Aqueous Methods for the Cleaning of Painted Surfaces

Day 1: pH, Conductivity, Chelating Agents

Matthew Cushman
1 August 2023

Baltic-American Freedom Foundation

Art Academy of Latvia

VALSTS KULTŪRKAPITĀLA FONDS

LATVIJAS RESTAURATORU BIEDRĪBA

1

Sergei Vinogradoff, Riga, 1924

2

Arshile Gorky, date unknown

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Course Outline

Day 1: pH, Conductivity, Chelating Agents
- Controlling swelling and surface dirt removal

Day 2: Thickeners, Spreadable Gels, Hydrogels
- Controlling movement of water

Day 3: Surfactants and Emulsions
- Removal of complex dirt; combining aqueous and solvent chemistry

Day 4: Designing a Cleaning Protocol
- Practical problem solving!

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Session Outline – Day 1, Part I

- **Introduction**
  - Why aqueous cleaning?
  - Nature of surface dirt
  - General questions to consider
- **pH**
  - Defining pH
  - Measuring pH
  - Adjusting pH
  - Controlling pH – **Buffers**
  - pH effects on object surfaces
- **Conductivity**
  - Defining conductivity
  - Measuring conductivity
  - Osmotic pressure and tonicity
  - Conductivity effects on object surfaces
- **Practicalities of testing**
  - Methods for estimating appropriate parameters for pH and conductivity

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Instructor Biases

UNIVERSITY OF DELAWARE

WINTERTHUR
MUSEUM, GARDEN & LIBRARY

OBJECTS EDITION

Independent Study: Materials and Methodologies for Cleaning Cultural Heritage Surfaces
ARTC 666 - Fall 2021

Syllabus and Course Information

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WHY AQUEOUS CLEANING?

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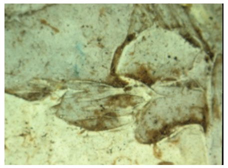
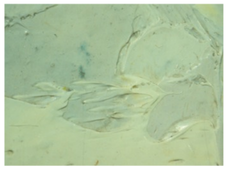
The Nature of Surface Dirt

Surface attraction

- Electrostatics (charged particles)
- Hydrogen & dipole bonding (polar interactions)
- Dispersion forces (hydrophobic interactions)
- Role of divalent metal ions





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The Nature of Aqueous Solutions

Forces within water

- High hydrogen bonding and dipole solvent parameters: **Great at disrupting electrostatic and hydrogen bonding**
- Good ability to dissociate salts
- Low dispersion solvent parameter: **poor interaction with oily, waxy, hydrophobic materials** (generally)

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The Nature of Aqueous Solutions

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Properties to tailor

- **pH**
- **Conductivity**
- **Use of chelating agents**
- **Use of surfactants**
- *Viscosity/rheological agents → gels*
- *Reactive additives: enzymes, redox reagents*

Additional factors:

- Time
- Mechanical action
- Temperature
- Addition of non-aqueous solvents

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General Considerations – Aqueous Cleaning

- Health & Safety
- Environmental concerns
- Material Sustainability
- Expense
- Possibility for residues
- Ease of preparation
- Ease of use
- Documentation

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pH: DEFINITION, MEASUREMENT, CONTROL

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pH: Autoionization of Water

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^{+}{}_{(aq)} + OH^{-}{}_{(aq)}$$

$$K = \frac{[H_3O^{+}][OH^{-}]}{[H_2O]^2} = [\mathrm{H}^{+}][\mathrm{OH}^{-}] = \mathrm{Kw}$$

$$K = [\mathrm{H}^{+}][\mathrm{OH}^{-}] = 1.0 \text{ x } 10 - 14$$

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pH: Definition

		$[H_3O^+]$	pH
MORE BASIC		1.0×10^{-15}	15.00
		1.0×10^{-14}	14.00
		1.0×10^{-13}	13.00
	BASIC	1.0×10^{-12}	12.00
		1.0×10^{-11}	11.00
		1.0×10^{-10}	10.00
		1.0×10^{-9}	9.00
		1.0×10^{-8}	8.00
	NEUTRAL	1.0×10^{-7}	7.00
		1.0×10^{-6}	6.00
		1.0×10^{-5}	5.00
		1.0×10^{-4}	4.00
	ACIDIC	1.0×10^{-3}	3.00
		1.0×10^{-2}	2.00
		1.0×10^{-1}	1.00
		1.0×10^{0}	0.00
MORE ACIDIC		1.0×10^{1}	−1.00

$$pH = -\log[H_3O^{+}] = -\log[H^{+}]$$

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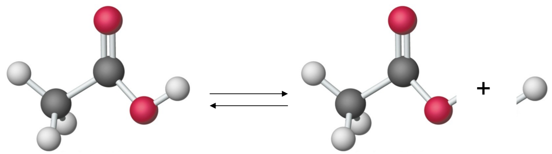
Strong and Weak Acids and Bases

A **strong acid or base** ionizes completely in water

A **weak acid or base** ionizes incompletely in water; the majority remains molecular in water at equilibrium



Strong and Weak Acids and Bases

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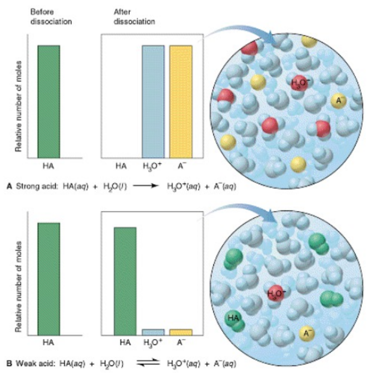
The Extent of Dissociation for Strong and Weak Acids



K_a: Acid Dissociation Constant

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

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Henderson-Hasselbalch Equation

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$-\log K_a = -\log[\mathrm{H}^+] - \log\frac{[A^-]}{[HA]}$$

$$\mathrm{p}Ka = \mathrm{pH} - \log\frac{[A^-]}{[HA]}$$

$$\mathrm{p}H = \mathrm{pK_a} - \log\frac{[A^-]}{[HA]}$$

If you know two of:

- Acid pKa
- Solution pH
- Ratio of acid and conjugate base

You can calculate/estimate the third!

