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Towards a new conservation method for ancient manuscripts by inactivation of iron via complexation and extraction

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Abstract The aim of this work was to study the efficiency of extraction of iron from model paper samples by use of different ligands (deferoxamine mesylate, the potassium–magnesium salt of phytic acid and diethylenetriaminepentaacetic acid) at varied concentrations (0.01, 0.005, and 0.001 mol L^{-1}) and pH (7, 8, 9). Graphite furnace atomic absorption spectrometry (GFAAS) was used to monitor the total amount of iron in solutions of the respective ligands. Two types of model were used to investigate the behaviour of various iron species present in ancient iron-gall ink. Requirements for the optimal procedure, which could possibly be used in the conservation of ancient manuscripts, included high effectiveness of iron extraction from samples which modelled free iron ions (samples "Fe"), while iron deposited in the form of ink (samples "A") should remain without any visible change of the ink's intensity. The best results were achieved with the solution of 0.005 mol L^{-1} diethylenetriaminepentaacetic acid (pH=9), which allowed extraction of 97±1% of iron from "Fe" model samples and only 64±1% from "A" samples.

Keywords Iron-gall ink corrosion · Paper · Iron extraction · GFAAS

Introduction

The chemical phenomenon of iron gall ink corrosion in ancient manuscripts, documents and drawings has been studied very intensively for many years [1, 2, 3, 4, 5, 6, 7, 8, 9]. Acid hydrolysis and after-effects of Fenton reactions were blamed for degradation caused by iron gall inks [10, 11, 12]. It is well known that these kinds of inks were produced by mixing aqueous solutions of iron(II) sulfate with extracts of gall nuts, but usually also variety of different, less important components, were added [13, 14, 15]. The colour of ink originates, according to Wunderlich [16, 17], from the complexes of iron(III) ions with gallic acid and according to Krekel [18] from the complexes with pyrogallol. It was found out that, taking into account the stoichiometry of those compounds, that most ancient iron-gall inks contain an excess of iron [6, 7, 8, 9, 10, 11, 19]. Therefore, it could be expected that iron is present not only in the form of non-organic (for example: ferrous sulfate) or organic compounds (for example: complexes with gallic acid, di-gallic acid or tannins), but as free ions as well. Iron ions present in the ink apart from the complexed form, can act as catalysts and promote the degradation of cellulose by participating in Fenton reactions [6, 10, 12].

The condition of the paper-support in ancient manuscripts depends on a state of cellulose, which can be influenced by several reactions. Iron-catalysed oxidation may occur simultaneously with acid hydrolysis, which can be slowed down by different deacidification procedures [20, 21, 22, 23]. None of the procedures which have been proposed for paper deacidification were sufficient to stop cellulose corrosion caused by iron gall inks [3, 11, 12, 24]. Conservation treatment of ancient manuscripts endangered by ink corrosion should be based not only on neutralising acids but the inactivation of active iron ions as well [10, 25]. Apart from iron other elements, mainly Cu and Mn, were found in ancient manuscripts and can take part in Fenton reactions, leading to the degradation of cellulose [8, 12, 25, 26]. From our previous investigation it is known that they are occurring in much lower concentrations than iron, therefore the inactivation of iron was found to be crucial for conservation of endangered documents [8, 27].

Among various ligands investigated by Graf et al. [28, 29] only few were found to block all available coordination sites at the iron ions, thus preventing the formation of hydroxyl radicals by the Fenton reaction. Phytic acid was then proposed by Neevel [10] to be used in conservation treatment for ancient manuscripts written with iron gall ink. Although phytates were found to have a beneficial effect on samples exposed to ink corrosion, the procedure has some drawbacks [12, 30]. The use of the ligand solu-

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tion has to be followed by a deacidification step, because when used alone the pH of the ligand solution is not sufficiently high to eliminate acid hydrolysis of cellulose. The low solubility of some phytates caused the appearance of a white deposit on the paper surface after the treatment, therefore searching for other ligands was found justified.

