IRON GALL INK CORROSION OF HISTORICAL DOCUMENTS PROBED BY X-RAY PHOTOELECTRON SPECTROSCOPY

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Preservation Science Symposia
New Research on Iron Gall Ink

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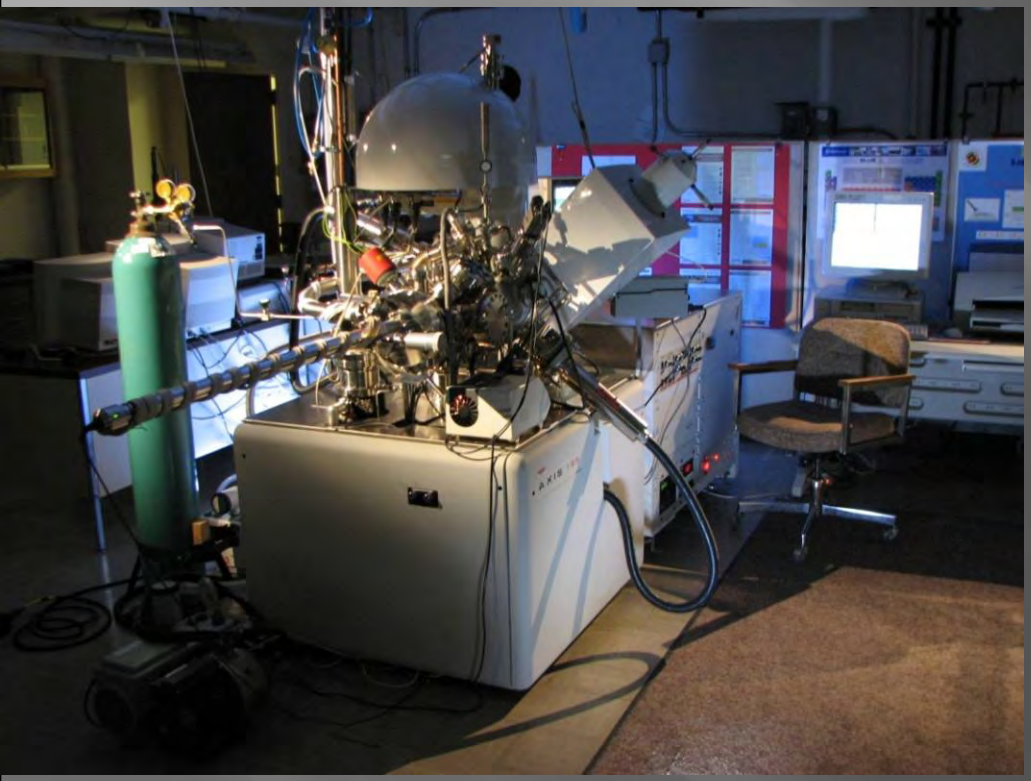
Outline

- X-ray Photoelectron Spectroscopy
- Part 1
  - XPS study of an 18th century Italian document
- Part 2
  - XPS clues regarding the chemistry of Iron Gall ink
  - Mossbauer

X-ray Photoelectron Spectroscopy (XPS)

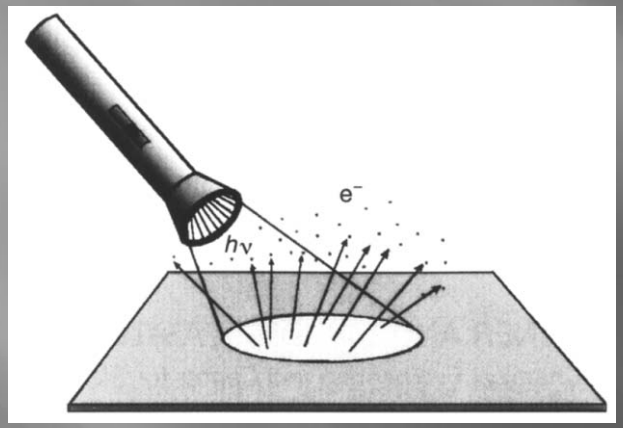
Kratos Axis 165



- Surface sensitive up to 10nm into surface
- Quantitative Information
  - Peak area α atomic % composition
- Qualitative
  - Peaks shift with change in oxidation state or chemical environment

X-ray Photoelectron Spectroscopy (XPS)