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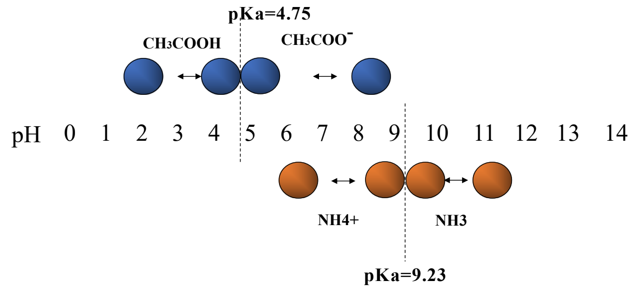
Henderson-Hasselbalch Equation: pK_a & Speciation

$$when\ [A^-] = [HA], \quad pKa = \text{pH}$$



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KEY CONCEPTS:

- As pH increases, acid groups become deprotonated (charged)
- If pK_a is known, we can predict the pH when the acid group becomes deprotonated (charged)
- Greater charge: increased solubility in water (generally)

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Measuring pH

pH meters convert the voltage ratio between a reference half-cell and a sensor half-cell to a pH value.

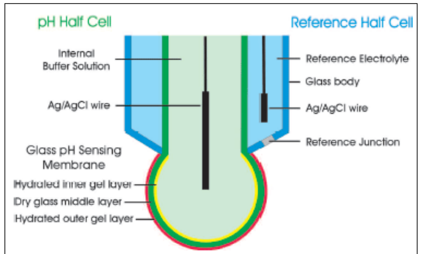

Figure 1 Typical combination pH electrode.

Half-cells can degrade over time!

Many pH meters feature replaceable electrodes.

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pH Measurement: Many Options!

The best pH meter is one that you are **comfortable using** and are **confident in its calibration**.

± 0.1 pH unit is great for most conservation cleaning applications!

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Measuring pH: Calibration

- Probe calibration requires at least two standard buffer solutions.
- Buffered solutions should cover the range of expected measurements.
- Buffered solutions should be at the same temperature as samples of unknown pH.

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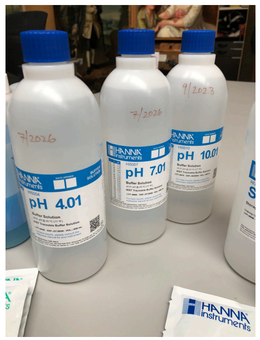
pH Measurement: Standards



Be sure to mark down date opened and 'use-by' dates!
pH 10.01 standard deteriorates faster than pH 4.01, 7.01...

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Buffers: Definition & Characteristics

Buffers are mixtures of a weak acid and its conjugate base (or weak base with its conjugate acid)

Buffers **maintain approximately constant pH** over a range of neutralization

Buffer effectiveness determined by:
- Buffering pH range (determined by **pK_a**)
- Buffering capacity (determined by **buffer concentration**)

For most conservation cleaning, a **buffer concentration of 0.05M** is sufficient!

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Buffers: How They Work

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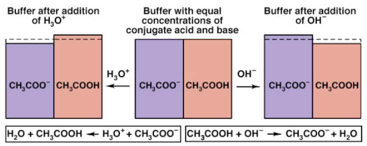
Given a weak acid buffer, the addition of OH^- neutralizes some hydronium ions

$$H_3O^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons H_2O$$

pH rises incrementally, causing dissociation of some buffer
- Produces more hydronium, recovering some of the pH change



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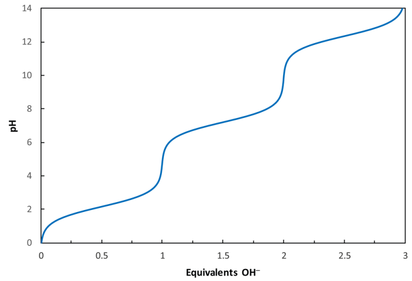
Polyprotic Acid Equilibria

- Acids with more than one hydrogen capable of deprotonation
- Examples: H_2SO_4, H_2CO_3, H_3PO_4
- Have multiple equivalence points



Titration curve of H_3PO_4

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Buffers: pK_a and Buffer Range

Buffer Range	pKa	Buffer
2.2-6.5	3.13	citrate (pK1)
3.0-6.2	4.76	citrate (pK2)
3.6-5.6	4.76	acetate
6.0-8.0	6.35	carbonate (pK1)
5.5-7.2	6.40	citrate (pK3)
5.8-8.0	7.20	phosphate (pK2)
7.0-8.3	7.76	triethanolamine (TEA)
7.5-9.0	8.06	Trizma (tris)
8.5-10.2	9.23	borate (pK1)
9.5-11.1	10.33	carbonate (pK2)

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pH: EFFECTS ON PAINTING STRUCTURES

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pH Effects

Influencing electronics

- Oxidation states of metals/ions
- Protonation/deprotonation of organic components

What organic components might we encounter?