Deactivation of iron ions could be achieved either by removing (extracting) active ions from the paper or by stabilising them in the form of very stable complexes. The desired ligands should form stable complexes with iron, preferable easily washed out from the paper. The complexes should be stable in a broad range of pH, however less stable than ink compounds and colourless, so they do not disturb the colour. It is important that the condition of cellulose should not be affected by the treatment and last but not least the procedure should be easy to prepare and apply. The complexation of an excess of iron ions could be followed by its extraction from paper into the washing solution. It would be preferred if the treatment could leave an alkaline reserve in the paper. The ideal ligand would extract nearly the entire excess amount of active iron, as the rest of ions should be left in the form of an inert and stable complex.

The aim of this study was to investigate the behaviour of iron species deposited on the paper support in the presence of chosen complexing agents. Work with ancient Works of Art is subject to a general rule that no harm should be done to the object [31], therefore the introduction of a new conservation procedure also requires its earlier approval with the use of model samples. Several experiments were provided in different conditions in order to find out the best procedure, and the usefulness of chosen chemical treatment for a conservation of ancient objects was examined. The importance of the performed investigations is based on a particular opportunity to use models, which were constructed according to results of previous investigations done for real documents endangered by ink corrosion [8, 27].

Experimental

Instrumentation

An atomic absorption spectrometer model 4100 ZL equipped with transverse heated graphite furnace THGA (Perkin–Elmer, Überlingen, Germany) with longitudinal Zeeman background correction was used. Hollow-cathode lamp for Fe (Narva, Germany) was 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 and samples were introduced into the atomiser with an AS-70 autosampler. The temperature programme for iron determination was used according to manual of the spectrometer. Integrated absorbances were measured.

A pH meter model N-517 (Poland) was used to monitor the pH of ligand solutions.

Chemicals

All reagents used were of analytical grade purity. Diethylenetriaminepentaacetic acid ($C_{14}H_{23}N_3O_{10}$), the potassium–magnesium salt of phytic acid ($C_6H_{15}O_{24}P_6KMg$), and deferoxamine mesylate ($C_{25}H_{48}N_6O_8.CH_4O_3S$; 95%, TLC) were from Sigma–Aldrich Chemie, Hungary, and ethyl alcohol (C_2H_6O) 96% vol. from POCh (Gliwice, Poland). Double-distilled water was used throughout. An iron stock standard solution of $FeCl_3$ containing 1.0 g L^{-1} of iron (Merck, Germany) was used. Working solutions used for the model samples were prepared gravimetrically by appropriate dilution with double-distilled water. Vessels (PP) and micropipette tips were cleaned with 0.1% m/v nitric acid Suprapure (Merck), washed in double-distilled water, and dried before use.

Complexing agent solutions

The aqueous solutions of complexing agents were prepared in double-distilled water at concentrations of 0.001, 0.005 and 0.01 mol L^{-1}. The aqueous/ethanol solutions of diethylenetriaminepentaacetic acid, potassium–magnesium salt of phytic acid and deferoxamine mesylate were prepared at concentrations of 0.005 mol L^{-1}. When required the pH of the solution was adjusted by adding powdered $Ca(OH)_2$ and the pH value of the solution of respective ligands was monitored.

Iron-gall ink solution

Iron-gall ink solution was prepared by mixing 4.20 g of ferrous sulfate p.a. (POCh), 4.86 g of tannin p.a. (POCh) and 3.14 g of gum arabicum (Kaspar, Austria) [27, 32]. Double-distilled water was used to dilute the solution to 100 mL.

Model samples

Model samples prepared on a support of a pure cotton paper, were used to simulate the phenomenon occurring in real artefacts [27]. In order to obtain two types of model samples (later referred as type "A" or "Fe") the set of the paper circles (ϕ=6 mm) was cut-off from the sheet of Whatman No.1 paper and 5 µL of respective solutions was deposited on their surface. Models "A" were created with the solution of a home-made iron-gall ink prepared according to the procedure described above; samples "Fe" were created with the aqueous solution of $FeCl_3$ containing 0.6 g L^{-1} of iron.

All samples were exposed to IR lamp for 15 min and then stored separately in closed vessels (1.5 mL).

Procedure

In order to investigate the extraction efficiency of iron from paper, each sample (type "A" or "Fe") was immersed into the freshly prepared complexing agent solution. In all experiments model paper samples were immersed into 20 mL of the solutions of the potassium–magnesium salt of phytic acid, deferoxamine mesylate or diethylenetriaminepentaacetic acid, for 20 min. Sampling was done every 20 s (within the first minute), then every minute (in the first 5 min) and then every 5 min. After stirring, 100 µL of the solution was taken out of the reaction vessel and the total concentration of iron was determined. GFAAS was chosen because this method allows the determination of a small amount of iron with the use of only minute amounts of liquids. The measurements were done according to the procedure described already by Bulska et al. [32].