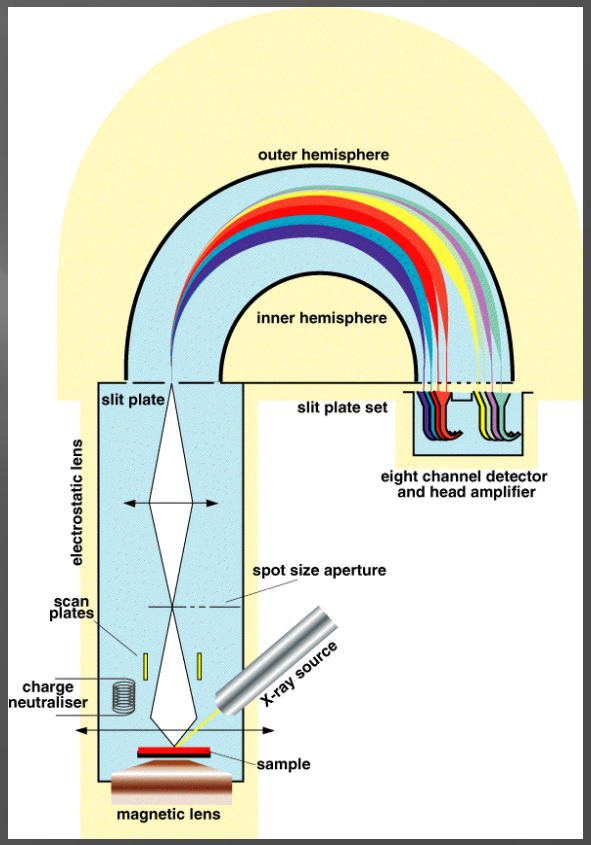
Photoelectric Effect



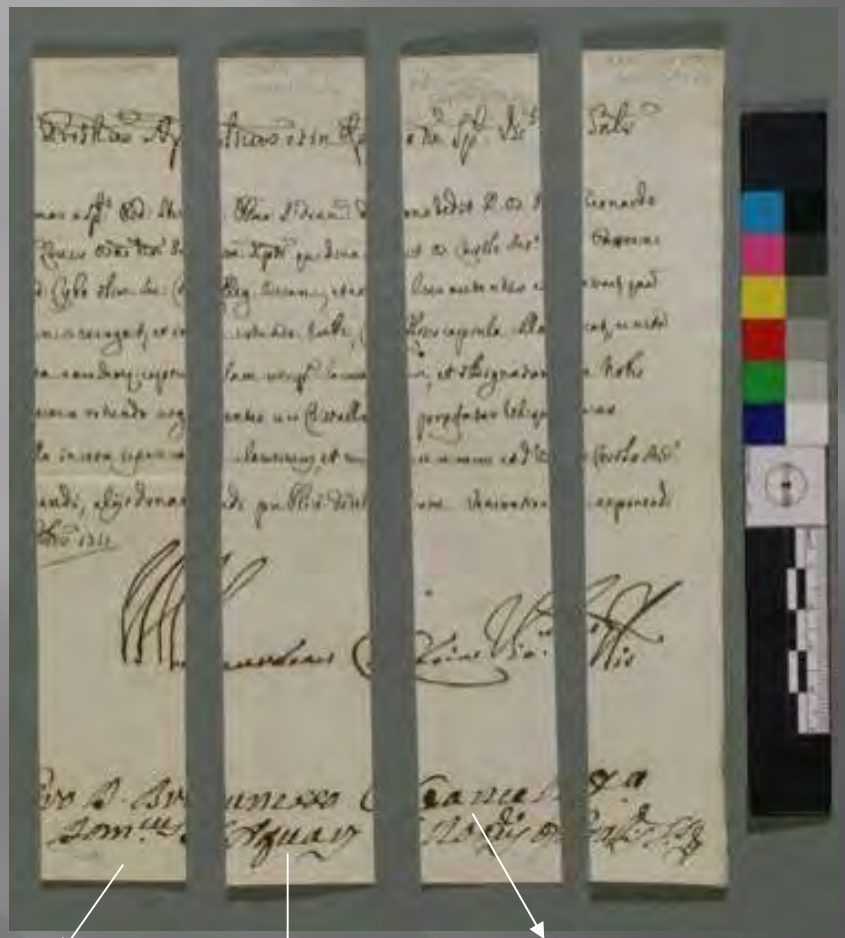
$$KE = h\nu - (E_B + \varphi)$$

Al Kα = hν = 1486.6 eV

Instrument Schematic



Preliminary Analysis of IGI by and XPS



control

Washed, de-acidified

+ phytate treatment

18th C Italian test document

(not LC coll.)

Treatments

- Washing + de-acidification (WD)

(calcium bicarbonate)

- Washing + de-acidification + phytate (WDP)

(calcium phytate)

Degradation Mechanisms

Two generally accepted mechanisms for the depolymerization of cellulose

1) Acid-catalyzed hydrolysis
   - Ink pH ~1.8-2.2
2) Iron(II)-catalyzed oxidation;

Formation of organic radicals:

$Fe^{2+} + O_2 \leftrightarrow Fe^{3+} + OO\bullet^-$

$Fe^{3+} + OO\bullet^- + RH \rightarrow R\bullet + HOO\bullet + Fe^{2+}$

Subsequent Oxidation

$R\bullet + O_2 \rightarrow ROO\bullet$ and $ROO\bullet + R'H \rightarrow ROOH + R'\bullet$

Production of H_2O_2

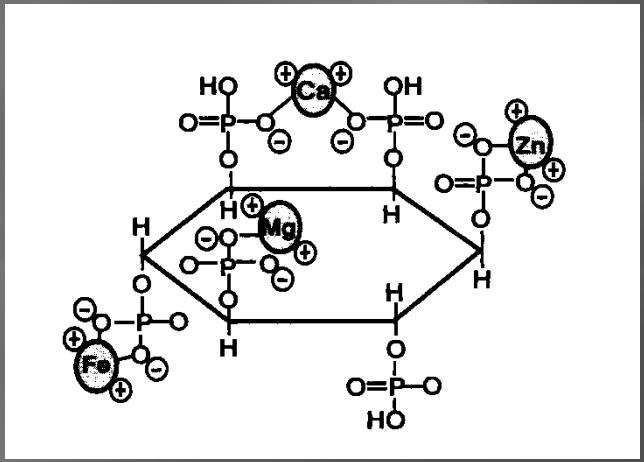
$Fe^{2+} + HOO\bullet + H^+ \rightarrow Fe^{3+} + H_2O_2$

