

# Viscometry determination of the kinetic of degradation of iron-gall inks

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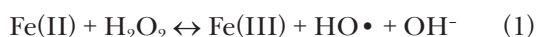
**Abstract:** Degradation of historical written documents, drawings and manuscripts containing iron-gall inks is a significant problem for years. Many researches proved that iron (II) ions and acids in the iron-gall inks cause damage of these documents. The purpose of this study was to assess the possibility of using degree of polymerization based on viscometric data in study of kinetic of degradation and determination of kinetic constant of degradation of model systems iron-gall inks – paper substrate. The obtained results were compared to the results obtained using degrees of polymerization based on gel permeation chromatography data. It was found, that the kinetic constants of degradation of model systems obtained from viscometric and from gel permeation chromatography data correlate.

**Keywords:** iron-gall inks, degradation of historical documents, viscometry, gel permeation chromatography

## Introduction

The iron-gall inks were used as the writing means from the Antique period to the middle of the last century (Budnar et al. 2006, Ďurovič 2002, Kolar et al. 2006). A lot of different written documents, drawings and manuscripts in which iron-gall inks were used can be found in many libraries, archives and museums worldwide. The iron-gall inks have been prepared according to a broad variety of recipes. The main components of the inks recipes were ferrous and copper sulphate, gallic acid and gum arabic. Unfortunately, these components cause severe damage or even complete destruction of historical artefacts due to the ink corrosion (Schölten 1997, Steemers 2006).

Main reasons of iron-gall inks corrosion are the acid hydrolysis of the glycosidic bonds and the cellulose oxidation (Ďurovič 2002, Wouters and Banik 2000). Acid hydrolysis is caused by the acids in the iron-gall inks and also by the sulfuric acid gradually formed during the curing of ink deposited on a paper substrate. Iron (II) ions are suspected to cause the oxidative degradation of cellulose by catalysing the formation of hydroxyl radicals ( $\text{HO}\cdot$ ) from hydrogen peroxide in the Fenton reaction (Emery and Schroeder 1994, Walling 1975):



Hydrogen peroxide is formed during the reduction of molecular oxygen by iron (II) ions. Hydroxyl radicals are very reactive and readily abstract hydrogen from cellulose, leading to the formation of organic radicals ( $\text{R}\cdot$ ) (Neevel 2003).

In the present study, two methods for analyzing degradation of cellulose and influence of iron-gall inks on the ageing of cellulose were compared. The first method was viscometry, which is often the preferred method to estimate the average degree of polymerization (DP) of paper samples. This method is fast and convenient. The second method was the gel permeation chromatography (GPC). The both methods allow to determine the degree of polymerization and consequently to study the kinetic of degradation of iron-gall inks – substrate systems. The aim of the paper was to find out, if the correlation between rate constants of degradation of model systems iron-gall inks – paper substrate based on viscometry and GPC data exists.

## Experimental

According to historical recipes of Neevel (Neevel 1975), we prepared two iron-gall inks (I1, I2) samples with the different ratios of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (Lachema) and gallic acid (Sigma-Aldrich) 0.25 and 4 respectively. The amount of other mean component, gum arabic (Sigma-Aldrich) – playing a role of suspension stabilizer and ink carrier, was kept constant (7.85 g/100 ml of deionized water) in all inks.

Freshly prepared inks were treated in ultrasound basin for 10 minutes for maximum homogeneity and then were kept in the dark for 7 days long. Consequently, model systems of iron-gall inks – substrate (WI1, WI2) with pH 3 and pH 10 for each iron-gall ink were prepared. As a substrate filter paper Whatman No. 1 (85 g.m<sup>2</sup>), which is consider to be a pure cotton linter cellulose, was used. Uniform

application of the inks on the substrate ( $5 \times 5$  cm) was obtained by immersion of the substrate into the inks samples. Soaked up samples of the paper were interposed between two filter papers and dried using a rubbery roller at a constant pressure.

The pH of model systems were modified using the standard acido-base agent 0.04 M  $\text{Mg}(\text{HCO}_3)_2$ . The samples were immersed into the properly diluted standard solutions for various times to obtain the pH values 3 and 10.

As a third system the pure paper Whatman No. 1 without applied inks was used. The paper Whatman No. 1 itself has the pH value 6.82. The pH value 3 was achieved treating the samples of paper with a damping solution (0.2 M  $\text{Na}_2\text{HPO}_4$  + 0.1 M citric acid diluted in deionized water) and pH value 10 by using an alkaline solution (0.04 M  $\text{Mg}(\text{HCO}_3)_2$  properly diluted in deionized water).