Results and discussion

It should be pointed out that the composition of each ancient iron gall ink is unique [33]. Various proportions between chemical species found in artefacts impede theoretical choice of ligands which could be possibly used. In this work the use of models, created on non-sized Whatman

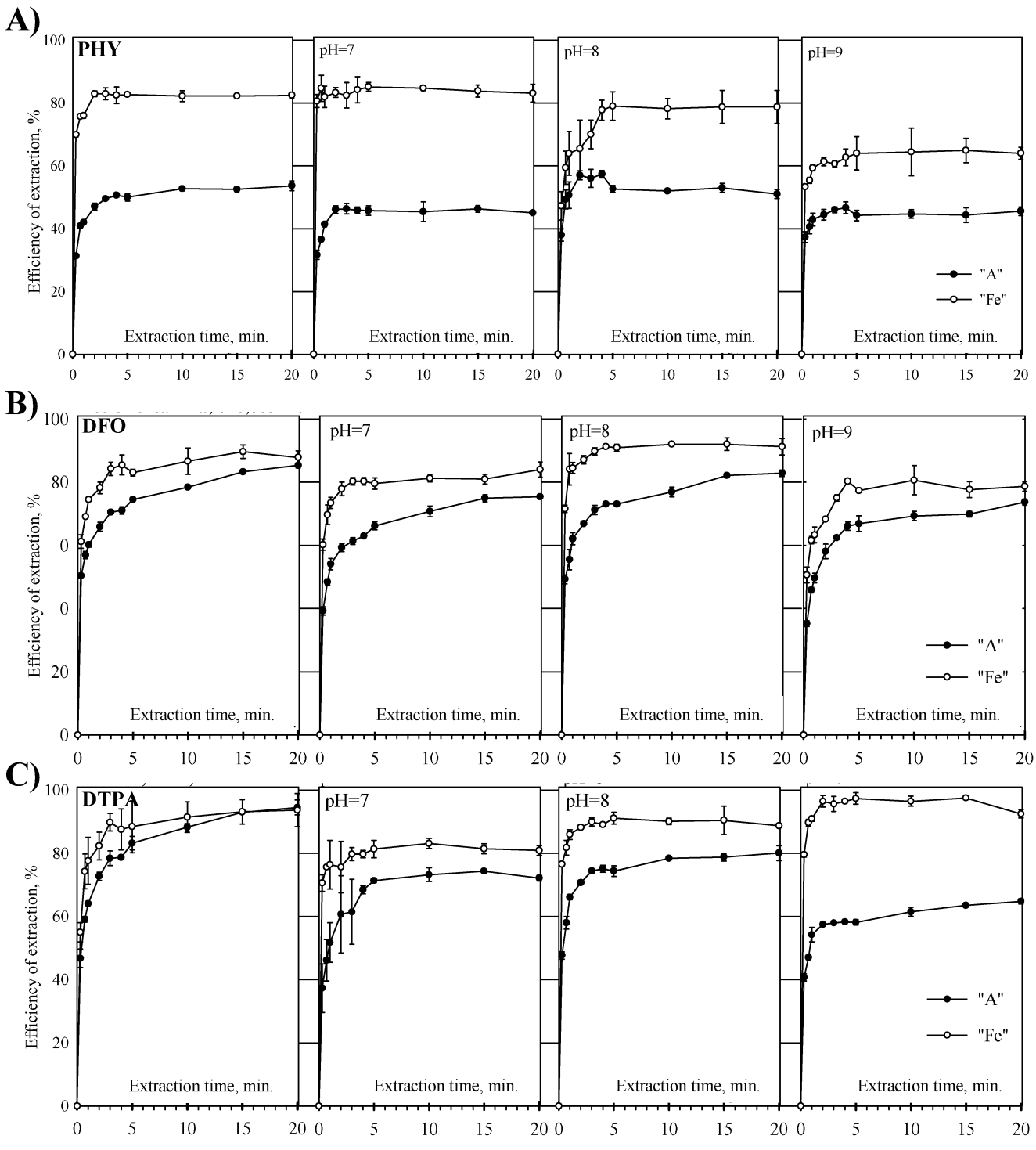

Fig. 1 The rate and efficiency of extraction of iron from "Fe" and "A" model samples into solutions of (**A**) magnesium-potassium phytate (PHY, c=0.005 mol L^{-1}), (**B**) deferoxamine mesylate (DFO, c=0.005 mol L^{-1}), and (**C**) diethylenetriaminepentaacetic acid (DTPA, c=0.005 mol L^{-1})