Fenton Reaction

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+}\ HO\bullet + OH^-$

Deacidification and Phytate Treatments

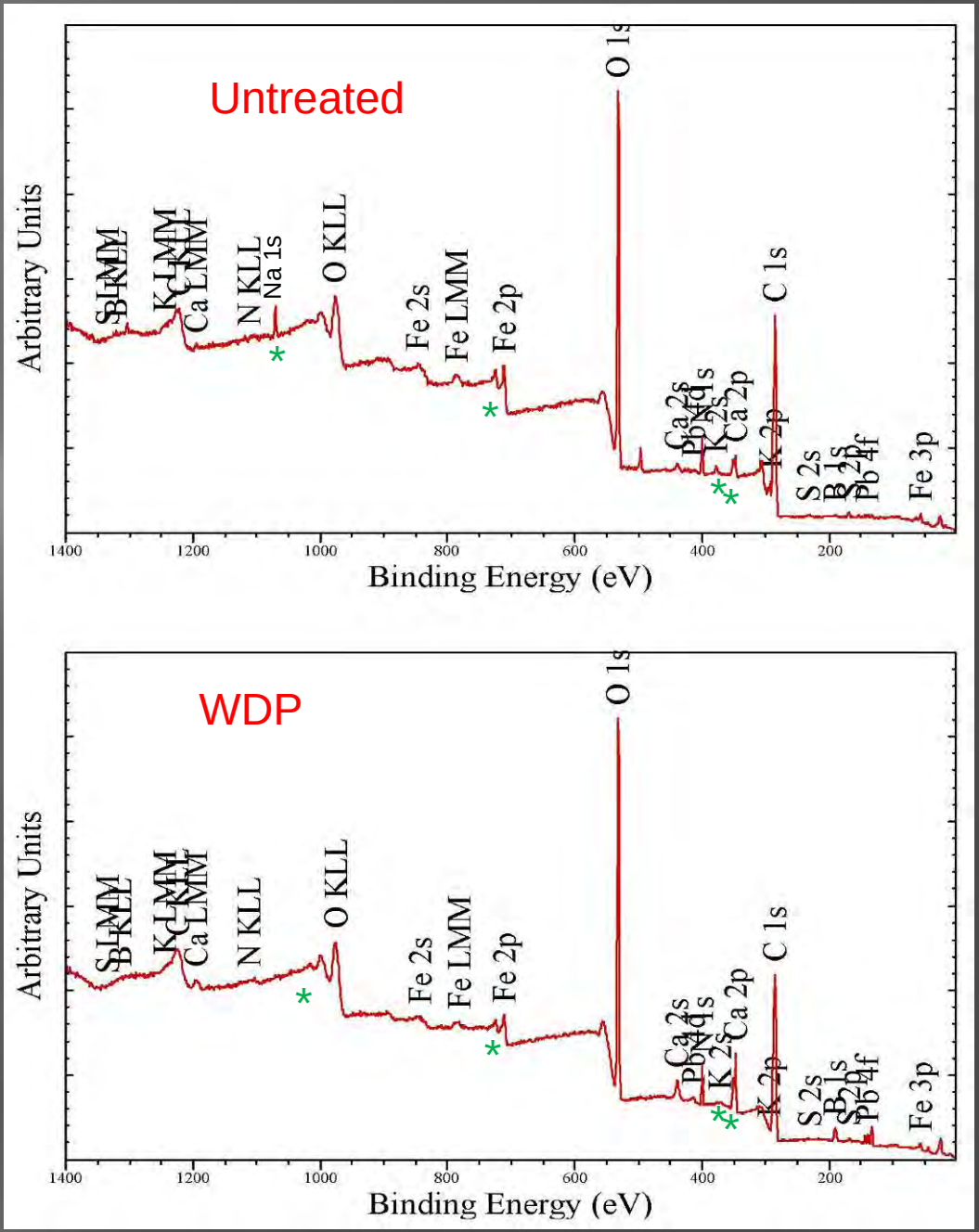
- Deacidification: Magnesium or calcium bicarbonate
- Phytate treatment: Magnesium or calcium Phytate



Johan Neevel, “Phytate: a potential conservation agent for the treatment of Ink corrosion caused by iron Gall Inks, *Restaurator* **(1995), 16, 143-160**

Ink Survey Spectra

- Na and K disappear after treatment
- Ca signal increases after treatments
- Fe signal decreases after treatments



