

Bathophenanthroline Indicator Paper

Development of a New Test for Iron Ions*

Due to their catalytic activity in oxidation processes, iron(II) ions are harmful to organic substrates like paper and parchment. The presence of iron ions in artefacts may require treatments to remove or inactivate them. A non-bleeding indicator paper to detect iron(II) ions has been developed. In direct contact with the area to be tested, the humidified indicator paper turns magenta when iron(II) ions are present. Since the indicator Bathophenanthroline is specific for iron(II) ions, iron(III) ions that have migrated to the indicator paper can only be detected indirectly by addition of a reductant to the indicator paper. This is referred to as modified iron(II) test. Suitable (micro) testing procedures are described. Examples of the application of the indicator paper in the field of paper conservation are given.

Bathophenanthroline-Indikatorpapier: Entwicklung eines neuen Tests für Eisenionen

Aufgrund ihrer katalytischen Aktivität in Oxidationsprozessen sind Eisen(II)-Ionen verhängnisvoll für organische Materialien wie z.B. Papier oder Pergament. Das Vorhandensein von Eisenionen in Objekten kann Behandlungen erfordern, um sie zu entfernen oder zu inaktivieren. Ein nicht blutendes Indikatorpapier zur Erfassung von Eisen(II)-Ionen wurde entwickelt. In direktem Kontakt mit dem zu testenden Bereich verfärbt sich das Indikatorpapier magenta, wenn Eisen(II)-Ionen vorhanden sind. Da der Indikator spezifisch für Eisen(II)-Ionen ist, können in das Indikatorpapier migrierte Eisen(III)-Ionen nur indirekt, durch Zufügung eines Reduktionsmittels auf die Reaktionszone des Indikatorpapiers, erfaßt werden. Dies wird als modifizierter Eisen(II)-Test bezeichnet. Geeignete (Mikro-)Testmethoden werden beschrieben. Beispiele zur Anwendung des Tests auf dem Gebiet der Papierrestaurierung werden erörtert.

Paper conservators need to have simple, quick and, preferably, non-destructive methods to evaluate the condition of artefacts, to determine the need for a conservation treatment and to assess associated requirements and risks. One of the things they want to test is the presence of iron ions in paper and other organic materials. Iron ions catalyse the oxidative degradation of organic substrates and they must be regarded as an inherent hazard. The presence of iron ions crucially influences the choice of a conservation treatment.

To detect iron ions, a contact test for soluble iron salts could be conducted with commercially available indicator papers. Unfortunately, these papers apply water-soluble indicators. Therefore, when the humid test paper is brought into contact with an original, the indicator might migrate to the original and develop an unacceptable discolouration in the presence of iron ions. In this publication, development and recommended application techniques of a non-staining indicator paper for water-soluble iron ions, applying the indicator bathophenanthroline, are described.

Sources of Iron Ions in Paper

Water: When derived from an iron-rich source, the water used for producing paper will have contained iron salts that are adsorbed to the paper fibres. This might cause overall or local iron contaminations, which will be perceptible over time as brown discolouration or stains. Closed water systems confront the modern paper maker with the problem of increasing metal ion contents of the water during the production process.

Additives: Non-purified additives that were derived from mineral sources, e.g. fillers like china clay could be contaminated with transition metal ions. This can cause severe formation of brown stains (Fig. 1 a); especially under oxidative conditions (Ligterink et al. 2004). Both, aluminium potassium sulfate and aluminium sulfate could be contaminated with iron ions (Brückle 1993).

Paper making machines: Iron-clad beaters as well as the iron cutting blades of early prototypes of the 'Hollanders', caused the deposition of metal inclusions within the paper (Hey 1988; Fig. 1 b).

Media: Iron containing pigments like Prussian Blue (Ferric Ferrocyanide $\text{Fe}_4(\text{Fe}[\text{CN}]_6)_3$ / Potassium Ferric-Ferrocyanide $\text{KFe}[\text{Fe}(\text{CN})_6]$), yellow/brown/red ochres (iron oxides), Green earth, or inks like iron gall inks (iron[III] tannates) form a source of iron in artefacts (Fig. 1 c). Attention should be drawn to the fact that media can contain iron by secondary sources like iron containing toners or fillers. Also, storage containers might be a source of iron contamination, as described in the case of bistre ink (Burandt 1994).

Sand: Sand, historically applied on fresh inks in order to decrease their drying time, can consist of iron containing minerals like Biotite, Magnetite or Stanekite. Mostly, iron-containing particles are dark-brown or black-coloured, and opaque. Also, pure iron particles can be applied to inks, appearing glittering under raking light (Reißland 2004; Fig. 1 d).