paper, allowed avoidance of the influence of any modern sizing or other paper additives on the investigated phenomena. As mentioned in Experimental, two sets of samples were prepared: type "A", was supposed to simulate the phenomenon occurring in written parts of ancient manuscripts while type "Fe", was supposed to model non-bound iron ions present in documents.

The preliminary selection of ligands was based on the paper of Graf et al. [28, 29] where the possibility of blocking the catalytic activity of iron was reported. The standard stability constants of selected ligands were as follows: for diethylenetriaminepentaacetic acid: $\log\beta Fe^{2+}L$=16.0, $\log\beta Fe^{3+}L$=27.5, for desferioxamine: $\log\beta Fe^{2+}L$=10.0, $\log\beta Fe^{3+}L$=30.7, and for phytic acid $\log\beta Fe^{2+}L$=18.2,

$\log\beta Fe^{3+}L=29.3$ [33]. It should however be stressed that the value of stability constants could be different in real solutions, as they depend much on pH as well as on the presence of other ions in the environment.

The preliminary investigations on complex formation in the solutions were done with the use of UV–VIS and on the elemental composition of real objects by ICP–MS, as described in our previous publications [27, 32]. Here the rate and kinetics of iron extraction from model samples were studied with the use of chosen complexing agents in varying concentrations, pH and both aqueous or aqueous/ethanol solutions. The main purpose of this work was to choose the most appropriate extraction procedure, which would preferably extract iron deposited in the form of $FeCl_3$ (which means the highest possible efficiency of extraction of iron from samples "Fe") than in the form of ink (which means the lowest efficiency of iron extraction from "A"). In this work special attention was given to the pH of the solutions providing simultaneous deacidification of the paper.

Determination of the efficiency of iron extraction

Although the catalytic activity of other elements (Cu and Mn) could be expected, it is iron which has mainly been described as responsible for the phenomenon of iron gall ink corrosion [6, 7, 9, 10, 11, 12]. Our preliminary investigation of the elemental composition of manuscripts from the XVIth century also proved the much higher concentration of iron than other elements in real documents [8, 27]. Therefore model samples, which have been used for the detailed investigation, were created by use of iron deposited in the form of either $FeCl_3$ or iron gall ink.

The dependence of the measured signals versus time was investigated for all ligands in three concentrations (0.01, 0.005 and 0.001 mol L^{-1}). The range of pH varied starting from that obtained directly after dissolution of ligand in the double-distilled water up to pH=9. The concentration of iron was determined by GFAAS and all absorbance values were related to the absorbance obtained for matrix-matched solutions. These solutions were supposed to contain the total amount of deposited iron that could be extracted from the model samples assuming 100% efficiency [32]. For this purpose 5 µL of the iron solution (as $FeCl_3$ or as iron-gall ink solution) was added to 20 mL of the respective complexing agent. The absorbance values obtained for such matrix-matched solutions were used as a 100% signal, according to procedure described by Bulska et al. [32].

The concentration of iron in complexing agent solutions was monitored within 20 min of extraction (Fig. 1). It was found that in all cases the extraction was almost complete within 5 min;, afterwards the total amount of iron stayed constant within the standard deviation. Table 1 summarises the maximum extraction efficiency and the results refer to the point after 20 min of extraction. All data represent the means for three independent samples. It should be noted that because of the low solubility of phytates at higher pH, calcium salts of phytic acid precipitated and in those cases and the comment "not anal." (not analysed samples) is inserted in Table 1.