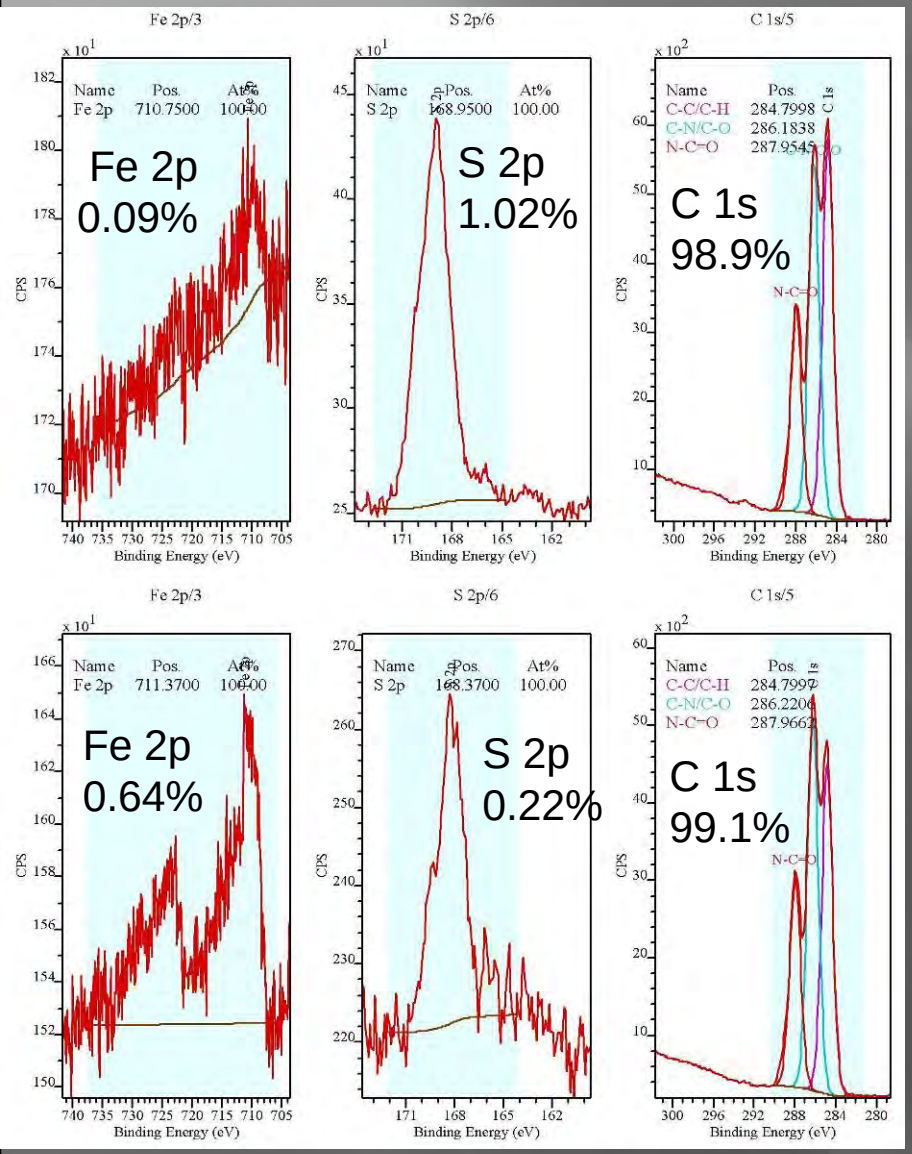
XPS Quantification of 18th C Italian Inks Before and After Treatments

Sample	Fe/At%	S/ At%	Fe/S	C/Fe
1:1 FE:GA fresh ink	8	10.2	0.8	-
Fe2(SO4)3, (ferric)	5.8	15.3	0.4	-
FeSO4, (ferrous)	12.5	14.8	0.8	-
Untreated	3.4	0.4	8.9	18.2
WD	2.0	0.2	8.9	31.4
WDP	2.1	0.3	8.4	27.9

- Large decrease in sulfate species ink on paper and with aging
  - Where does sulfur go? (answered in the next slide)
- Significant decrease ~40% in surface iron concentration after treatments
  - Iron washed away, chelated or organic residue left behind
- The C:Fe =~18 in untreated inks, after treatment C:Fe=~30.

  Iron concentration at the surface of the historic ink has reduced by ~40% after treatments, consistent with Fe^{+2} indicator results?

What about the Paper?