Complicating factors

- **Formation of insoluble salts**
- **Substrate effects**

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pH Effects - Proteins

Amino Acid Chemical Properties

- Polar amino acids: greater interactions with water
- Charged amino acids: pH-sensitive

AMINO ACID			SIDE CHAIN	AMINO ACID			SIDE CHAIN
Aspartic acid	Asp	D	negative	Alanine	Ala	A	nonpolar
Glutamic acid	Glu	E	negative	Glycine	Gly	G	nonpolar
Arginine	Arg	R	positive	Valine	Val	V	nonpolar
Lysine	Lys	K	positive	Leucine	Leu	L	nonpolar
Histidine	His	H	positive	Isoleucine	Ile	I	nonpolar
Asparagine	Asn	N	uncharged polar	Proline	Pro	P	nonpolar
Glutamine	Gln	Q	uncharged polar	Phenylalanine	Phe	F	nonpolar
Serine	Ser	S	uncharged polar	Methionine	Met	M	nonpolar
Threonine	Thr	T	uncharged polar	Tryptophan	Trp	W	nonpolar
Tyrosine	Tyr	Y	uncharged polar	Cysteine	Cys	C	nonpolar

POLAR AMINO ACIDS — NONPOLAR AMINO ACIDS

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pH Effects - Proteins

Influencing electronics

- **Iso-electric point** (IEP): pH range where a protein has zero net charge
- IEP: pH where the protein will be most stable
- Example: Collagen IEP: pH ~5.5

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pH Effects - Proteins

Typical pKa values in proteins

Group	Amino Acid	Approx. pKa
α-carboxyl	(free, C-terminal)	3
β-carboxyl	aspartic acid	4
γ-carboxyl	glutamic acid	4
imidazole	histidine	6
sulfhydryl	cysteine	8
1°α-amino	(free, N-terminal)	8
2° α-amino	(free, N-terminal)	9
ε-amino	lysine	10
hydroxyl	tyrosine	10
guanido	arginine	12

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pH Effects - Proteins

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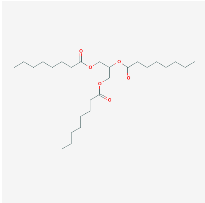
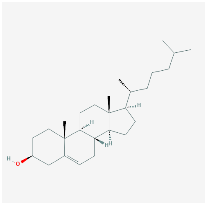
pH Effects – Oils, Resins, Waxes

pH-sensitive Components

- Fatty acids
- Plant/animal sterols



Triglycerides



Sterols

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Drying Oils - Prevalence

- Inks
- Coatings
- Paint binders
- Hardboard binders
- Compo formulations
- Epoxidized oils
- Plastic stabilizers
- UV Absorbers for UV-curing polymers
- Historical restoration materials!

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Chemical Characteristics: Oils

	Linseed	Tung	Oiticia	Castor	Fish	Safflower	Soya	Tall Oil	Cottonseed	Coconut
Iodine Value	180	165	150	135	175	145	130	133	106	8
Viscosity (lb/gal)	7.76	7.85	8.10	7.81	7.69	7.70	7.7	7.53	7.65	7.68
Color (Gardner)	11	10	9	5	12	10	10	4	8	5
Acid Value	4	8	8	4	6	4	3	194	1	2
Saponification Number	190	190	190	190	190	190	190	196	190	250

Acid Value: mM OH^- to titrate to pH 7
Saponification Number: mg OH^- needed to de-esterify 1g oil

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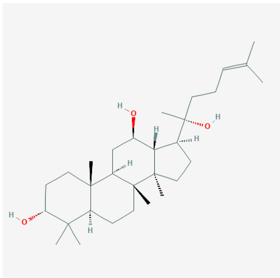
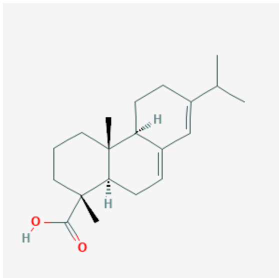
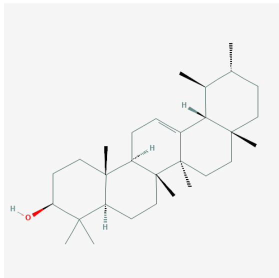
Plant Resin Components



Dammarenes
pKa: 4.3-4.8



Abietic Acid
pKa: 4.3



Labdanes (C30)
Plant waxes

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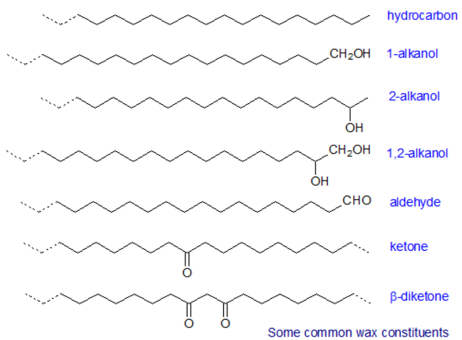
Natural Wax Components



Some common wax constituents

Only minor pH sensitivity!

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The Role of pH - Summary

Key factor in removal and retention of materials

- Proteins are least soluble at their isoelectric point
- Oils are sensitive to both acid hydrolysis and saponification
- Natural resins are sensitive to elevated pH
- Elevated pH can assist in picking up acidic soiling
- Elevated pH generally increases chelation effect

Considerations

- pH sensitivity of pigments, colorants
- Elevated pH: increase in surfactant residues
- Elevated pH: increased production of metal hydroxides

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CONDUCTIVITY

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Conductivity: Definition

Conductivity is the ability of a material to conduct electric current.

Experimentally, measured by placing two plates in a sample, one of which has an applied potential. **Current is measured**.

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Measuring Conductivity

Conductivity measurements are temperature-dependent.
Some conductivity meters account for T dependence, but many assume a standard temperature – usually 25°C.

Conductivity meters require calibration with standard solutions.
Standard solutions are chosen according to the expected measurement range.