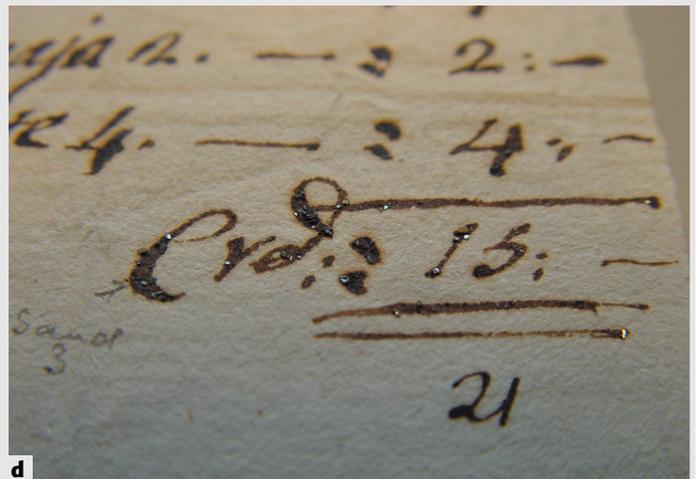
External sources: Iron nails, tacks or staples used to mount objects, iron-contaminated water (e.g. leakage water; Owen 1994), blood stains etc. can be a source of iron in paper.

The Risks of Iron Ions in Paper or Parchment

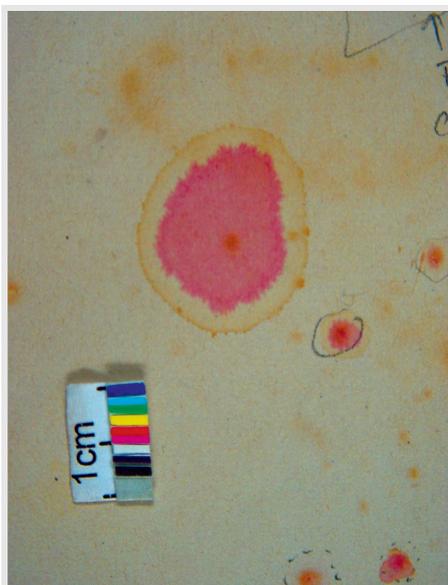
Like most transition metal ions, iron ions are harmful to paper and parchment (Strlič et al. 2003; Banik 1997; Shahani et al. 1986). They can be present in two oxidation states: as iron(II) or as iron(III) ions. Iron(II) ions catalyse the decay of cellulose (e.g. paper) and collagen (e.g. parchment) by promoting the decomposition of pre-formed peroxides to hydroxyl- and alkoxy radicals. Those species initiate the oxidation of the substrate, which results in discolouration and loss of mechanical strength (Neevel 1995). Iron(II) ions can be transported to reactive sites on the cellulose or collagen within the water absorbed to the substrate. Iron(III) ions tend to exist predominately as hydro-

xides, which have low water solubility (Pourbaix 1963). Unfortunately, iron(III) ions can be 'recycled' to iron(II) ions by reducing substances such as cellulose degradation products present in the paper, like low-molecular carbohydrates (Ntshile et al. 1994) or tannic and gallic acid present in iron gall inks (Theis and Singer 1974; Powell and Taylor 1982; Hynes and Coin-

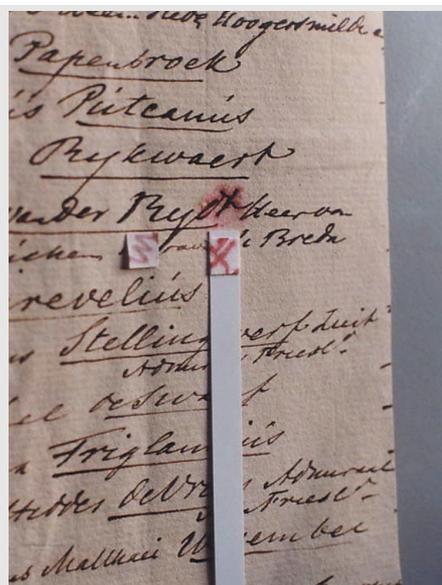
ceanainn 2001). This conversion is accelerated under acid conditions, e.g. those prevailing in iron gall inks (Powell and Taylor 1982). The oxidation / reduction reactions will always continue in the presence of air and reducing substances. Iron(II) ions have to be considered as a direct threat to the permanence of the substrate, whereas iron(III) hydroxides are a future hazard,



1 Sources of iron in paper: Filler used for paper making that has been contaminated with an iron-containing mineral (a); iron particle inclusion with halo (b); iron gall ink (c); 'sand' containing iron particles (\varnothing 150-250 μ m) on an iron gall ink (d).