The highest differentiation of extraction efficiency from samples "A" and "Fe" should be achieved by washing out nearly the total amount of iron from "Fe" samples, while the extraction efficiency from "A" samples should be as low as possible. The best results were obtained for 0.005 mol L^{-1} diethylenetriaminepentaacetic acid (pH=9), 0.005 mol L^{-1} deferoxamine (pH=8) or 0.005 mol L^{-1} potassium–magnesium salt of phytic acid (pH=7). Diethylenetriaminepentaacetic acid was found to be the best ligand; it could extract iron to a different extent from "A" and "Fe" samples. Almost the total amount of iron was extracted from "Fe" samples, while nearly 45% of iron was still left in "A" samples, when 0.01 mol L^{-1} or 0.005 mol L^{-1} solution was used (Table 1). The 0.005 mol L^{-1} diethylenetriaminepentaacetic acid solution effective at pH=9 was found to be the most convenient, as it gave the possibility

Table 1 The maximum efficiency of Fe extraction into solutions of the chosen ligands

Concentration (mol L^{-1})	Efficiency of extraction from "A" samples (%)			Efficiency of extraction from "Fe" samples (%)		
	PHY	DFO	DTPA	PHY	DFO	DTPA
0.001, pH≤3	62.7±1.0	79.8±1.3	74.7±1.5	74.1±1.0	83.2±1.7	84.3±1.1
0.001, pH=7	57.4±0.5	82.4±0.8	50.9±3.0	61.2±3.0	87.4±1.8	83.1±3.8
0.001, pH=8	48.1±0.4	56.0±3.0	63.2±0.8	67.5±0.5	83.5±2.0	80.3±1.6
0.001, pH=9	51.2±0.7	59.1±1.4	60.6±1.3	79.7±2.0	85.1±1.6	87.0±1.6
0.005, pH≤3	53.6+1.5	85.3±0.8	94.5±2.3	82.4±1.0	87.8±2.0	93.1±3.0
0.005, pH=7	45.0+0.5	75.4±0.3	72.1±0.9	83.1±3.0	84.0±2.0	80.9±1.5
0.005, pH=8	51.1±3.0	82.8±0.3	80.1±2.3	78.8±5.1	91.2±2.3	90.4±2.0
0.005, pH=9	45.5±2.5	85.3±0.8	64.1±1.0	64.0±3.0	87.8±1.5	97.1±1.0
0.01, pH≤3	55.2±1.3	89.9±0.2	93.4±1.5	89.2±2.0	98.8±2.0	96.0±1.0
0.01, pH=7	61.0±2	62.6±1.0	64.6±0.5	80.0±2.6	67.8±1.3	98.7±0.4
0.01, pH=8	"not anal."	65.3±0.4	68.4±2.3	"not anal."	71.8±3.0	89.8±1.6
0.01, pH=9	"not anal."	52.9±0.5	56.7±1.5	"not anal."	67.1±1.3	80.8±0.4

PHY, magnesium-potassium phytate; DFO, deferoxamine mesylate; DTPA, diethylenetriaminepentaacetic acid