The samples were submitted to the thermal accelerated ageing in closed vessels according the standard ISO 5630-5 (ISO 2006). Samples were conditioned for 24 hours in a climatic room with temperature 23 °C and relative humidity of 50 % in the opened special flasks with the volume of 130 cm<sup>3</sup>. After 24 hours all flasks were closed and put into the oven (multiple-function oven APT Line Series FED, Czech Republic). The samples were aged at temperature 100 °C for 1, 4, 8, 16 and 24 hours. The times of accelerated ageing for samples of paper Whatman without the inks were 1, 4, 8, 16, 24, 96, 120 and 192 hours.

Estimation of correspondence of time of thermal accelerated ageing with the amount of time of ageing under normal conditions is rather difficult because of two reasons. Such equivalence of time of accelerated ageing and the time of ageing under normal conditions was established only for accelerated ageing according to the standard ISO 5630-1 for dry heat treatment at 105 °C (ISO 1999) and for the paper substrate only. Similar equivalence for the accelerated ageing according to the standard ISO 5630-5 for exposure to elevated temperature at 100 °C (ISO 2006) used in this study has not been established even not for a pure paper. So, few researchers estimated, that the 3 days of accelerated ageing at 105 °C is equivalent to 25 years of natural ageing at 20 °C (18 °C) (Barrow 1963, Wilson et al. 1955).

The average degrees of polymerization of the aged samples were determined from viscometric and from GPC data. Viscometry measurements were realized in the capillary viscometer (UNITEX viscometer for the determination of the cellulose polymerization, Effeci di Vincenzo Formenti, Italy; complying to the standard ISO 5351-1 for determination of limiting viscosity number of cellulose (ISO 1994)). The

procedure, solvent (cupriethylenediamine (CED, Sigma-Aldrich)) and calculations according to the standard ISO 5351-1 (ISO 1994) were followed and the constants and the parameters data listed in tables of this standard were used in the calculations. Degrees of polymerization were calculated from the intrinsic viscosity data using Mark-Houwink-Sakurada equation and the constants according to Evans and Willis (Evans and Wallis 1987, Kolar and Strlic 2004). The rate constants of degradation of samples “k” were calculated using the Ekenstam equation (Ekenstam 1936):

$$1/DP = (1/DP_0) + kt \quad (2)$$

where  $DP$  = degree of polymerization after ageing,  $DP_0$  = degree of polymerization at the beginning of ageing,  $k$  = rate constant of degradation [ $\text{h}^{-1}$ ],  $t$  = time of ageing [h].

The gel permeation chromatography (GPC) is a type of liquid chromatography and allows us to characterize different average molecular weights such as the number molecular weight ( $M_n$ ) and the weight molecular weight ( $M_w$ ).

The degrees of polymerization of all samples were determined also from the gel permeation chromatography (GPC) data using the equation (Halajová and Kačík 2011, Kačík et al. 2009):

$$DP = M_w/162 \quad (3)$$

where  $M_w$  is the average molecular weight from GPC data. As in the previous case the rate constant of degradation “ $k$ ” was calculated from  $DP$  using the Ekenstam equation (2).

### GPC method

The following parameters were used in the GPC measurements – flow: 1.00 mL/min.; columns: four PL gel mixed ALS, 20  $\mu\text{m}$ ,  $7.5 \times 300$  mm; injection volume: 100  $\mu\text{L}$ ; run time: 45 min.; mobile phase: DMAc/LiCl (0.9 %, w/v) filtered through a 0.02  $\mu\text{m}$  filter.

The samples were dissolved in the solution of DMAc/LiCl.

