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Investigation of Complexation and Solid–liquid Extraction of Iron from Paper by UV/VIS and Atomic Absorption Spectrometry

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Abstract. The aim of this study was to evaluate the strategy for the investigation the possibility of diminishing the *iron-gall ink corrosion* process occurring often in ancient manuscripts. In order to understand the respective processes, the efficiency of iron complex formation as well as solid–liquid extraction of iron compounds from the paper was investigated by UV/VIS spectrometry and by graphite furnace atomic absorption spectrometry (GFAAS) as well. Acetylacetone, dibenzoylmethane and deferoxamine mesylate were chosen as they are known to form strong complexes with iron and they exhibit a broad absorbance band in the range of 390–600 nm. UV/VIS spectrometry was used for the determination of that part of iron, which was bound with the respective complexing agent. Parallel, the total amount of iron in the solution was measured by GFAAS. The efficiency and rate of the process were investigated for $FeCl_3$ as well as for iron compounds present in the iron-gall ink solution. It was demonstrated, that the process is based on the fast extraction of the iron from the paper followed by the iron-complex formation in the solution.

Key words: Iron-gall ink corrosion; paper; iron complex formation; UV/VIS; GFAAS.

In recent years growing attention has been observed to use various instrumental analytical methods to analysis and to support the conservation of works of art [1–7]. Manuscripts are among the antique works of art, which are endangered by several destructive processes [8–11]. Ancient manuscripts were commonly written with iron-gall inks, which were basically produced by mixing aqueous solutions of iron(II) sulphate with gallotannin-containing extracts of gallnuts [12–14]. Most ancient iron-gall inks contain an excess of iron, partly present as iron(II) ions. That form of iron could take part in redox reactions catalysing the oxidation of cellulose. The process, known as *iron-gall ink corrosion*, leads to loss in mechanical strength of the paper [12–15].

It must be pointed out that the degradation of cellulose could be caused by several mechanisms among which acid-catalysed hydrolysis and metal-catalysed oxidation are the most commonly described ones. These two processes may take place not only separately, but very often they can occur simultaneously as well. Therefore, in order to diminish the unwanted destruction of cellulose chains, the conservation treatment of the paper should be based on the removal of an excess of iron and/or neutralising acid [15]. In recent years several successful deacidification methods have been proposed, not only for the conservation of individual items but for mass-conservation as well [16–18]. This however is not sufficient to achieve the total protection of manuscript papers. It was found that metal-catalysed oxidation can take place independently from acid hydrolysis and therefore a special conservation strategy should be developed for *iron-gall ink corrosion* [13, 15, 21].

Our studies were stimulated by the co-operation with Polish National Library (Warsaw, Poland) where a number of manuscripts are endangered by the corrosion process [19, 20]. Based on actual knowledge concerning the *iron-gall ink corrosion* [13, 15, 21] it could be concluded that the successful conservation strategy should be based on following procedures:

- To bind iron ions into a persistent complex in paper
- To remove the excess of iron ions from the paper
- To remove excess of iron partially and bind the residual ions in the form of stable compounds that would not accelerate degradation processes.

The complexing agents which could be potentially used for the conservation of manuscripts endangered

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by *iron-gall ink corrosion* should fulfil various requirements. The first criterion is that they form stable complexes with iron, however less stable than ink compounds, so they do not bleach the colour. These complexes, preferably colourless, should be easily washed-out from the paper. The complexing agents should be stable in a broad range of pH. They should also be non-destructive for cellulose and, last but not least, be easy to prepare and apply. The conservation procedures should therefore be based on the complexation of an excess of iron followed by extraction of the iron complex from paper into the washing solution.