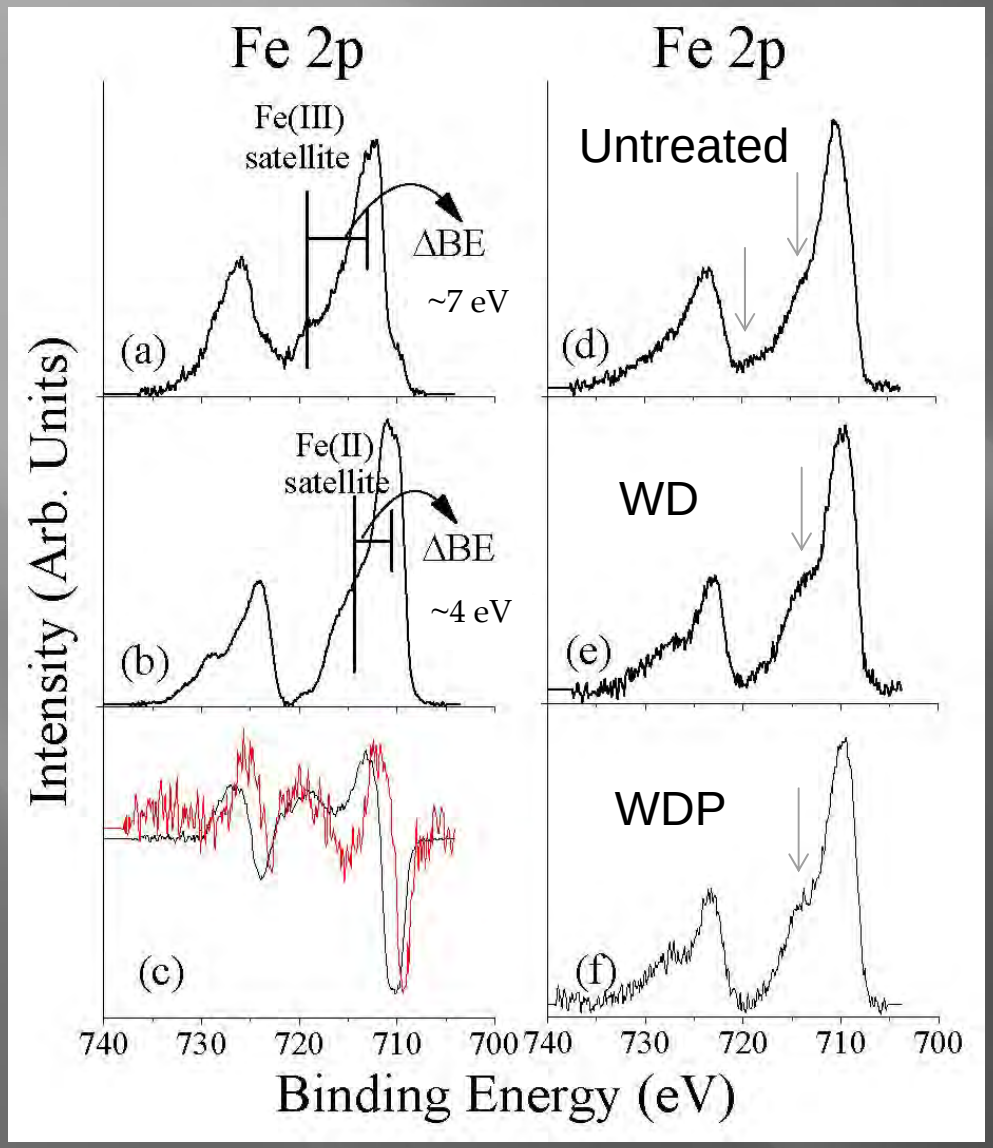
Untreated
Fe/S=
0.09

WDP
Fe/S=
2.9

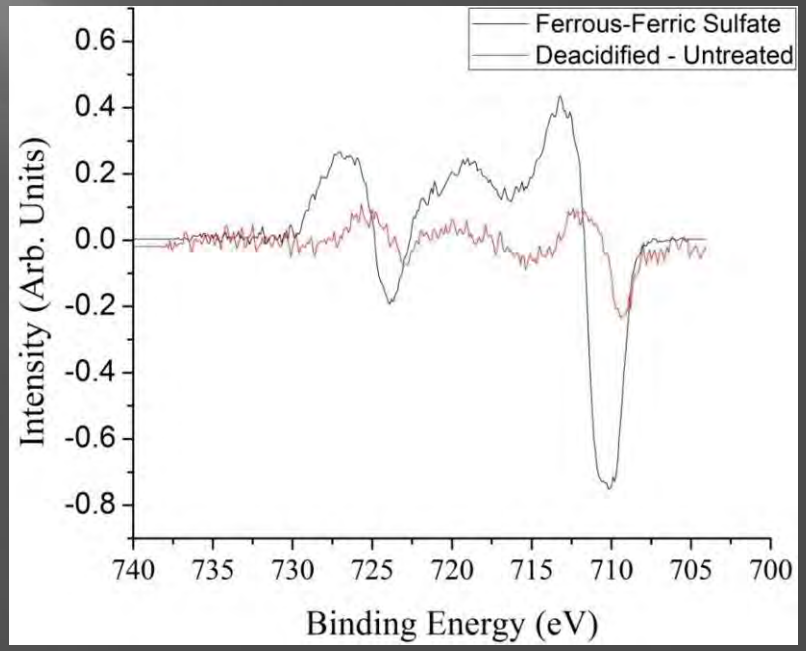
- XPS was taken at ~ 2mm Away from the ink line
- Paper was found to be sized with gelatin – significant nitrogen concentration
- Sulfur in the form of sulfate (~168.9 eV has migrated through the paper)
- Sulfur is removed from paper during treatments
- Iron concentration in paper is Increased after treatment by ~ 7x

Not desirable!!!