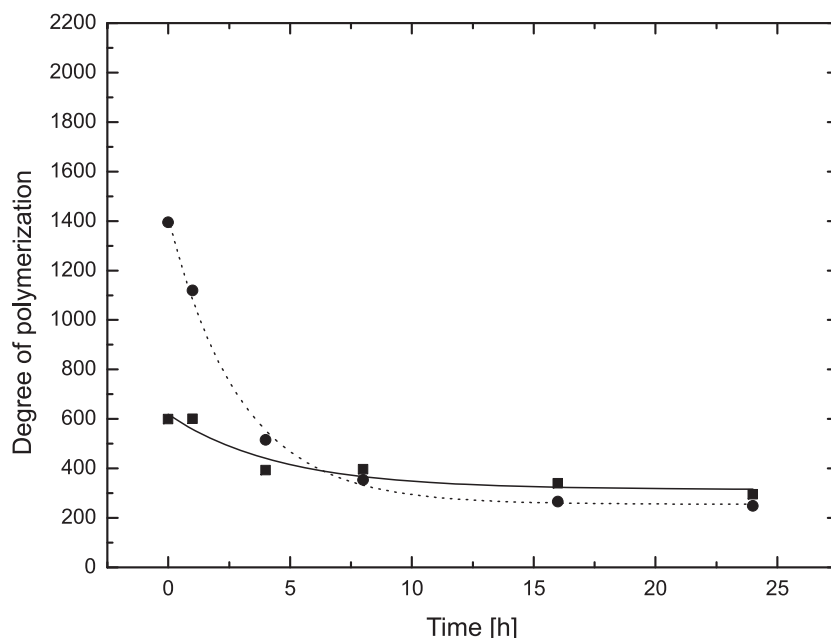
## Results and discussion

Fig. 1, 2 show the dependence of the degree of polymerization (DP) on the time of accelerated ageing for the system iron-gall ink – Whatman (W11) with pH 3 and pH 10. Degradation curves obtained from viscometric and GPC data respectively differs. The degrees of polymerization based on viscometric data are in most cases higher (or not significantly greater) than the corresponding degrees of polymerization based on GPC data. The situation was the same for the degradation lines of the other samples.

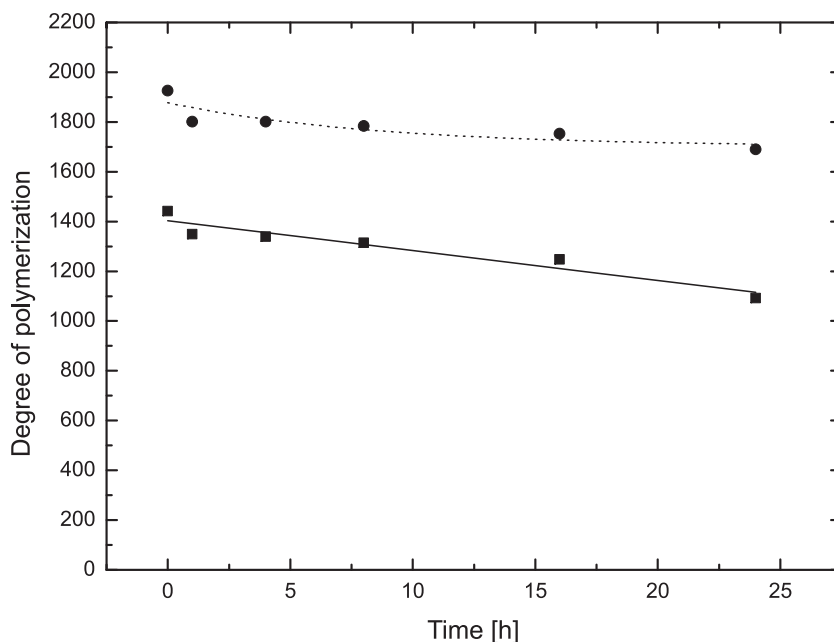
One of the possible explanations of this difference is that the used constants of Mark-Houwling-Sakurada equation for calculation of degrees of polymerization according to Evans and Willis were determined for pure cellulose and thus the hydrodynamic conditions in viscometer should correspond to the dissolved pure cellulose. Samples of the systems iron-gall ink – paper Whatman create slightly different hydrodynamic conditions in viscometer, what leads to the different

absolute values of the measured degrees of polymerization. Another reason of difference can be attributed to different solvents used in respective methods.

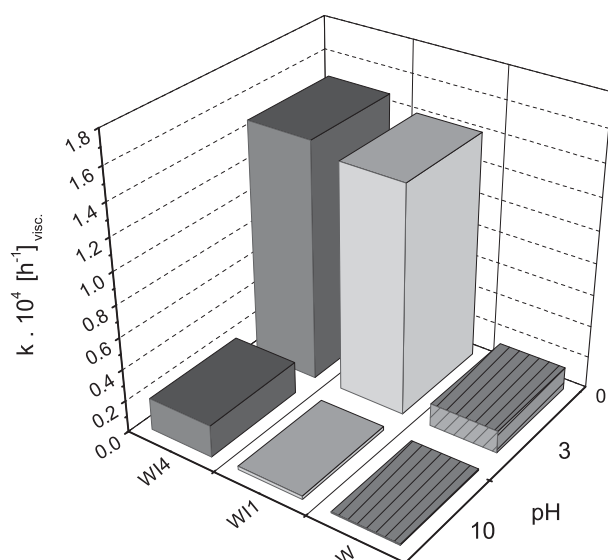
The rate constants of degradation of the model systems iron-gall inks – paper Whatman (WI1, WI2) and pure paper Whatman (W) in the region pH 3 and pH 10 obtained using two methods, viscometry and gel permeation chromatography, are on the Fig. 3 and 4. Although the values of rate constants