2 Application of an indicator solution caused a stain.



3 Application of an indicator paper. Staining of the original by a water-soluble indicator (right) in comparison with a water-insoluble indicator (left).

especially when acidity increases. Raised humidity or local wetting of papers contaminated with iron ions will cause migration of soluble iron ions and leads to accumulation of iron salts in the evaporating area, e.g. in the area of tide lines. It has been reported that the use of oxidizing bleaching agents, esp. hydrogen peroxide on originals containing iron ions caused the formation of intolerable brown stains within a period of several months (Ligterink et al. 2004).

Methods to Detect Iron in Paper or Parchment

Analytical Methods

There are several instrumental methods available to detect iron in paper and parchment. μ -XRF analysis (X-ray Fluorescence Analysis; Hahn et al. 2003; Jembrih-Simbürger 2004), EDX-Analysis (Electron Dispersive X-ray Analysis) usually combined with Scanning Electron Microscopy (Stachelberger et al. 1983) and PIXE (Particle Induced X-ray Emission; Del Carmine et al. 1996; Budnar et al. 2003) have been used for analysis of inks on manuscripts. However, these only detect the *total* iron content and they do not give information about the form in which iron is present nor do they discern between the iron(II) and the iron(III) oxidation state. Typical detection limits for XRF are 20 ppm (Bronk et al. 2001) and for PIXE: 2 ppm (Budnar et al. 2003). ESCA (Electron Spectroscopy for Chemical Analysis) provides information about the chemical substance to which the iron is bound and, therefore, is suitable for ink identification (Griebenow et al. 1983). Mössbauer spectroscopy (Darbour et al. 1981; Bulska and Wagner 2002) and μ -XANES (Micro X-Ray Absorption Near Edge Structure; Proost et al. 2004) are the only instrumental analytical techniques that can analyse the relative amounts of the iron(II) and iron(III) oxidation state. While Mössbauer spectroscopy has a relatively low sensitivity and needs large amounts of sample (up to half a page), μ -XANES can be carried out in situ.

In general, the accessibility of instrumental techniques to the paper conservator is usually impeded by high costs, the

necessity to transport the object to the equipment and their low sensibility. Of all these techniques, XRF, EDX, PIXE and μ XANES can be conducted in a non-destructive way, without the need to take a sample of the original.

Indicators

A more convenient method, which can be carried out in any paper-conservation studio, is the application of specific iron indicators. In the presence of water, absorbed to the paper, such reagents form intensely coloured complexes with iron(II) and iron(III) salts. In order to be able to detect iron ions that are part of a complex, like in the case of Prussian Blue, it is important that the iron/indicator complexes to be formed should be more stable than the iron complex to be tested. Historically, many applications of iron indicators are presented in the field of forensic science (Witte 1963; Rhodes 1940). One of the oldest forensic test for iron is mentioned by Plinius the Younger (23-79 A.D.), who described the use of papyrus impregnated with tannic acid for detecting iron in adulterated verdigris (Rackham 1961: 211). In Table 1 some examples of reagents used for the detection of iron ions in iron gall inks are given.

Application Techniques

Indicator solutions: The easiest technique is a direct application of the reagent onto the testing area (one step application). The colour change is observed right away (Fig. 2). This method is applied in situations where damage to the original is not an issue, e.g. testing conservation materials or application in forensic science. If staining of the material is not tolerable, the test must be carried out indirectly by applying a drop of distilled water or, even more effective, in the case of iron ions, a dilute acid solution on the original. The surplus solution containing the dissolved iron ions is soaked up with a blotting paper. The reagent solution is applied onto the blotting paper (two step application). After some seconds, the colour develops in the presence of iron ions (Cunha and Cunha 1971; Snow and Zammit 1987). *Indicator test papers:* The reaction zone of commercially avail-

Tab. 1 Some analytical reagents used for the detection of iron ions especially in inks.