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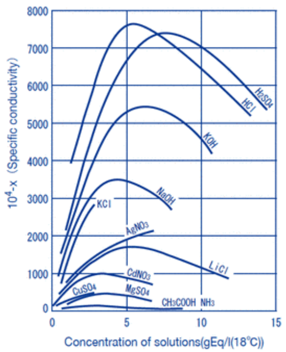
Conductivity: Deviations from Ion Concentration



N.Kameyama 「Denkikagaku no Riron Oyobi Ouyou Part I」
(Theory and Applications of Electrochemistry Part I), P31.1963. (Maruzen Pub.)

Basic unit of conductivity: Siemens (S)

Standardized measurements reported in specific conductivity units **(S/cm)**

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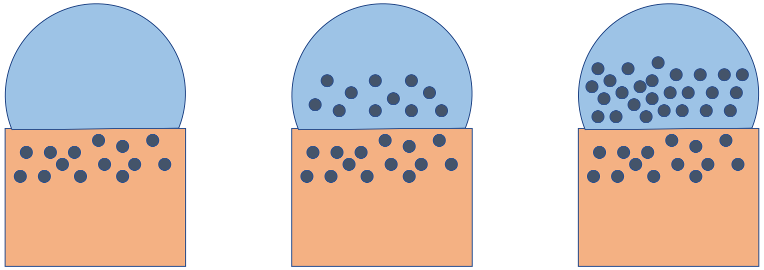
The Role of Conductivity



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Tonicity Effects

Hypotonic solutions will cause the surface to gain water and swell through osmosis and/or ions will be removed from the surface

Isotonic solutions will cause the minimal swelling of the surface as there is no osmotic pressure to move water or salts

Hypertonic solutions will cause the surface to lose water and shrink through osmosis and/or ions will move into the surface

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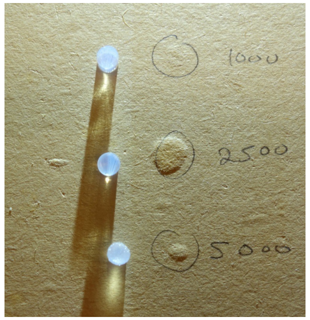
Testing Surface Response to Conductivity – Cellulosic Board



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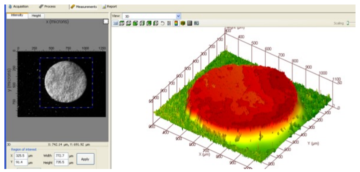
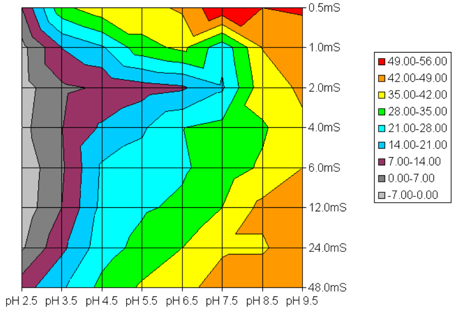
Conductivity, pH, and Paper Swelling





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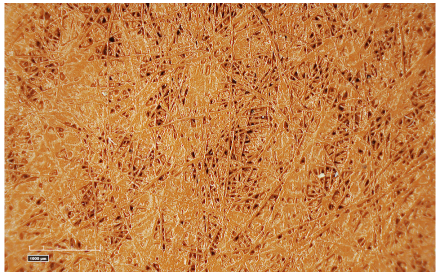
Influence of pH & Conductivity on Surface Swelling – Acrylic Paint



Red ochre acrylic paint,
nonwoven polyester support
15 years of natural aging

After application of 3mm dia. agarose gel, deionized water

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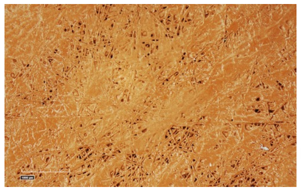
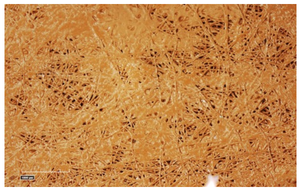
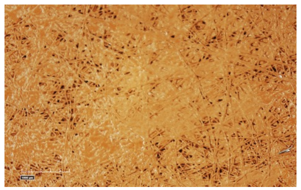
Influence of pH & Conductivity on Surface Swelling – Acrylic Paint



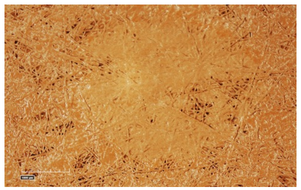
pH 5.1
1000 µS/cm



pH 6.0
1000 µS/cm



pH 7.5
1000 µS/cm



pH 9.1
1000 µS/cm

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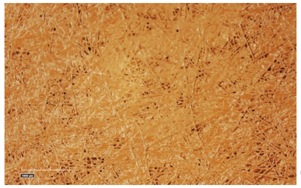
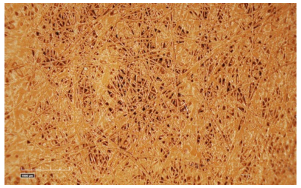
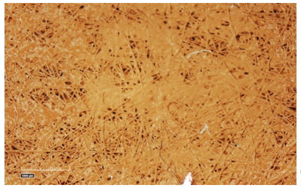
Influence of pH & Conductivity on Surface Swelling – Acrylic Paint



pH 5.1
6000 µS/cm



pH 6.0
6000 µS/cm



pH 7.5
6000 µS/cm

pH 9.1
6000 µS/cm

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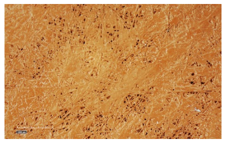
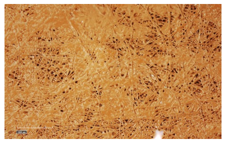
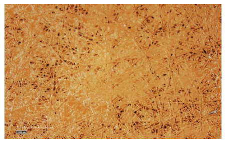
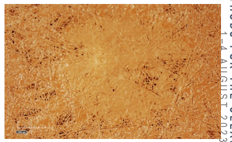
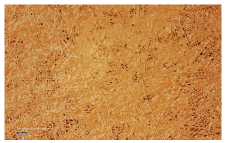
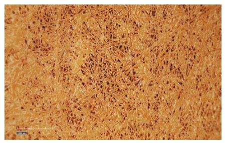
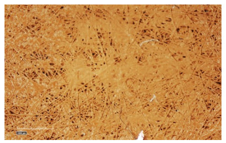
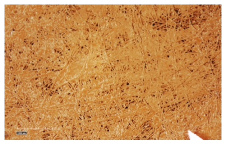
Influence of pH & Conductivity on Surface Swelling – Acrylic Paint

1000 µS/cm

pH 5.1 **pH 6.0** **pH 7.5** **pH 9.1**

6000 µS/cm

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Expect Varied Response!