The aim of this work was to evaluate the strategy for studying the efficiency and rate of the formation as well as solid-liquid extraction of several iron complexes from paper. For that purpose UV/VIS spectrometry and GFAAS were used. This strategy was based on the use of model samples without necessity of taking any sample from artefacts. The investigated model samples were chosen according to Whitmore and Bogaard [9], where a Whatman chromatographic paper, made of cotton fibres, was used. Although various artificial ageing of paper are described [9, 13, 21] for the investigation carried out in this work paper samples were exposed under IR lamp. This treatment was found to be sufficient for described purposes.

Experimental

Instrumentation

Shimadzu UV-2401 PC UV/VIS recording spectrophotometer (Japan) was used for the UV/VIS investigation. Slit width was set to 2 nm, wavelength range was 390 to 600 nm and 1.000 cm quartz-cells were used in all measurements.

An atomic absorption spectrometer model 4100 ZL equipped with THGA graphite furnace (Perkin Elmer, Überlingen, Germany) with longitudinal Zeeman background correction was used. Integrated absorbances were measured. Samples were introduced into the atomiser with AS-70 autosampler. Hollow cathode lamps for Fe (Narva, Germany) were run at 12 mA with recording of analytical lines at 248.3 nm using spectral bandwidths of 0.2 nm. The injection volume was always 20 µl. The temperature programme for iron determination was used according to the manual of the spectrometer.

Reagents

All reagents used were of analytical grade purity. Acetylacetone ($C_5H_8O_2$) p.a. (Fluka Chemie AG, Switzerland), dibenzoylmethane ($C_{15}H_{12}O_2$) (Fluka Chemie AG, Switzerland), deferoxamine mesylate ($C_{25}H_{48}N_6O_8 \cdot CH_4O_3S$) 95% (TLC) (Sigma-Aldrich Chemie GmbH, Hungary), ethyl alcohol (C_2H_6O) 96% vol. (POCh, Poland). Double distilled water was used throughout. An iron standard solution of $FeCl_3$ containing 1.0 gl^{-1} of iron (Merck, Darmstadt, Germany) was used. Working solutions used for the preparation of the model samples were prepared by appropriate dilution with double distilled water. Vessels (PP) and micropipette tips were cleaned with 0.1% m/v nitric acid Suprapur™ (Merck, Germany), washed in double distilled water and dried before use.

Complexing Agents Solutions

(i) solution of deferoxamine mesylate in double distilled water was prepared in the concentration of 0.001 mol l^{-1}
(ii) solutions of acetylacetone and dibenzoylmethane were prepared in double distilled water and in ethanol, respectively, at concentration of 0.001 mol l^{-1} and 0.003 mol l^{-1}

Iron-Gall Ink Solution. To prepare iron-gall ink solution 4.20 g of ferrous sulphate p.a. (P.O.Ch. Gliwice, Poland) were added to 4.86 g of tannin p.a. (P.O.Ch. Gliwice, Poland) and 3.14 g of gum arabicum (Kaspar & Co., Austria). Double distilled water was used to fill the solution up to 100 ml. After 24 hours the solution was filtered and analysed by GFAAS for iron content.

Model Samples Preparation Procedure. In this work we applied Whatman paper for the preparation of *model samples*, which were used to study the efficiency of complexation and solid–liquid extraction of iron. For these purpose two types of *model samples* were prepared: Model sample *No. I* – from the solution of iron-gall ink 5 µl was deposited onto the paper small circle (f = 6 mm). Model sample *No. II* – from the solution of $FeCl_3$ ($C_{Fe} = 0.6$ g/l), 5 µl was deposited onto the paper small circle. After the deposition of the respective solution, all paper samples were exposed to IR lamp for 15 min, then stored separately in closed vessels (a 1.5 ml). All model samples were prepared in a clean box under laminar air flow conditions.