Reagent	Reagent dissolves in water	Specific for	Product formed	Product colour	Product dissolves in water	Application
Tannic acid	Yes	Iron (II) and Iron (III)	Iron(III) tannates (Iron gall ink)	Bluish	No	Indicator solution, one step application (Plinius)
Potassium ferrocyanide	Yes	Iron(III)	KFeIII ₂ (CN) ₆ (Prussian Blue)	Blue	No	Indicator solution (5 % sol.) + 5 % sulphuric acid, one step application (Witte 1963) Indicator solution (1 % sol.) + 5 % acetic acid, two step application (Witte 1963)
Potassium thiocyanate	Yes	Iron(III)	1:1 iron(III)-thiocyanate	Red	Yes	Indicator solution, (1 % sol.) + 5 % acetic acid two step application (Cunha and Cunha 1971)
2,2'-Bipyridyl	Yes	Iron(II)	1:3 iron(II)-bipyridyl	Red	Yes	Indicator solution (1 % sol.) + 1.8 % hydrochloric acid, one step application (Rhodes 1940) Indicator solution (2 % sol. In Ethanol) 5 % acetic acid, two step application (Snow and Zammit 1987) Indicator paper (Merck test), two step application (Haberdtz 1999)

able analytical test strips consists of a highly pure paper that has been impregnated with an indicator. Usually, these test strips are dipped in a sample solution and after a certain reaction time, the colour of the test strip is compared with a colour scale. This application technique can be modified by moistening the test strip with water and pressing it against a surface to be tested. However, if the indicator is water soluble, the risk that the indicator migrates to the original, forming unacceptable stains in the presence of iron ions is quite high. This has been observed with commercially available Merckoquant[®] Fe-Test strips using 2,2'-bipyridil as an indicator (Fig. 3). Therefore, such indicator strips should only be used indirectly on originals by applying a drop of distilled water on the surface and absorbing the surplus solution with a blotting paper which then is brought into contact with the indicator paper (Haberdtzl 1999). This second migration step for iron ions from the blotting paper to the indicator paper might reduce the sensitivity of this test.

It can be concluded, that none of the available methods meets the demands for a regular use on artefacts in a conservation laboratory. In order to make a thorough treatment decision, the detection of the presence of detrimental iron ions is essential for paper conservators. Therefore, a fast, sensitive, cheap, easily interpretable test, that should not require sampling and leave no residues on the object, needed to be developed.

Choice of an Appropriate Iron Indicator

Migration of water-soluble indicators to the artefact can be avoided by using a reagent, which is not water-soluble. In this way coloured products are only formed on the test paper in the presence of iron ions. Consequently, the indicator paper can be applied directly to the surface of an object. Due to the direct contact, such a test is expected to be more sensitive. For iron ions, however, such indicator papers are not commercially available. The literature was searched for an indicator with a low water-solubility, a high sensitivity for iron ions and a low sensitivity for other metal ions. 4,7-Diphenyl-1,10-phenanthroline or bathophenanthroline (Fig. 4) is used in extraction procedures for very sensitive determinations of iron in high-purity non-ferro metals (Penner and Inman 1962). It is a derivative of 1,10-phenanthroline, which in itself is an iron(II) indicator (Schilt 1969). The compound is soluble in ethanol, benzene or acetone, but only sparingly in water. Like 2,2'-bipyridyl (used in the Merckoquant[®] Fe Test), Bathophenanthroline forms a magenta coloured, 1:3 complex with iron(II) ions where 1 iron(II) ion is bound to 3 indicator molecules. Moreover, it has a much higher molar extinction coefficient ($\epsilon = 22\,400 \text{ l} / [\text{mol} \times \text{cm}]$ at $\gamma_{\text{max}} = 533 \text{ nm}$, instead of $\epsilon = 8700 \text{ l} / [\text{mol} \times \text{cm}]$ at

$\gamma_{\text{max}} = 522 \text{ nm}$) than 2,2'-bipyridil (Schilt 1969). Therefore, Bathophenanthroline is about 2.6 times as sensitive as 2,2'-bipyridyl.

The magenta coloured complex has a very good colour stability, even over years (own observation). It has a very low solubility in water, but easily dissolves in a range of organic solvents, e.g. ethanol, isoamyl alcohol, isoamyl acetate, chloroform and n-hexanol, with which it can be extracted from the aqueous phase (Schilt 1969). The complexation is specific for iron(II) ions, which can be determined even in the presence of a high excess of iron(III) ions (Schilt 1969).

Because of its high sensitivity and specificity for iron(II) ions, the low water solubility of the compound itself and its iron(II) complex, bathophenanthroline was chosen as the most suitable indicator for the preparation of a non-bleeding indicator paper for iron(II) ions.

Modification to Detect Iron(III) Ions

As already stated, bathophenanthroline only forms complexes with iron(II) ions. Iron(III) ions, migrating to the test strip during its contact with the tested area, are not detected. To be detected, they have to be reduced to iron(II) ions, which can be achieved by applying a solution of a reducing agent to the strip after it has been in contact with the tested area. Reducing agents can be acid compounds, e.g. ascorbic and citric acid, or neutral compounds, e.g. sodium dithionite.