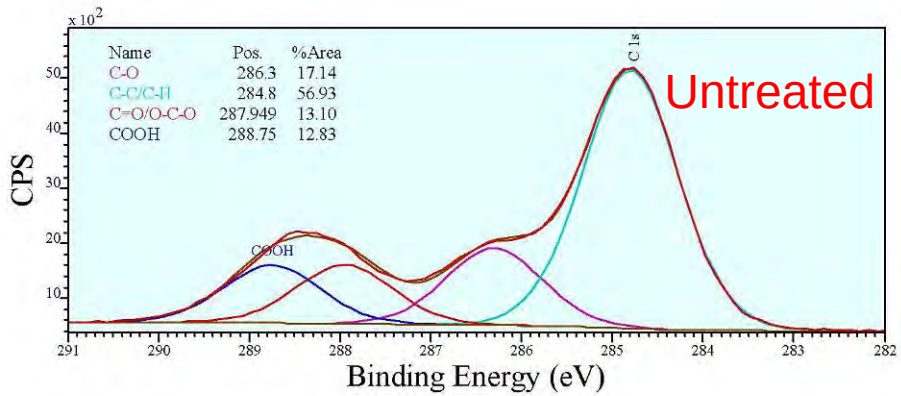
XPS of Ink – Fe 2p

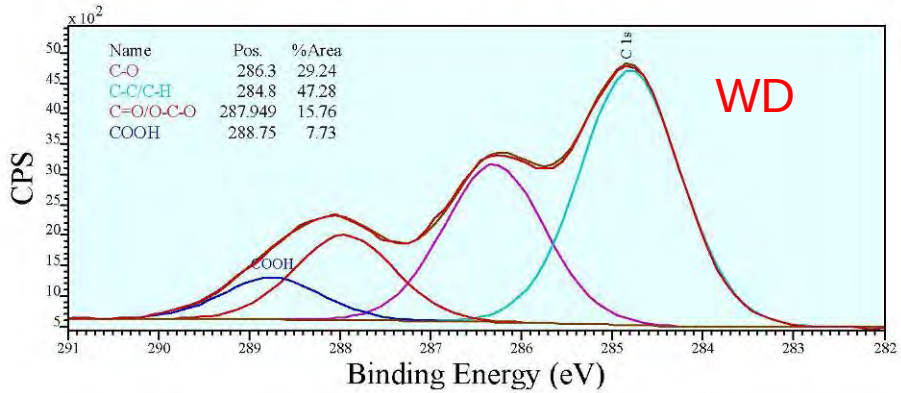


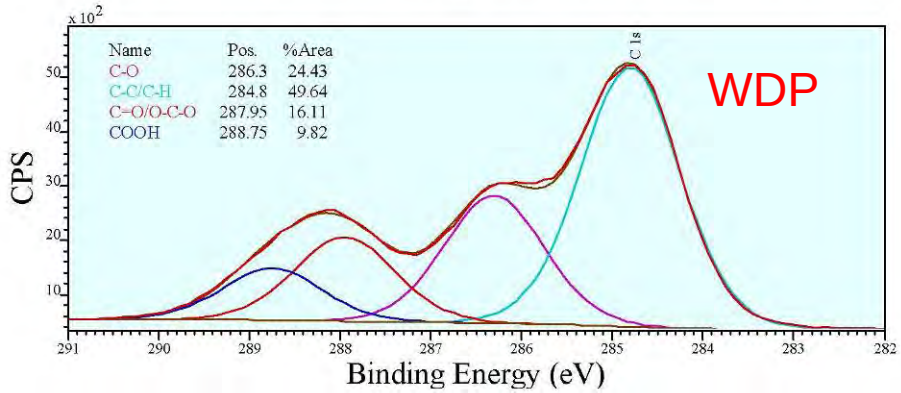
- Rough estimate of increase in Fe(II) / Fe (III) ratio based on Spectral subtraction is ~10% +/- 5%
- Perhaps surprising that the remaining iron has a greater Proportion of Fe^{2+}



Organic – Historic Ink







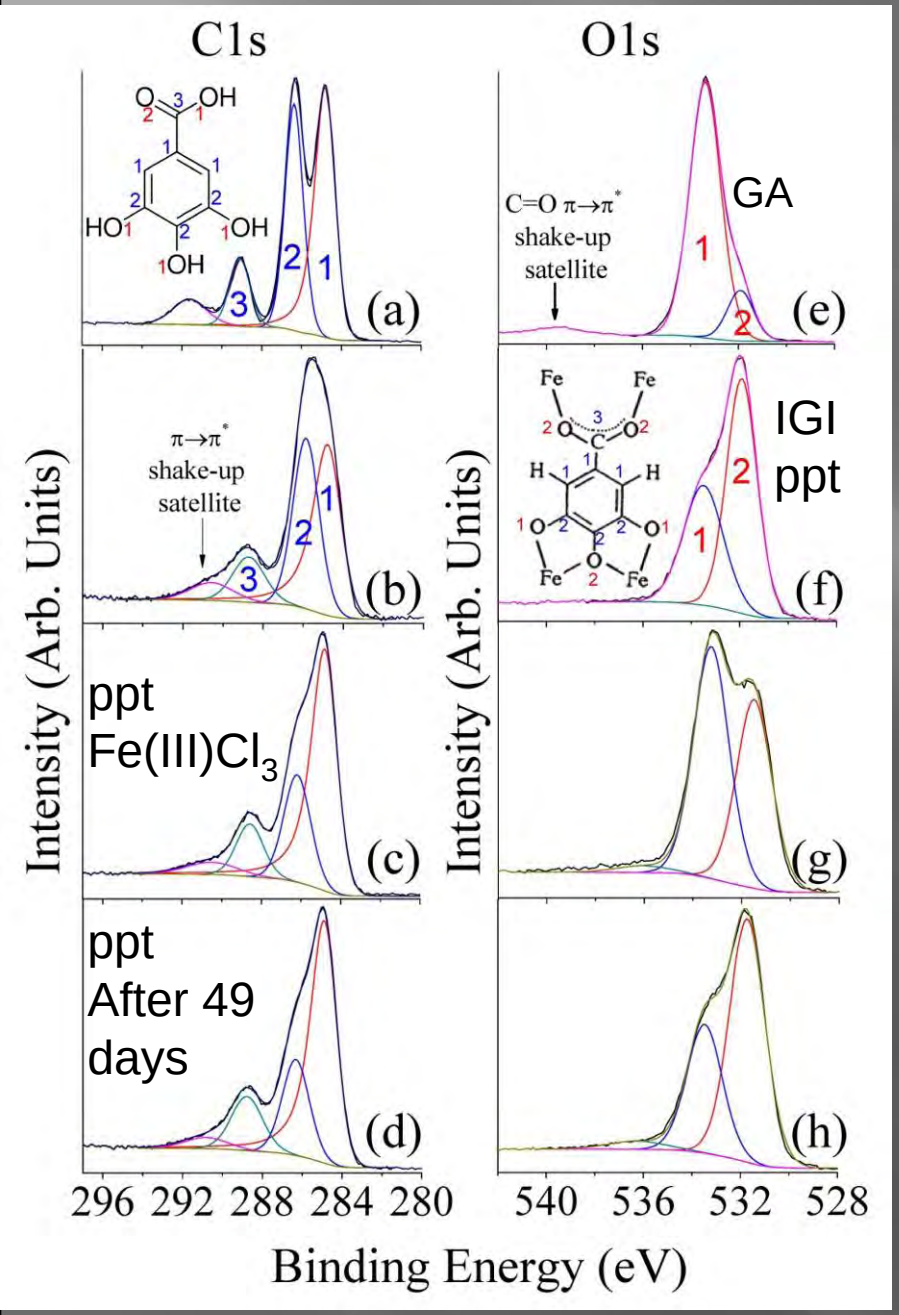
- Deacidification has reduced number of surface carboxylic groups
- Carboxylic containing molecules reduced particularly after deacidification

Sample	Atomic Percentage			
Functional group	C-O	O-C-O/C=O	COOH	COOH/C-O
Untreated	17.1	13.0	12.8	0.75
WD	29.2	15.8	7.7	0.26
WDP	24.4	16.1	9.8	0.40

