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www.elsevier.com/locate/talanta

PII: S0039-9140(17)30268-0
DOI: http://dx.doi.org/10.1016/j.talanta.2017.02.053
Reference: TAL17329

To appear in: *Talanta*

Received date: 22 November 2016
Revised date: 22 February 2017
Accepted date: 24 February 2017

Cite this article as: A. Schedl, T. Zweckmair, F. Kikul, U. Henniges, T. Rosenau and A. Potthast, Aging of paper - Ultra-fast quantification of 2,5 dihydroxyacetophenone, as a key chromophore in cellulosics, by reactive pape spray-mass spectrometry, *Talanta* http://dx.doi.org/10.1016/j.talanta.2017.02.053

Aging of paper - Ultra-fast quantification of 2,5-dihydroxyacetophenone, as a key chromophore in cellulosics, by reactive paper spray-mass spectrometry

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Abbreviations

ACN: Acetonitrile, DHAP: 2,5-dihydroxyacetophenone, DMAP: 3,4–dimethoxyacetophenone, GT: Girard's reagent T, PS-MS: Paper spray mass spectrometry, TFA: Trifluoroacetic acid

Keywords: paper aging, chromophores, yellowing, 2,5-dihydroxyacetophenone, artificial aging, experimental design, Girard's reagent T, reactive paper spray-MS

Abstract: The detection of individual chromophores that contribute to the overall discoloration of paper or pulp ("yellowing") is a challenge because these substances are only present in extremely small amounts (ppm to ppb range). In this work, paper spray (PS) coupled with mass spectrometry was used to detect a low-concentrated cellulosic key-chromophore, 2,5-dihydroxyacetophenone (DHAP). Sensitivity was enhanced by derivatization with Girard's reagent T (GT). DHAP was successfully detected in historic paper samples and also was applied to model papers in order to investigate different factors that influence its generation: temperature, time, relative humidity, and the presence of iron ions, by means of a full factorial design. The main factors, temperature and relative humidity, have the most impact on the generation of DHAP, but the interactions between the factors are also significant and are therefore important for the degradation process. The historical papers containing DHAP were then compared to the artificially aged samples. The results were confirmed by independent, accurate mass measurements.

Introduction

Many commodities nowadays are based on pulp derived from wood: paper, tissues, and fibers are the most prominent examples. As a white color is associated with purity and cleanliness in the customers´ notion, pulp producers aim for materials with very high brightness indices. However, upon exposure to different kinds of stress (thermal, irradiation, and chemical) and even upon storage under ambient conditions, new chromophores—literally "carriers of color"—are generated from carbohydrate degradation products [1, 2]. Extensive research has been done to clarify structure, occurrence, and formation pathways of these chromophores [3-5]. It turns out that