- **Deterioration variation due to material instability**
- **Deterioration variation due to differing exposure to light, heat, humidity, etc.**
- **Past restoration – pros and cons**
- ***Similar objects may respond differently!***

AQUEOUS METHODS FOR THE CLEANING OF PAINTED SURFACES
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Session Outline – Day 1, Part II

- **Introduction**
  - Metal ions, "dirt", and staining
  - General properties of chelators
  - Practical considerations
- **Improvements/refinements**
  - Improved pH ranges
  - Selectivity
  - Biodegradability
- **"Classic" chelators**
  - EDTA
  - Citrate
  - NTA
- **Balancing practical use vs.**
  - Health & environmental safety
  - Economic considerations

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Metal ions, dirt, and staining

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Sources of surface contamination

- Original materials
- Water, solvent contaminants
- Pollutants
- Restoration materials

And degradation products resulting from interactions between the above!

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Metal ions, dirt, and staining

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Divalent metal ions

- Often present at surfaces, interacting with anionic sites
- Can form bridges between surfaces and weakly acidic materials, pollutants, particulate
- Can be present as components of complex mixtures (colorants, cross-linking agents in coatings, e.g.)
- Often very difficult to solubilize

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Metal ions, dirt, and staining

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Metal ions and staining

- Transition metal ions (Fe, Cu, e.g.) can present as colored stains on/within surfaces
- Possible bridge between original surface and organic staining
- Potential for catalysis of oxidative reactions

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Metal ions, dirt, and staining

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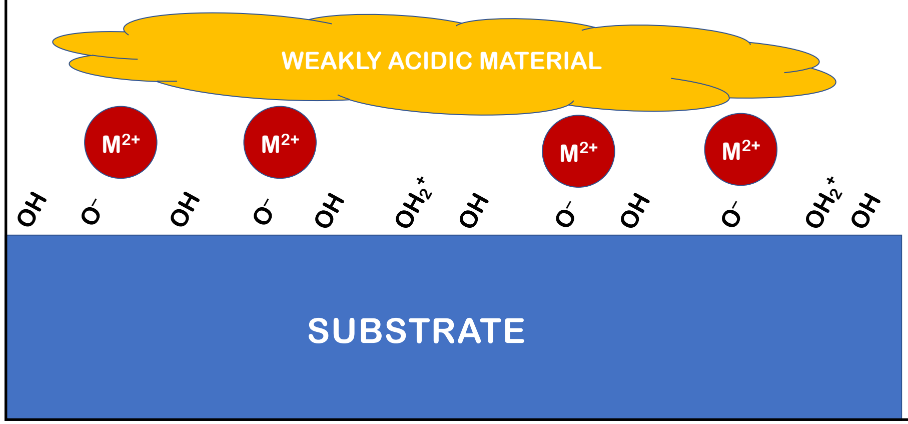

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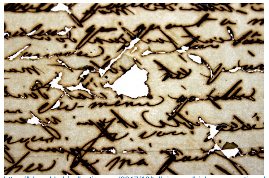
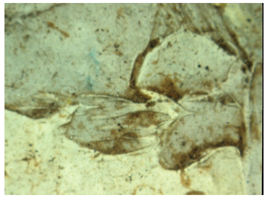
Metal ions, dirt, and staining



https://blogs.bl.uk/collectioncare/2017/10/talk-iron-gall-ink-conservation-challenges-and-research.html

https://www.fieldmuseum.org/blog/what-hundred-year-old-birds-tell-us-about-environment



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Chelation: Definitions

Chelation is the binding/complexation of bi- or multi-dentate ligands specifically to metal ions.

Chelate effect is the increased stability of metal-chelate complexes arising from the low probability that all donor/binding sites will dissociate from the metal ion

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Chelating Agents

Structure

- **Polydentate** molecules: multiple acid groups & donor atoms
- Each acid group has an associated equilibrium constant (pK_a)
- Increasing pH: increased number of deprotonated sites
- Deprotonated sites coordinate around metal ions

Number of binding sites & geometry determine binding strength for different metal ions

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Example: EDTA

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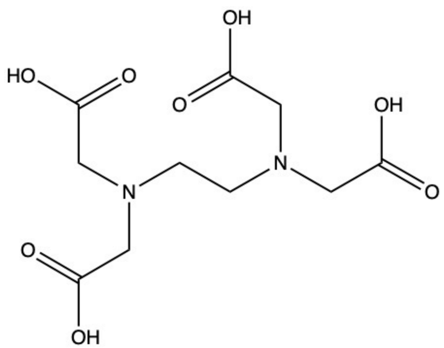