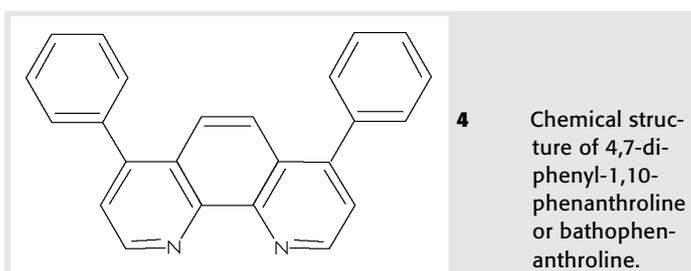
Care should be taken, as also water-insoluble, iron-containing substances, like iron gall ink, Prussian blue, iron(III) oxide or iron(III) phytate can be transferred to the test strip. Adding acid reducing agents can release iron(III) ions from such substances. After reduction, they will be detected as iron(II) ions. If the test is intended to detect only free iron(III) ions, a neutral reducing agent should be chosen.

Materials and Methods

A test batch of indicator paper was prepared by impregnating filter papers (589/2, Ø 70 mm: Schleicher & Schuell) with a solution of bathophenanthroline (Fluka, p.a.) in ethanol (Nedalco, 99.9%), containing 1.6 g/l of the indicator. With a capillary pipette 10 drops of this solution were placed on the centre of the filter paper with in-between evaporation of the solvent. To be able to retrace it, the border of the impregnated part was marked with a pencil. Later, a larger amount of indicator paper was prepared by the German firm Schleicher & Schuell. In one batch process, 4.3 m² of filter paper were impregnated by immersion in a solution of bathophenanthroline in ethanol (1.6 g/l). The surface concentration of the indicator was about 1 g/m².

Micro Testing Procedures

The bathophenanthroline indicator papers were applied to define the most suitable testing procedures. Originals where the presence of iron(II) ions was expected—e.g. metal inclusions, foxing stains, tide lines and iron gall inks—were tested before, and the ink corroded papers also during and after treatment, applying the indicator paper on the original's surface. The bathophenanthroline indicator paper has also been used to test



aqueous treatment solutions aiming for the removal or immobilisation of iron(II) ions. The recommended procedures are described here:

Detection of Iron Ions in Solution

The test can be used in order to find out if a treatment solution (e.g. tap water) is contaminated with iron ions. Furthermore, the efficacy of a treatment can be tested by determination of iron ions that dissolved in the treatment solution during treatment.

Needed equipment: Iron(II) indicator paper, pair of scissors (stainless steel), tweezers (stainless steel or plastic), blotting paper (filter paper, ash free).

Procedure: A piece of indicator paper is dipped into the treatment solution for some seconds until it is fully wetted. It should be blotted and placed on a white support such as filter paper. The colour will intensify and be complete after 2-5 min. To get an estimation of the iron(II) concentration in solution, the strip can be compared with a colour chart developed by the Canadian Conservation Institute (Vuori and Tse in press).

Detection of Iron Ions on Surfaces

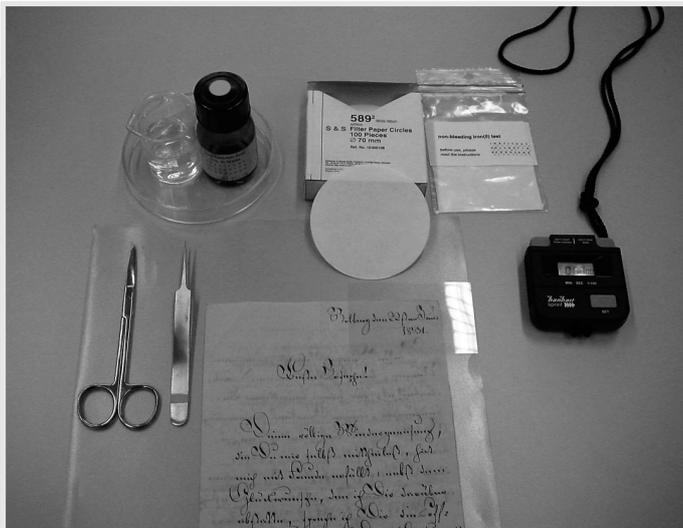
All kinds of surfaces like paper, parchment, media, inks can be tested for the presence of iron ions. Recently published studies confirmed that the bathophenanthroline indicator paper is quite

useful to test textile surfaces of cellulosic-, silk- or acidic collagen fibres (Vuori and Tse in press). Also, the test is quite useful for testing if tools are stainless steel or if they are contaminated with soluble iron salts.