Summary

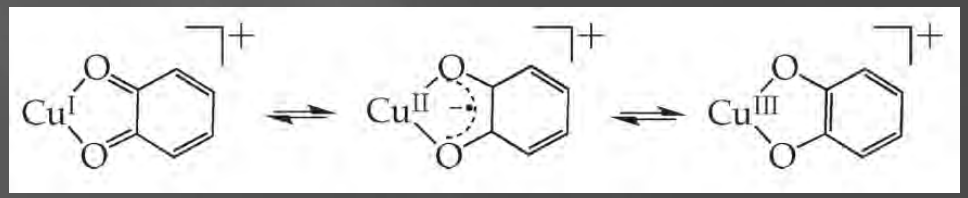
- XPS was able to give valuable insight into both treatments of historical documents
- Increased iron in paper after treatments
- Increased Fe(II)/Fe(III) ratio after treatments
- Sulfate washed away
- Increase in Calcium
- Na and K impurities washed away

IGI Chemistry

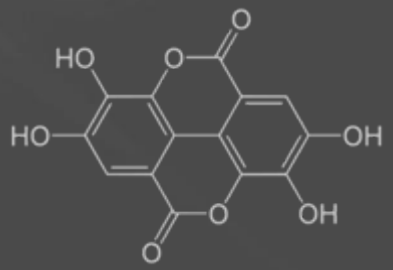


- IGI ppt blue/black
- Fe(III) / 49 day Brown black
- Big change in C-OR/C:COOR ratio
- C/Fe ratio of brown black ppt double IGI precipitate
- Redox isomers

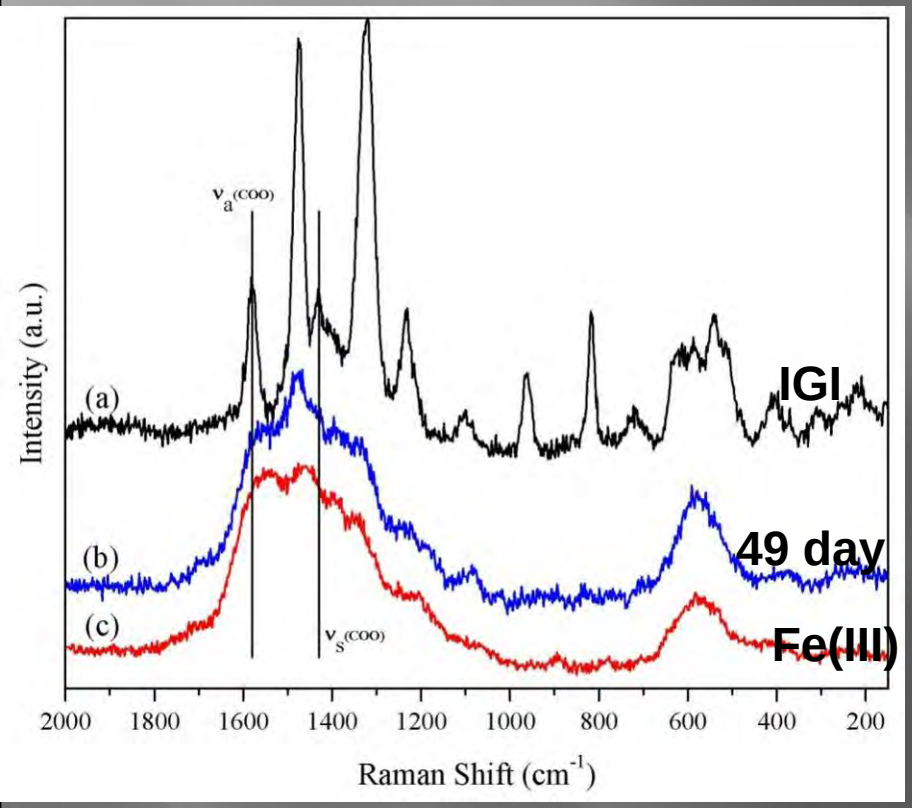
Fe(III) + 1/2phenol → Fe(II) 1/2 o-quinone + H+