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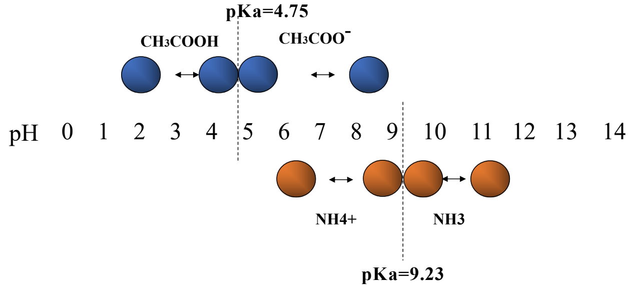
pK_a & Speciation

$$when\ [A^-] = [HA], \qquad pKa = \mathrm{pH}$$



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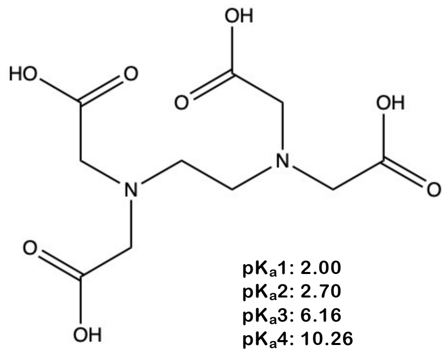
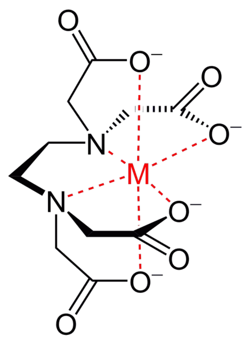
Example: EDTA



pK_a1: 2.00
pK_a2: 2.70
pK_a3: 6.16
pK_a4: 10.26



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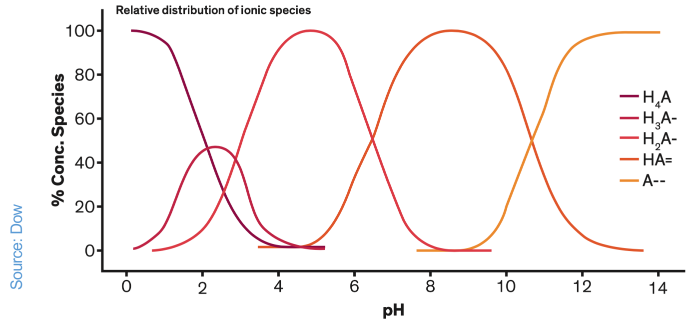
Example: EDTA



pK_a1: 2.00
pK_a2: 2.70
pK_a3: 6.16
pK_a4: 10.26

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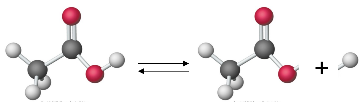
pH Effects



Influencing electronics

- Oxidation states of metals/ions
- Protonation/deprotonation of organic components

Complicating factors

- **Formation of insoluble salts**
- **Substrate effects**

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We can **control pH** (buffer) to **minimize risk** to the substrate while **improving efficacy** of our chosen chelating agent.

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Chelation: pH Dependence

	EDTA	EGTA	HEDTA	NTA	DTPA	Citrate
pk_1	1.99	2.00	2.51	1.89	1.8	3.13
pk_2	2.67	2.65	5.31	2.49	2.6	4.76
pK_3	6.16	8.85	9.86	9.73	4.4	6.4
pK_4	10.26	9.46			8.8	
pK_5					10.5	

EDTA--Ethylenediamine-tetraacetic acid Disodium salt

EGTA-Ethyleneglycol-O, O'-bis(2-aminoethyl)-N, N, N', N'-tetraacetic acid

HEDTA- N-(2-Hydroxyethyl)ethylenediamine-N, N', N'-triacetic acid Trisodium salt

NTA- Nitrilotriacetic acid

DTPA- Diethylenetriaminepentaacetic acid

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"Strong" vs. "Weak" Chelating Agents

Number of binding sites & geometry determine binding strength for different metal ions

- Binding sites determined by speciation (pH)
- Geometry determined by molecule size, freedom of rotation
- Chelator geometry must match metal ionic radius for strong binding

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Chelation: Bite Angle

If the ionization of the chelating agent satisfies the electronic "needs" of the crystalline/ionic/metallic material, what determines the stability of the complex?

Ligand bite angle
- **Preferred coordination number of ion**
- **Ring size**
- **Bond lengths**
- **Hybridization & bond angles**

Matching geometry with ionic radius gives opportunities for selective chelation!

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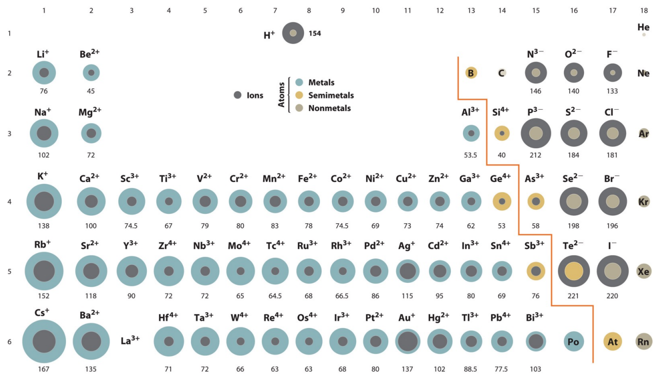
Ionic Radius – General Trends



saylordotorg.github.io/text_general-chemistry-principles-patterns-and-applications-v1.0/s11-02-sizes-of-atoms-and-ions.html

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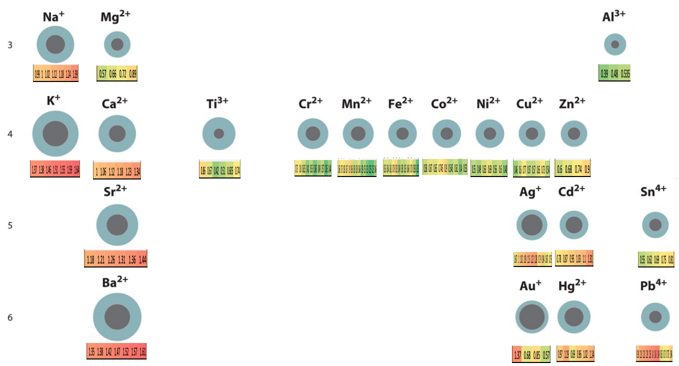
Ionic Radius – General Trends



saylordotorg.github.io/text_general-chemistry-principles-patterns-and-applications-v1.0/s11-02-sizes-of-atoms-and-ions.html