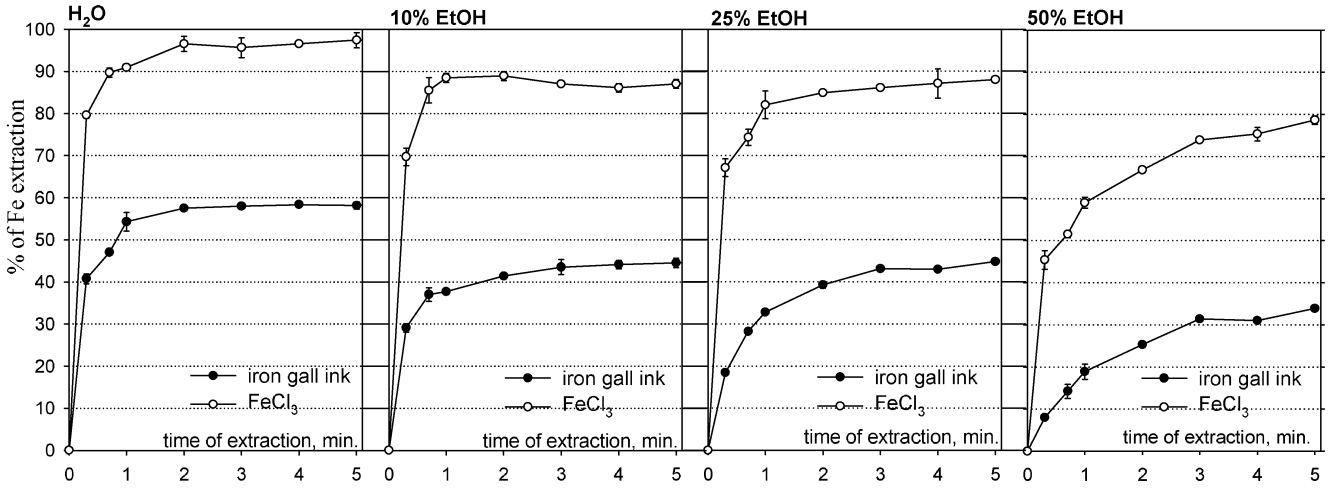

Fig. 2 The influence of ethanol on the rate and efficiency of extraction of iron from "Fe" and "A" model samples into a solution of DTPA (c=0.005 mol L^{-1}), pH=9

of deacidification of the paper in the treatment. Moreover this chelating agent is commonly used in the paper industry, therefore it is expected to be neutral for cellulose [34]. It is important to note that, beside iron, the stability constants for complexes of copper and manganese with this ligand are also high [35]. Both elements, which can also catalyse the degradation of cellulose simultaneously with iron ions would then possibly be inactivated in a side-reaction [34].

Some ancient iron gall inks were found to be soluble in water to a certain degree. To overcome this problem addition of alcohol to the aqueous solutions is recommended in conservation practice [24]. It has been proven that by adding ethanol to the distilled water more uniform migration of soluble compounds from ink could be achieved. Therefore, the possibility of using an aqueous/ethanol solution of diethylenetriaminepentaacetic acid was investigated. Figure 2 shows the influence of increasing the amount of ethanol in the solution of diethylenetriaminepentaacetic acid on its extraction performance. It is clear that the addition of ethanol reduced the amount of extracted iron. The same extraction efficiency as for the aqueous solution could be achieved by using double washing (Fig. 3). Therefore when the addition of ethanol is necessary, the reduction of extraction efficiency could be overcome by the immersion of the sample again in a fresh solution of the ligand.

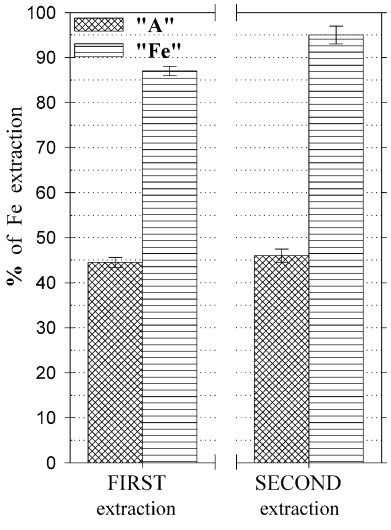

Fig. 3 The efficiency of extraction of Fe from "Fe" and "A" model samples into solutions of 0.005 mol L^{-1} diethylenetriaminepentaacetic acid (pH=9)

Conclusion

Diethylenetriaminepentaacetic acid used at pH=9 was found to be the best ligand among investigated complexing agents, in respect of defined pre-requirements for the conservation procedure. In this case most pronounced differences of the extraction efficiency for two forms of iron, deposited on the surface of "A" and "Fe" model samples, were observed. The extraction of iron by deferoxamine from "Fe" model samples was also satisfactory, but the extraction efficiency from "A" samples was too high, and the use of deferoxamine in consequence influenced the intensity of the ink's colour. The use of phytic acid gave good results, but the value of pH of the solution was too low for conservation purposes.

Diethylenetriaminepentaacetic acid allowed not only extraction of active iron ions from model samples, but deactivation of the residual amount of iron in the form of a stable complex. The pH of the solution was high enough to allow simultaneous deacidification of paper. Although the main scope of this study was to investigate the extraction of iron by different ligands, the high stability constants for Cu and Mn complexes with diethylenetriaminepentaacetic acid were also found to be important. The conservation procedure would only benefit from a side-reaction, such as inactivation of copper and manganese. Therefore, on the basis of results obtained, we can conclude that it is possible to develop a new method, which could slow down corrosive processes in written documents

by extracting part of the iron ions present in the ink, apart from colourful compounds, which are responsible for the visual appearance of a written text.

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