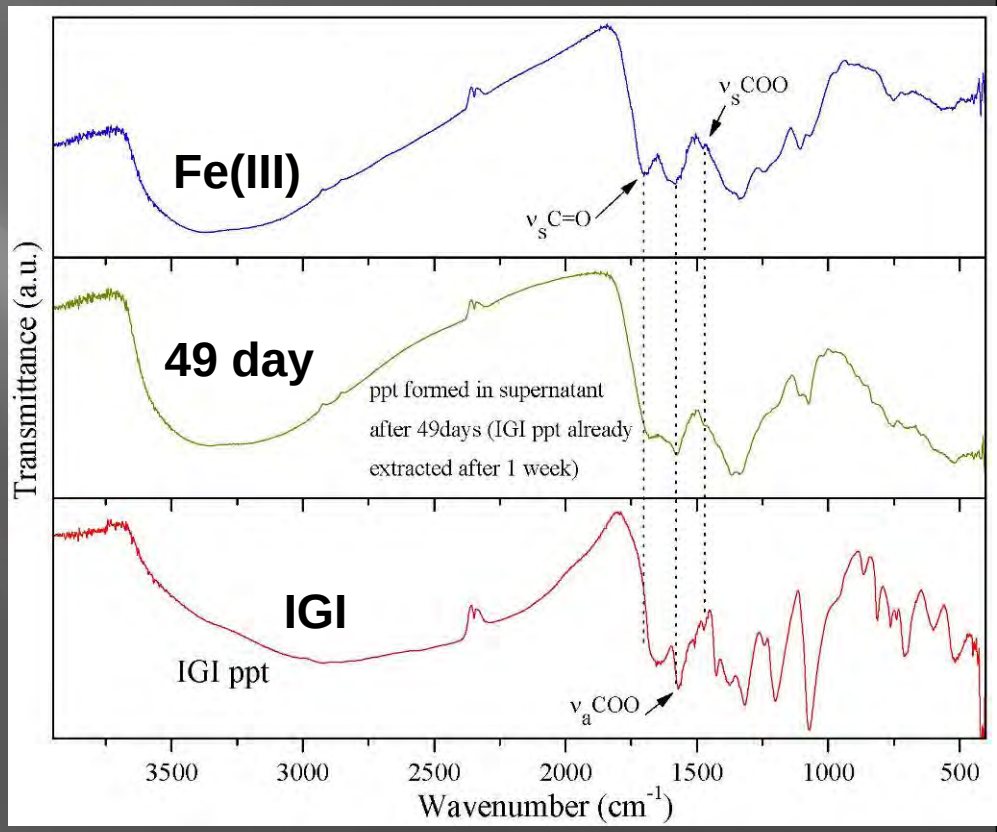


Ellagic acid



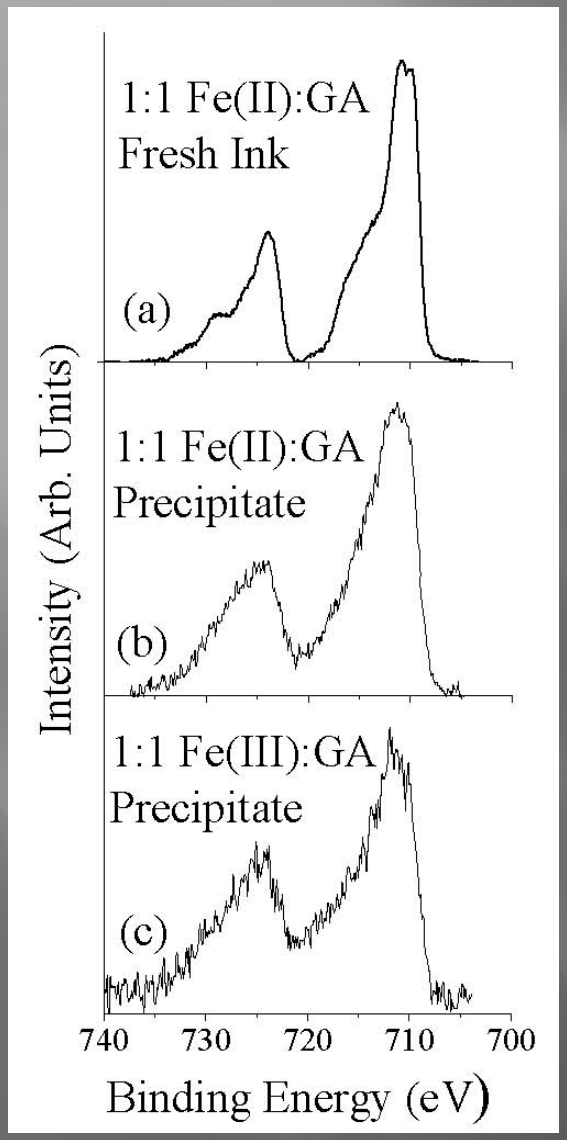
Infra Red and Raman Spectroscopy





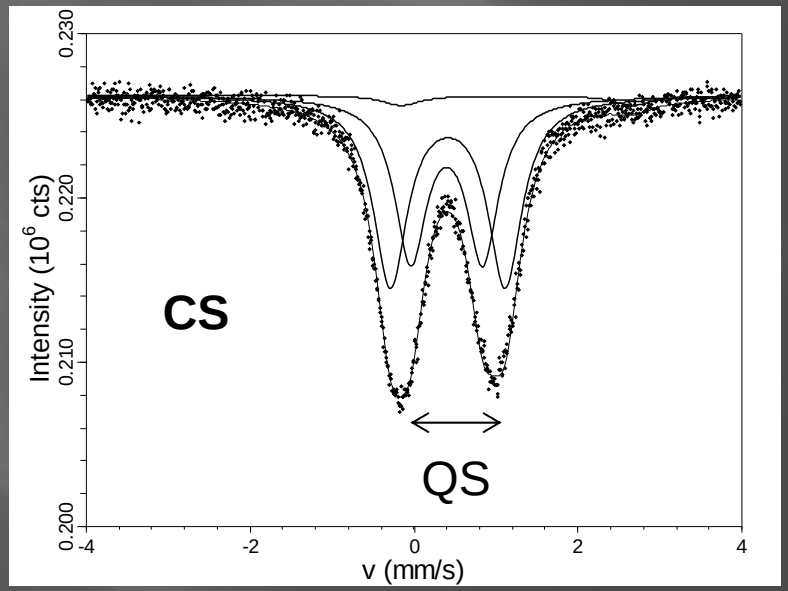
Note: Krekel was able to obtain brown / black precipitates

XPS / Mössbauer Iron oxidation state



We can conclude that in all these samples there is a relatively wide distribution of distorted mostly octahedral sites for Fe^{3+} and even more distorted and more likely octahedral sites for Fe^{2+}.

Sample	GA:IS 1:9	GA:IS 1:6	GA:IS 1:4
Fe^{2+} /Σ Fe	6%	8%	4%



Fe(III)
High spin
complex

Conclusions

- XPS was able to compliment other techniques and provide us valuable structural information
- Initial XPS, Raman and IR results indicate that with change in experimental conditions very different complexes can be formed
- Mössbauer showed the complex to be predominantly a high-spin Fe(III) but also containing an ~4-8% high-spin Fe(II)

Acknowledgments

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