Needed equipment: Iron(II) indicator paper, distilled or deionised water, ascorbic acid (1 % w/w aqueous solution), pair of scissors (stainless steel), tweezers (stainless steel or plastic), inert plastic foil (Mylar, Melinex), blotting paper (filter paper, ash free), pipette and a timer (Fig. 5).

Procedure: The object should be placed on an inert, clean support like glass or plastic. To reduce the contact area between indicator paper and original, the size of the test strip should be kept to the minimum, which can be handled conveniently, preferably a triangle. Then, the indicator paper is dipped in distilled water using stainless steel tweezers. The excess water is removed by blotting the strip on filter paper—the indicator paper must be damp, not wet. This step limits the risk of water stain formation on the object. The damp indicator paper is placed on the area to be tested (e.g. an iron gall ink line)—attention should be paid that one part covers the testing zone, while the other part covers the blank paper. Then the test strip must be covered with a piece of inert plastic foil (Fig. 6 a) which is gently pressed down on the support for 30 s, using a weight or just a finger (Fig. 6 b). During this period, soluble products (e.g. Fe(II) ions) migrate into the test paper. After 30 s, the indicator paper should be removed from the object and placed on a white support like filter paper. The colour change is followed visually during drying. The colour will intensify and be complete after 2-5 min. A magenta coloured complex is formed if iron(II) ions are present. For indirect determination of iron(III) ions, the test is modified: a drop of ascorbic acid (1 % w/w aqueous solution) is applied on the indicator paper (Fig. 6 c). For interpretation of the colour change, again, the indicator paper should be placed on a white support (filter paper). During drying, any iron(III) ions present, are reduced to iron(II) ions. The extra iron(II) ions produced will react with the indicator, leading to an intensification of the magenta colour (Fig. 7).

If a comparison between the direct iron(II) test and the modified iron(II) test is wanted, initially the test strip should be cut larger. While the direct test is carried out on the whole test strip, it is cut in the middle after the colour change (Vuori and Tse in press). The modified iron(II) test is carried out just on one half (Fig. 7 and 9 b). Both pieces are compared after the colour has developed fully.



5 Equipment for detection of iron ions on surfaces: Iron(II) indicator paper, distilled or deionised water, ascorbic acid, pair of scissors, tweezers, inert plastic foil, blotting paper, pipette and a timer.



6 Determination of iron ions on surface test strip covers half the ink, half the blank paper (a); gently press down the Melinex using a finger (b); a drop of ascorbic acid is added to the indicator paper (c).

Detection of Iron Ions on Surfaces during Treatment

In order to judge if a treatment has been successful or if it has to be repeated, originals can be tested during treatment. The procedure is different from the surface determination on dry surfaces. *Needed equipment:* Iron(II) indicator paper, pair of scissors (stainless steel), tweezers (stainless steel or plastic), blotting paper (filter paper, ash free).

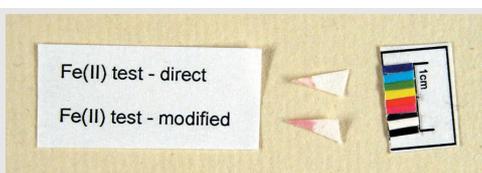
Procedure: A piece of indicator paper should be cut. The object must be lifted a bit out of the treatment solution. The *dry* indicator paper is brought into contact with the testing area. Some treatment solution is absorbed by the test strip (Fig. 8). In this way, the risk of transferring the indicator onto the object is negligible. The indicator paper should be immediately removed from the object and placed on a white support like filter paper. The colour will intensify and be complete after 2-5 min. For indirect determination of iron(III) ions, a drop of ascorbic acid (1 % w/w aqueous solution) is applied on the indicator paper. For interpretation of the colour change, the indicator paper should be placed on a white support (filter paper). The modification of the test using ascorbic acid should not be carried out for Ca-Phytate treatments, since the low pH of the ascorbic acid solution destroys iron(III) phytate complexes, causing a misleading positive result.

Interpretation

If the indicator paper turns magenta, iron(II) ions are present in the tested area. The intensity of the magenta colour formed on the indicator paper depends on several factors—some are directly related to the testing area of the object, others to the test method. Factors that are inherent to the testing area are (1) the concentration of iron(II) ions present, (2) its pH, since higher acidity causes more iron salts to dissolve (Fuori and Tse in press) as well as (3) its wettability. For instance, foxing stains or tide-lines have an increased wettability in comparison to the surrounding areas, causing more water to be present as solvent for iron ions. Factors that are inherent to the testing method are especially (1) the amount of water applied, (2) the contact time and (3) the contact pressure. Therefore, under non-standardised circumstances, a contact test cannot be used as a quantitative test.