Determination of Iron Complex by UV/VIS Spectrometry. The spectra of the investigated ligands with iron (added as $FeCl_3$ or as gall-ink solution) were recorded in the range of 390–700 nm. The wavelengths for maximum absorbance (λ_{max}) (1) were used for further measurements of the content of the iron-complex in the solution after extraction of iron from the paper. For all investigated model samples, each paper dot was immersed into a quartz-cell (of 3 ml). The first measurement was done after the solution of the respective ligand was added into the cell. Then, a measurement was provided every minute, with acquisition time fixed to 1 second. The total amount of iron in the form of complex was determined for respective ligands by measuring the "reference absorbance value" for the mixture of 5 µl of the iron solution (as $FeCl_3$ or as iron-gall ink solution) with 3 ml of complexing agents solution. To this reference value (100% of iron-complex), the absorbance values for iron-complex that has been washed out from the paper samples, were always referred. Every point in the Fig. 1 represents the mean of absorbance values for three independent samples.

Determination of Iron by GFAAS. For all investigated model samples, each paper sample was immersed in 20 ml of the solution of respective complexing agents. Every minute (within first 5 minutes) and then every 5 minutes, 200 µl of the solution was taken out from the reaction vessel. Before sampling, the solution was always stirred for 3 seconds. The concentration of iron was determined by GFAAS.

In order to avoid the influence of the complexing agent on atomic absorption measurements, all data were recalculated in respect to the absorbance of the defined amount of iron mixed with the ligand solution. For this purpose 5 µl of the iron solution (as $FeCl_3$ or as

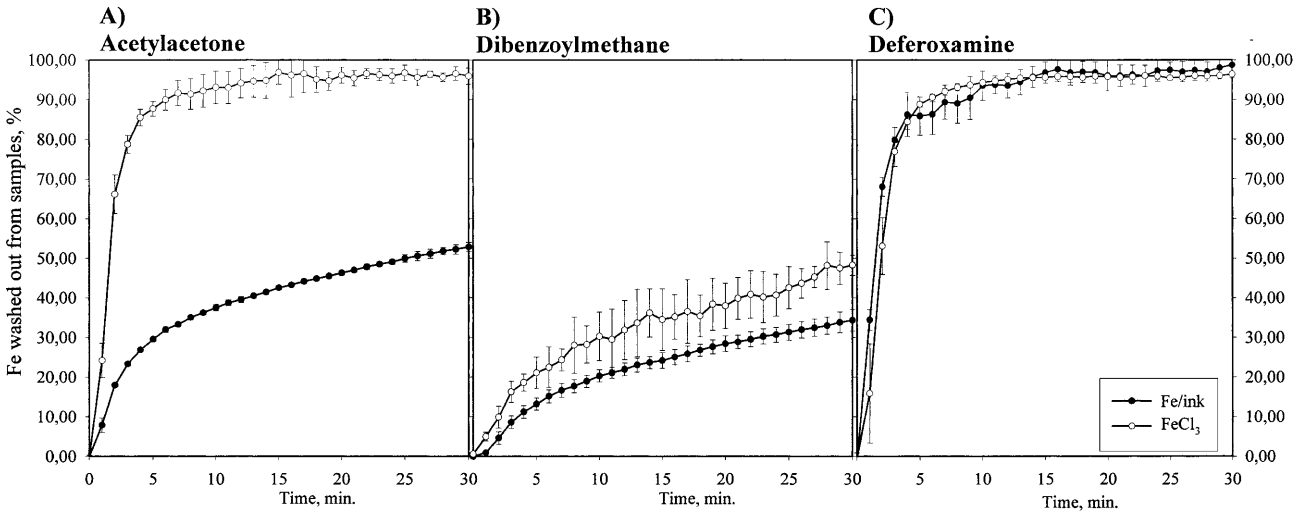

Fig. 1. Efficiency of iron-complex formation in the solutions: (A) acetylacetone; (B) dibenzoylmethane; (C) deferoxamine. The model sample were used: (—●—) with iron-gall ink; (—○—) with $FeCl_3$. Results are expressed as the percentage of respective "reference absorbance values" (see experimental)