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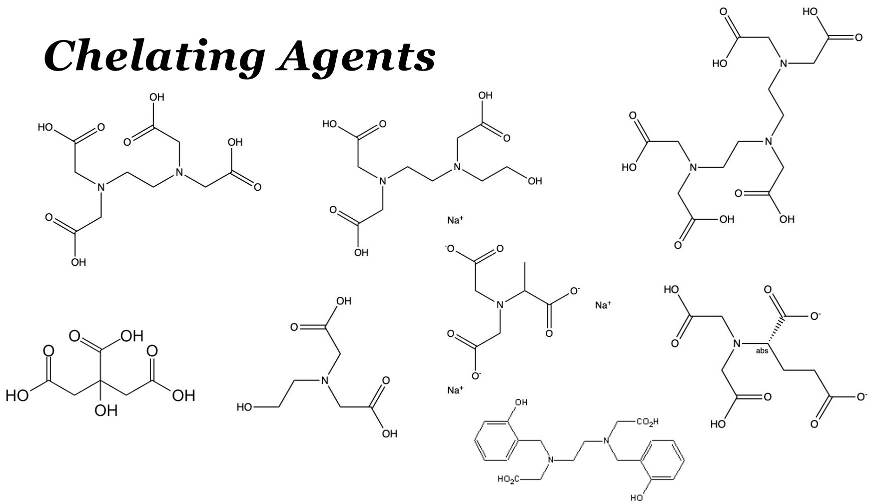
Chelating Agents



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Chelation: Stability Constants

Table 30.2 Common chelators and pK_f for selected metal ions (Wolbers, 2008)

	EDTA	EGTA	HEDTA	NTA	DTPA	Citrate
Ag(I)	7.32	6.88	6.71	5.16		7.1
Ca(II)	10.96	11.00	8.14	6.41	10.9	4.68
Cd(II)	16.46	16.70	13.6	9.54	19.3	3.98
Co(II)	16.31	12.50	14.4	10.38	19.3	4.8
Cr(III)	23.40			>10		
Cu(II)	18.80	17.88	17.55	12.96	21.5	4.35
Fe(II)	14.33	11.92	12.2	8.84	16.0	3.08
Fe(III)	25.1	20.5	19.8	15.87	27.9	12.5
Hg(I)	21.8	23.12	20.1	14.6	26.7	
Li(I)	2.79	1.17		2.51		
Mg(II)	8.69	5.21	7.0	5.46	9.0	3.29
Mn(II)	14.04	12.3	10.7	7.44	15.6	3.67
Na(I)	1.66	1.38	2.15			
Ni(II)	8.62	13.55	17.0	11.54	20.2	5.11
Pb(II)	18.04	14.71	15.5	11.39	18.9	6.50
Sn(II)	18.3	23.85				
Tl(III)	22.5			18.0		

Compare pK_f of metal-chelate complexes to pK_{sp} of expected metal salts to estimate likelihood of successful chelation

If $pK_f \geq pK_{sp}$, chelation is favorable

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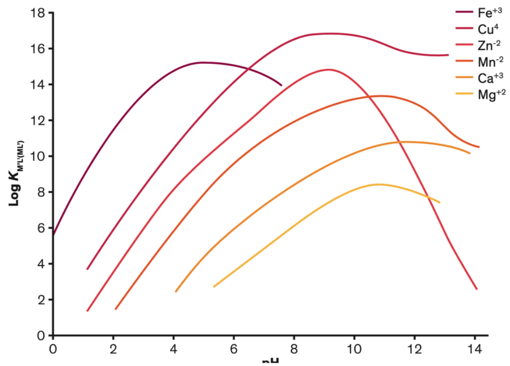
Conditional Stability – Influence of Competing Equilibria



Source: Dow

Figure 18: EDTA Conditional Stability Constants vs. pH for Select Metals

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We can select chelating agents according to the metal ions we wish to target and the aqueous parameters needed for treatment.

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Practical Considerations: Purchasing Options

Chelating agents can be purchased as **free acids**, **salts**, or in **concentrated solutions**

Free acids: requires some pH manipulation to solubilize, but you can choose your cation

Salts: easier to solubilize, but the cation may be problematic – do you really want to buy different salts of the same chelator?

Concentrated solutions: generally good shelf life, very easy to solubilize, but introduces some extra math, and you're paying to ship water

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Practical Considerations: Delivery Modalities

As components of aqueous solutions (typical concentrations of 0.25-2.0% w/v), chelating agents can be delivered:

On dampened swabs, loaded into cosmetic sponges, in thickened solutions, in rigid hydrogels, in emulsions, in poultices, in tissues, etc. etc. etc.

Caveats: less predictable stability in w/o emulsions, in preparations with polyionic polymers, in rigid gels that are strengthened by the presence of divalent metal ions

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Practical Considerations: Rinsing/Clearing

Questions to consider:

- How porous is the substrate/structure?
- Are there any sensitivities to moisture to anticipate?
- Does the delivery method work well with the structure and condition of the surface?
- How likely is clearance? Are you willing to leave material behind as part of your treatment?

