery, for those leathers that have been processed under good manufacturing practices.

On the one hand, if the test does not detect hexavalent chromium in a given sample, this result is considered completely reliable. The advantage is that this sample would not have to be sent to an external laboratory to be analyzed.

On the other hand, the samples where the test detects hexavalent chromium would need to be sent to an accredited laboratory to define whether they really contain substantial amounts of Cr(VI) or show some tendency to develop it, or whether it is a false positives of the kit.

The validation of the method has been carried out assessing qualitatively the results of the test in comparison with the results of the ISO 17075-2:2017. It has been done in two stages. Firstly, it has been carried out in our laboratory, testing 36 samples of leather. Afterwards, the LeatherKit_Cr6 was deployed at a tannery. The staff of this company has not found any trouble in the application of the method. All together, more than 300 samples of leather have been tested. The kit performed very well and only gave 5% of false positives. The kit detected risk of hexavalent chromium in the 100% of the tested samples that contained Cr(VI) or had propensity to develop it. In other words, the kit made 0% of false negatives.

For the test, simple equipment is needed: a laboratory oven, a balance of 0.01g readability, and a shaker. Highly-qualified analysts are not necessary to carry out the tests.

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