It should be noticed, that the argumentation can not be reversed. A negative test result does not necessarily mean that no iron is present. It can also implicate that (1) iron ions were hindered to migrate into the test strip (for instance iron ions were 'trapped' under a surface sizing film, or the binding media prevented a migration) or (2) iron-containing substances which migrated into the test strip did not react with the indicator (for instance some iron oxides might not react; Fuori and Tse in press).

7 Result of the direct test (above), intensified after adding ascorbic acid (below)



Caution / Interference

Obviously, only stainless steel tools / equipment should be used and any contact with iron and rust must be avoided. The test strips should not come in contact with bare fingers. The indicator is soluble in organic solvents like ethanol, therefore any contact with such solvents should be avoided. Interference of the reading is expected from water-soluble, coloured substances like paper- or ink degradation products or coloured additives (e.g. dyes like logwood) that could migrate to the indicator paper and disturb the observation of the magenta colour. As the coloured iron(II) bathophenanthroline complex is not soluble in water, these interfering substances can be removed by rinsing the strip with distilled water.

Shelf Life

After four years, we discovered a slight yellowing of the test strips and a decreased wettability. Anyway, testing the same iron-containing solution using old and new strips, the results proved to be comparable. The function of the bathophenanthroline indicator paper can be conveniently checked by conducting the test on a rusty nail or staple.

Fields of Application

Iron Gall Inks

The test is very useful for objects containing iron gall ink (Fig. 1 c). 126 inks on manuscripts from the possession of the National Archive (Den Haag, The Netherlands) and 60 drawing inks on master drawings from the collection of the Teylers Museum (Haarlem, The Netherlands) dating between the 16th and the 20th century, all of Dutch origin, were tested. Those tests showed no correlation between the state of ink corrosion and the presence or absence of iron(II) ions (Reißland 2004). This is in contradiction to the fact, that iron has indeed a significant detrimental effect on the stability of cellulose (Strlic et al. 2003: 622). Recently, Kolar et al. determined that papers show a strong decrease in Degree of Polymerisation (DP) until an iron content of 35 mmol g⁻¹ is reached. Further increase in iron content did not decrease the DP any further (Kolar et al. in press).



8 Determination of iron ions on surfaces during treatment using a dry indicator paper..

Interestingly, 90 % of the manuscript inks tested positive for iron(II) ions. Adding ascorbic acid to the test strips even increased this number to 96 %. Therefore, the test is considered to be indicative for the presence of iron ions in manuscript inks. Testing the drawing inks showed that only 15 % tested positive for the presence of iron(II) ions, while 70 % tested positive after adding ascorbic acid. Since the identification of non-corroded brown drawing inks remains still a problem, some selected drawing inks of good condition could have been based on non-iron containing inks like bister or sepia. Interestingly, six very corroded drawing inks did not test positive. Assuming, that these objects at least contained some iron ions, this could be an indication that the testing procedure was carried out more carefully (less water, lower pressure) for drawings than on manuscripts.

Metal Inclusions and Rust Stains

Inclusions of metal particles (\varnothing 0,5-1 mm) in five 17th and 18th-century rag papers tested positive for iron(II) ions (Fig. 9 a). Also, rust stains can be tested for the presence of iron ions (Fig. 9 b).

Foxing and Brown Stains

Analysis by Hey (1988) proved that some foxing stains contain high iron concentrations. Application of the iron(II) indicator paper supported her results. Iron(II) ions were positively identified in several foxing stains in different 18th and 19th-century rag papers. In the case of a contemporary art object, dating from 1992, iron ions were detected in brown stains (Fig. 1 a) by applying the bathophenanthroline test strips. The stains occurred some months after an oxidative bleaching treatment using hydrogen peroxide. The presence of iron was confirmed by SEM-EDX and XRD analysis (Ligterink et al. 2004).

Tidelines

A tideline on a 19th century lithography tested negative for iron(II) ions. However, when the indicator paper was dipped in an ascorbic acid solution, a magenta colour developed, indicating the presence of soluble iron(III) salts in the tideline (Fig. 9 c).