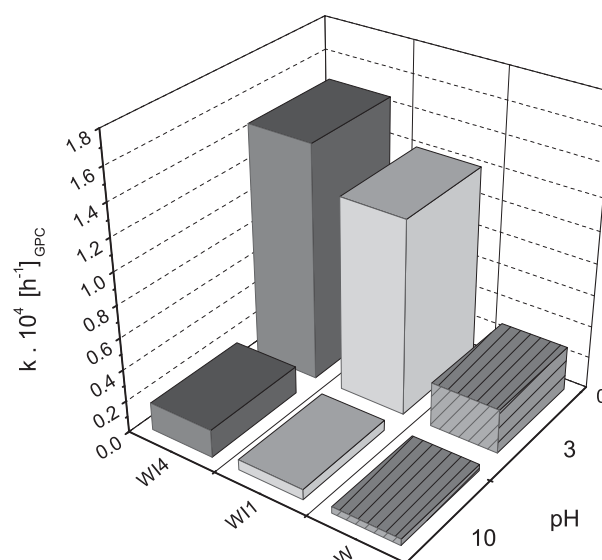
**Fig. 1.** Degradation curves (degrees of polymerization determined viscometrically and from GPC data); model system WI1 – Whatman; iron-gall ink Fe(II):gallic acid = 0.25; pH 3, (GPC: solid squares, solid line; viscometry: solid circles, dot line).



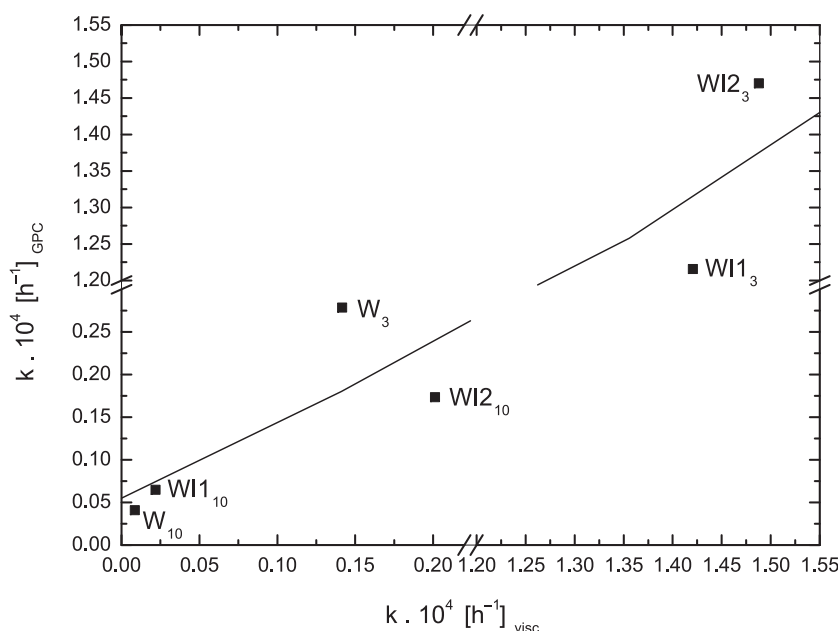
**Fig. 2.** Degradation curves (degrees of polymerization determined viscometrically and from GPC data); model system WI1 – Whatman; iron-gall ink Fe(II):gallic acid = 0.25; pH 10, ((GPC: solid squares, solid line; viscometry: solid circles, dot line).



**Fig. 3.** The rate constants of degradation, viscometry; paper Whatman No. 1 (W), model systems (WI1, WI2), pH 3 and pH 10.



**Fig. 4.** The rate constants of degradation, GPC; paper Whatman No. 1 (W), model systems (WI1, WI2), pH 3 and pH 10.



**Fig. 5.** Dependence of the rate constants of GPC on the rate constants of viscometry; paper Whatman No. 1 (W), model systems (WI1, WI2), pH 3 and pH 10.

obtained by these methods are not equal, both sets of rate constants follow the same general trends: the rate of degradation of all samples is higher in the acid region pH 3 comparing to the alkaline region pH 10; the rate of degradation of samples containing iron-gall inks is higher comparing to the rate of degradation of pure substrate and depends on the composition of the inks, this behavior is more significant in the acid region.

The correlation of the rate constants of degradation of studied samples determined viscometric and the rate constants based on GPC data is on the

Fig. 5. The correlation is linear with the coefficient of correlation 0.99.

## Conclusions

The study deals with the comparison rate constants of degradation of model systems iron-gall ink – paper substrate using two methods for determination of degrees of polymerization: viscometry and gel permeation chromatography.

The results obtained in this study demonstrates, that the kinetic constants of degradation of systems

iron-gall ink – paper substrate obtained from degradation curves based on viscometric data and GPC data correlate. Thus, the simpler viscometric method of determination of degree of polymerization can be used in study of kinetic of degradation model samples of systems iron-gall ink – paper substrate.

This finding corresponds to the conclusion of the study of correlation between viscometrically determined degrees of polymerization and Mw determined from GPC data for carbanilated cellulose (Kolar et al. 2006).

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