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Formaldehyde in leather: what are we really chasing?

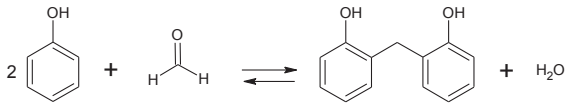
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Abstract

The content of formaldehyde in leather is determined by chromatographic (HPLC) or colorimetric analysis after extraction with a water solution of a surfactant and subsequent derivatization. Both the extraction and the derivatization procedure are potentially capable to trigger hydrolytic phenomena in certain chemical compounds that are widely used in the leather processing, thus influencing the analytical outcome. In this research work the effect of some selected retanning agents and of the HPLC derivatization time on the analytical result is investigated, showing that such factors can heavily impair inter- and intra-laboratory numerical comparisons. As a consequence, the formaldehyde content in leather should be considered as the result of an operational procedure rather than the estimation of an absolute measurand, suggesting that the analytical methods should be better focused on the concept of usage scenario.

Introduction

Formaldehyde is a highly biodegradable gaseous compound (boiling point = -19°C) that, at ordinary conditions, occurs in different interchangeable forms (1,3,5 trioxane, paraformaldehyde, methanediol and various oligomers). Despite it finds no direct use in the tanning process due to toxicity issues, its ability of forming molecular bridges (ether- or methylene-based) is widely exploited in the synthesis of a number of polymeric specialties used in leather manufacturing, especially for the production of syntans and dicyandiamide resins. In the presence of water these compounds can undergo hydrolytic phenomena and are consequently capable of releasing variable amounts of free formaldehyde (reversible reactions).
The reaction between phenol and formaldehyde is illustrated below as a simple example of a formaldehyde-releasing system.



Phenol Formaldehyde Bisphenol F

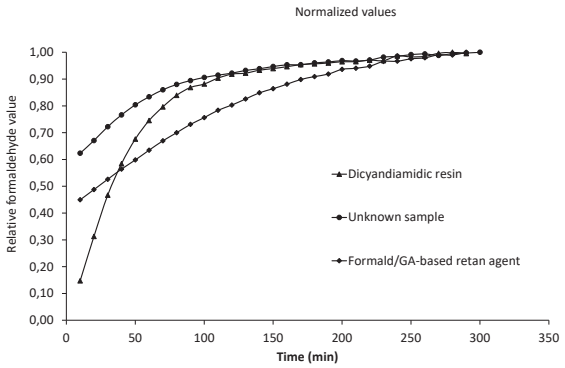
A remarkable consequence is that the concentration of formaldehyde detected in leather is potentially subjected to variations depending on the sample history, especially if the leather has been exposed to conditions that promote hydrolytic processes. Besides, the extraction and the derivatization procedures may themselves accelerate the decomposition of formaldehyde-condensed chemicals and further increase the amount of free formaldehyde. For example, the derivatization with 2,4-dinitrophenylhydrazine (DNPH) described in the older versions of ISO 17226-1 standard method takes place in the presence of phosphoric acid; this latter acts as a catalyst of the above mentioned decomposition processes and leads to a progressive increase of the formaldehyde concentration within the analysis time interval (60-180 minutes in the 2008 version, 60-80 minutes in the 2018 version). In the newest edition of the method (2021) only acetonitrile is used as derivatization medium, and a pre-treatment at 50°C for 180 minutes is prescribed before the chromatographic analysis with the aim to bring all reactions to completion

Materials and methods

For this research work some samples of leather have been prepared with specific retanning agents that are known to potentially release formaldehyde, namely a dicyandiamide resin and a formaldehyde-glutaraldehyde mixture. An unknown leather sample from the market has been also included in the analytical sessions.
An HPLC system with ODS column and UV detector was used for the chromatographic analysis.

Result and discussion

The diagram below shows the increase of formaldehyde concentration upon analyzing the same sample at different derivatization times in the presence of phosphoric acid (older versions of ISO 17226-1). It is clearly visible how the chemical nature of the retanning agent affects the dynamics of formaldehyde release; as we are only interested to relative variations, each single result has been normalized with respect to the maximum values.



The reduction of the analytical time slot from 60-180 minutes (ISO 17226-1:2008) to 60-80 minutes (ISO 17226-1:2018) led to the differences reported in the following table:

Values at t =	60	80	180	% @80	% @180
Dicyandiamide resin	0,75	0,84	0,96	12,6%	28,4%
Unknown sample	0,83	0,88	0,96	5,5%	15,2%
Formald/GA-based retan agent	0,63	0,70	0,91	10,3%	43,3%

It is apparent that, even in the best case, the analytical result for the same sample delivered by the same laboratory at the same conditions would be subjected to a systematic bias of over 5% in the formaldehyde value as an additive component of the repeatability uncertainty. Considering the variety of retanning agents used in the process, a higher bias is expected on average when it comes to formaldehyde analysis.

The last edition of ISO 17226-1 tries to limit hydrolysis by avoiding the presence phosphoric acid in the derivatization solution, using only acetonitrile as solvent. The graph below shows the result of an interlaboratory proficiency testing where the participants adopted this latter version of the standard method (ppm of formaldehyde are reported in the ordinate and laboratory number in the horizontal axis). In this case, despite the hydrolytic processes are not enhanced by the presence of phosphoric acid, statistically acceptable values range in the considerably wide interval 20 - 60 ppm, with an average of 40 ppm.



In the colorimetric procedure (ISO 17226-2) the derivatization is done with acetylacetone in a buffered solution and the contribution of hydrolysis is therefore expected to be less influent. In fact, once the interferences due to color are ruled out, the results obtained with this latter procedure are generally lower than with the DNPH-HPLC method, as is visible in the following table:

Method	Unit	N of participants	Average	R
HPLC 2021	mg/kg	42	39.4	24.3
HPLC 2008/2018	mg/kg	7	68.1	41.0
Colorimetric	mg/kg	57	41.6	11.3

With reference to the results above, the remarkably higher values obtained by the laboratories that applied the older versions of the ISO 17226-1 method provide the evidence that the presence of phosphoric acid in the derivatizing medium promotes further release of formaldehyde from the leather. When the DNPH derivatization takes place in a non-acidified medium (2021 version), the results are similar to the ones obtained with the colorimetric (acetylacetone) method, indicating that the hydrolytic processes act in a similar way in the two instances. However, the reproducibility is noticeably high in all cases.

Aknowldegements

The authors are grateful to the R&D staff of Gruppo Mastrotto.

References

Data and graph of the proficiency testing has been kindly provided by IIS (Institute for Interlaboratory Studies) and are taken from the published PT report of Formaldehyde in Leather iis21A08 organized in November 2021 by the same Institute.