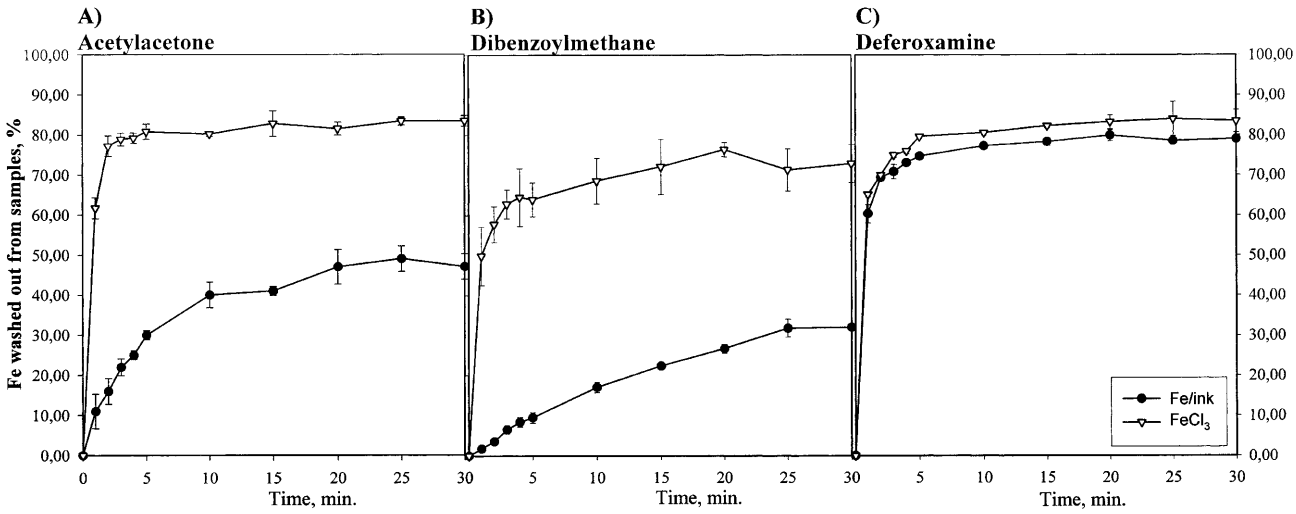

Fig. 2. Efficiency of iron extraction from the model samples by the ligand solutions (see experimental): (A) acetylacetone; (B) dibenzoylmethane; (C) deferoxamine. The model sample were used: (—●—) with iron-gall ink; (—○—) with $FeCl_3$. Results are expressed as the percentage of the "iron equivalent" in respective ligand solutions (see experimental)

iron-gall ink solution) was pipetted into 20 ml of the solution of the respective complexing agent. Absorbance values, for the matrix matched solutions were used as 100% of the iron equivalent. The amount of iron that has been washed out from the paper samples was referred to that value. Every point in the Fig. 2 represents the means of three measurements for three independent samples.

Results and Discussion

In order to choose the proper conservation procedure for works of art, detailed physico-chemical investigations are always required. It is not possible to use the original ancient object as it would in consequence lead to its destruction. Therefore in this work we provide an extensive investigation by using model samples (see Experimental) in order to understand the phenomena occurring when an excess of iron has been washed-out from the paper by complexing agent. After wetting of the paper by the liquid phase, two processes could occur in the investigated system:

(i) The preliminary diffusion of the complexing agents in the cellulose followed by iron-complex extraction into the solutions, or

Table 1. Wavelength of maximum absorbance for iron complexes with respective ligands

Ligand	Wavelength of maximum absorbance*), nm	
	Mixture of ligand with iron-gall ink	Mixture of ligand with $FeCl_3$
Deferoxamine	425.60	435.80
Dibenzoylmethane	502.40	414.00
Acetylacetone	443.00	461.20

*) Note that the wavelengths for maximum absorbance differ for both solutions of iron.