Treatment Evaluation

Besides applying the iron(II) test on untreated objects, the test can also be applied to follow the removal of soluble iron salts by a conservation treatment and to decide whether the treatment has to be repeated or not. Fig. 8 gives an example of application during a treatment. Eusman (2002) applied the indicator paper to compare the effects of different application techniques of aqueous solutions on the migration behaviour and removal of

iron(II) ions from iron gall inks. He considered the test to be very useful. Kolbe (1999) and Huhsmann (2000) used the prepared indicator papers to follow the iron(II) migration in originals during artificial ageing and different aqueous treatments. They also sprayed a 0.1 ethanolic solution of bathophenanthroline directly on their samples.

A positive identification of iron (II) ions means the presence of an intrinsic threat to an object. This has definite consequences in the choice of conservation treatments for the object. Research confirmed that a small amount of moisture is able to promote the migration of iron(II) ions in the porous paper support, causing spreading of soluble iron and the degradation they induce (Eusman 2002: 127-129). Therefore, all moisturising treatments have to be considered to be very hazardous to objects that contain free iron(II) ions, when not combined with a treatment that completely removes or deactivates these ions (Reißland 2001). Iron(II) ions are water-soluble and can partly be removed by immersion, spraying on a suction table or local washing techniques. In order to deactivate iron(II) and iron(III) ions, they can be complexed by phytate (Neevel 1995). This complexing agent has been proven to inhibit radical formation. The use of any oxidative bleaching agent strictly should be avoided, as these enhance the oxidative degradation in the iron-containing areas (Ligterink et al. 2004).

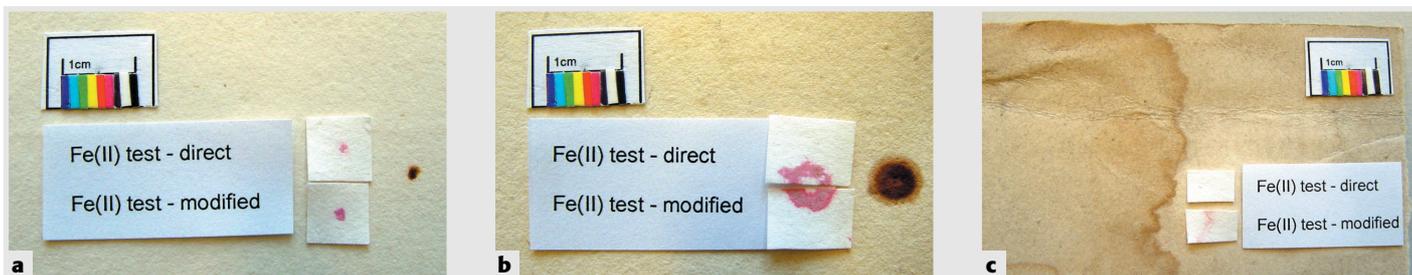
Conclusions

The Bathophenanthroline indicator paper for soluble iron(II) ions is a useful tool for the paper conservator to evaluate the condition of objects, and to identify the objects at risk and therefore in need for removal of the catalytically active iron(II) ions. The indicator paper can be applied directly to the area to be tested without the danger of staining the original. In the presence of iron(II) ions, the indicator turns magenta. Because iron(III) ions can easily be reduced to iron(II) ions in paper, they form a potential hazard to the original. By adding ascorbic acid to the indicator paper, iron(III) ions can be indirectly detected as well.

Apart from using the test to identify the presence of iron ions on surfaces, it can be used to follow the progress and efficacy of various treatments to remove iron ions.

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9 Examples for testing the presence of iron(II) ions on paper: metal inclusion (a); rust stain (b); tideline (c).

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Endnote

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Suppliers

Preservation Equipment Ltd, Vines Rd, Diss, Norfolk, IP22 4HQ, United Kingdom, Tel. +44-1379-647400, Fax +44-1379-650582. www.preservationequipment.com (Bathophenanthroline test paper: Product referred to as 'Iron Gall Ink Test Paper', Product Code 539-3000, package containing 100 strips 75 x 10 mm).

Fluka Chemie GmbH, Industriestr. 25, 9470 Buchs, Switzerland, Tel. +41-81-7552511, Fax +41-81-7565449, for local suppliers: see website www.sigma-aldrich.com (Bathophenanthroline, puriss.p.a. Product No. 11880; Ascorbic acid, puriss. p.a., Product No. 95210; Citric Acid, puriss. p.a., Product No. 27488, Sodium dithionite, referred to as "Sodium hydrosulfite", BioChemika, > 85 %, Product No. 71699).

Schleicher & Schuell GmbH, Postfach 4, 37582 Dassel, Germany, Tel +49-5561-791676, Fax +49-5561-791583, www.schleicher-schuell.de (Filter paper, Product No. 10 300 108, Grade 589/2, White band, round filter, Ø 70 mm).

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