(ii) the preliminary extraction of iron into the liquid phase followed by complex formation in the solution.

All investigated ligands have no chromophoric groups, therefore the spectra of iron-complexes show the broad spectra band characteristic for charge-transfer transitions with relative high values of absorbance coefficients ($\varepsilon = 500$–1500). From preliminary results small shifts in maximum absorbance wavelength were found when the iron was introduced as $FeCl_3$ in comparison to the iron in the ink solution. Therefore two wavelengths were used for further experiments (Table 1).

UV/VIS Measurements

From UV/VIS measurements (Fig.1) it was found that nearly 100% (see Experimental) of iron deposited onto the paper dots as $FeCl_3$ could be washed-out by acetylacetone and deferoxamine solutions. For both compounds, the plateau was achieved within 10 min (Fig. 1, A and C). In the case of dibenzoylmethane solution, the rate of the investigated process was much slower. The respective curve for $FeCl_3$ as well as for iron-gall ink solutions have not reached plateau even after 30 min. Additionally, the efficiency of iron-complex formation (as compared to Fig. 2B) within this time was less than 50% for $FeCl_3$.

In the case of iron deposited on the paper in the form of iron-gall ink solution, when acetylacetone and dibenzoylmethane were investigated, the amount of the iron-complex measured by UV/VIS was around 50% and 35% respectively, in comparison to the signal which has been measured for the same amount of iron and complexing agent in the solution of $FeCl_3$. Only for deferoxamine solution, the efficiency of iron-complex formation was close to 100%, as it was also observed for $FeCl_3$. It could be therefore concluded, that iron bound to compounds present in iron-gall ink could nearly completely be washed-out from the paper by $0.001\ mol\,l^{-1}$ solution of deferoxamine. Also from the visual observation of the paper samples after 30 min of extraction, it was found that the ink colour was weakened. When dibenzoylmethane solution was used, for both iron form ($FeCl_3$ or in the solution of gall ink) the similar type of the dependence of iron–dibenzoylmethane complex formation, measured by UV/VIS, was observed. This in turn means, that such conditions are not sufficient for distinguishing between two forms of iron. Moreover, the iron–dibenzoylmethane complex is coloured and is not easily washed-out from the paper.

In contrary to dibenzoylmethane and deferoxamine, acetylacetone solution (Fig. 1A) shows the most pronounced difference between the behaviour of both investigated forms of iron. This leads to the conclusion that the process of iron–acetylacetone complex formation is not competitive to iron-complex present in iron-gall ink. In fact, after 30 minutes of extraction from the samples with deposited iron-gall ink, the colour of the ink remains unchanged.

Measurements of Total Iron Concentration

In order to get the complete picture of the process, when the sample of paper was immersed into the complexing agent solutions, the GFAAS determination of total amount of iron in the solution was additionally performed (Fig. 2). In the case of acetylacetone and deferoxamine solutions a similar shape of the dependence of the measured signal *versus* time was obtained. This indicates, that nearly the total amount of iron ions washed-out from the paper samples appears in the solutions in the form of the respective complexes. The results were different when dibenzoylmethane was used for $FeCl_3$ deposited onto the paper surface (Fig. 2B). The amount of iron in the solution increased rapidly within 2 min, as parallel measurements by UV/VIS (Fig. 1B) of the amount of iron-dibenzoylmethane complex indicate the much slower reaction. This could be explained by assuming that the process is based on the extraction of iron ions from the paper into the liquid phase followed by the complex formation in the solution and that the rate of iron extraction is slower than the iron-complex formation.

In order to examine whether such a tendency is also valid for two other investigated compounds, both sets of results (UV/VIS and GFAAS) obtained within first minute were compared (Fig. 3). In all cases the slopes

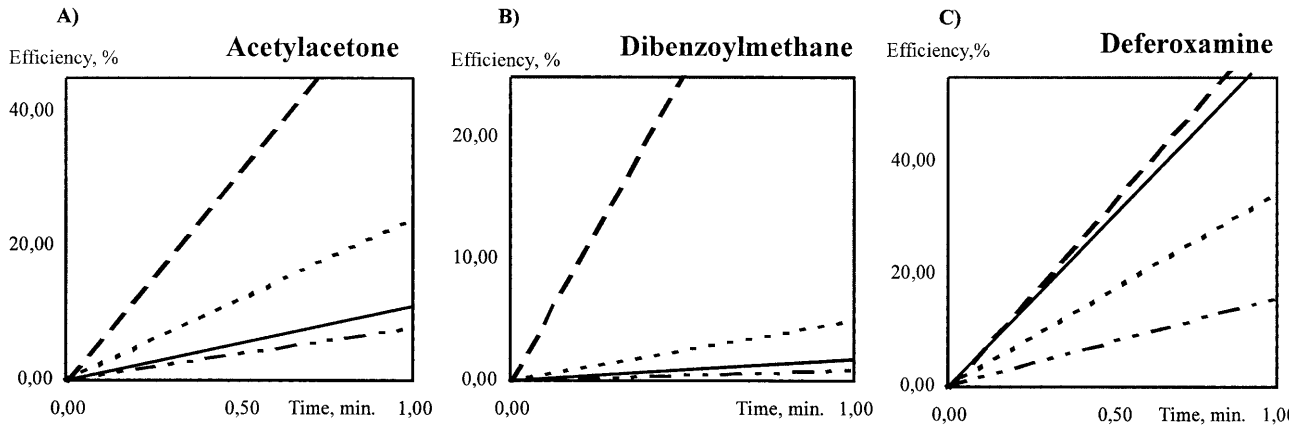

Fig. 3. Comparison of the initial (within the first minute) rate of iron extraction from model samples and iron-complex formation in the solutions: (A) Acetylacetone; (B) dibenzoylmethane; (C) deferoxamine. The model samples were used: (– – –) $FeCl_3$ and (—) gall ink [GFAAS] (· · · · ·) $FeCl_3$ and (–· ·–) gall ink [UV/VIS]

were lower when the amount of iron-complex *vs.* time was measured by UV/VIS, when compared with that for the amount of total iron *vs.* time measured by GFAAS. Most pronounced differences were observed for all investigated complexing agents when iron was added in the form of $FeCl_3$. This means, that in this case, iron ions are extracted from the paper, then they react with the respective complexing agent directly in the solution. The picture is different when iron was introduced in the form of ink solution. Only for deferoxamine the behaviour of iron extracted from the ink is similar to that observed when introduced as $FeCl_3$. The increase of iron concentration is faster than the increase of iron-deferoxamine complex formation in the solution. For two other compounds the difference is much less pronounced.

Conclusions

The rate of iron-complex formation was investigated by UV/VIS spectrometry. Parallel the total amount of iron, washed-out from the paper was determined directly in the solution by GFAAS. It was demonstrated that in all investigated solutions, the process is based on the fast extraction of the iron ions from the paper followed by the iron-complex formation in the solution.

The best behaviour with respect to defined requirements for the conservation procedure was found for acetylacetone solutions. In this case the best selectivity between two forms of iron was observed: acetylacetone was found to form the stable complexes with iron introduced as $FeCl_3$, but was not sufficient to displace iron from the gall ink compounds as it was observed for deferoxamine. The disadvantage, however is, that nearly 20% of residual iron can still be left in the paper sample and participate in the destruction of cellulose.

The described procedure based on UV/VIS and GFAAS measurements was found to be useful for the investigation of the phenomena occurring in the paper with deposited iron solutions used as a model sample of ancient manuscript. Although the investigated ligands could not satisfactorily fulfil the described requirements for conservation treatment, the analytical strategy evaluated in this work will be used for further investigation relating to the conservation of manuscripts endangered by ink corrosion.

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