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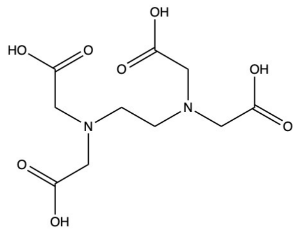
Comparing Common Chelating Agents – EDTA



Broad use chelator: "strong" for most metals; non-selective

Effective pH > 6.1

Inexpensive: ~25USD/100g

Hazard statements:
Harmful if swallowed; causes serious eye irritation; harmful to aquatic life with long lasting effects

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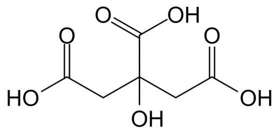
Comparing Common Chelating Agents – Citric Acid



Considered a "mild" chelator: fairly good for most metals, "weak" for calcium

Effective pH > 6.4

Inexpensive: ~25USD/100g

Hazard statements:
Causes skin irritation; causes serious eye damage; may cause respiratory irritation

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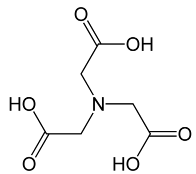
Comparing Common Chelating Agents – NTA



Fairly broad chelator, generally "stronger" than citric acid and "weaker" than EDTA

Effective pH > 9.7

Fairly inexpensive: ~45USD/100g

Recommend phasing out!

Hazard statements:
Harmful if swallowed; causes skin irritation; causes serious eye irritation; suspected of causing cancer; may cause respiratory irritation

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Comparing Common Chelating Agents

General trends:

- Broad, non-selective utility
- Require near-neutral or alkaline pH
- Relatively inexpensive
- Poor biodegradability; concerns about environmental impact
- Significant health and safety concerns

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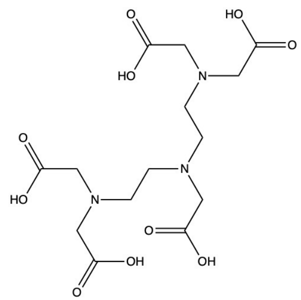
Additions to the toolkit: DTPA



Broad chelator, comparable to or "stronger" than EDTA

Effective pH > 4.4

Fairly expensive: ~65USD/100g

Hazard statements:
Harmful if swallowed; causes skin irritation; causes serious eye irritation; suspected of causing cancer; may cause respiratory irritation

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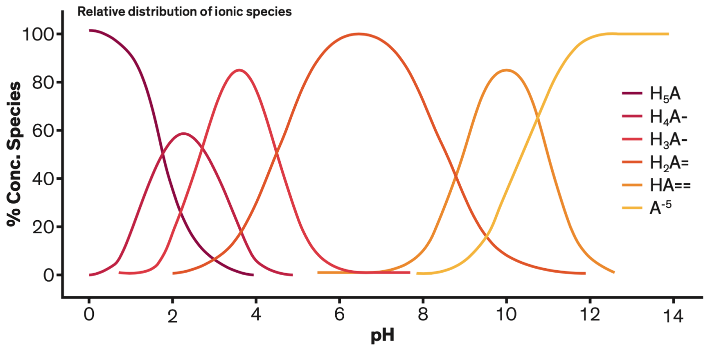
DTPA Speciation



Source: Dow

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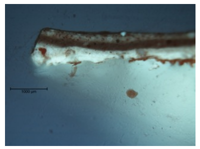
DTPA Case Study: Washington Portrait, c. 1810.



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DTPA Case Study: Washington Portrait, c. 1810.

- 0.5% DTPA, buffered to pH 5.5, 1.5% xanthan gum
- Hydrophobic solvent applied to inhibit gel ingress
- Agitation with a brush under magnification
- Cleared with pH 5.5 ‘pH adjusted water’ from MCP

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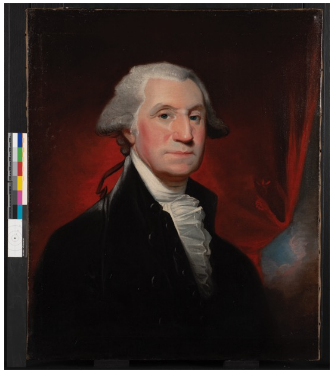
DTPA Case Study: Washington Portrait, c. 1810.



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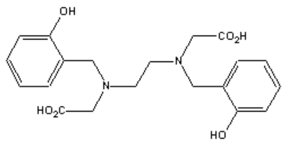
Additions to the toolkit: HBED



N,N'-Di(2-hydroxybenzyl)ethylenediamine-N,N'-diacetic acid

HBED: High affinity for iron (III) and other transition metals

Effective pH > 8

Truly expensive: ~65USD/1g

Hazards not adequately studied. Temporarily: "safe".

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Additions to the toolkit: HBED

Metal ion	pK_f, citric acid	pK_f, EDTA	pK_f, HBED
Ca^{2+}	4.7	11.0	9.3
Fe^{2+}	3.1	14.3	
Fe^{3+}	12.5	25.1	39.6
Cu^{2+}	4.3	18.8	21.4

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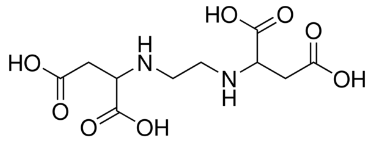
Additions to the toolkit: Biodegradable chelating agents



Ethylenediamine-N,N'-disuccinic acid

EDDS: Biodegradable alternative to EDTA

Effective pH 3-9

Expensive: ~35USD/1g

pKf, Fe(III): 20.6
EDTA: 25.1

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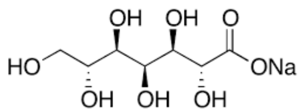
Additions to the toolkit: Biodegradable chelating agents



Glucoheptonic acid: broadly effective chelator for divalent and trivalent metals.

Effective pH > 4

Fairly inexpensive: ~50USD/100g

Hazard: Causes eye irritation

AQUEOUS METHODS FOR THE CLEANING OF PAINTED SURFACES
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We can explore options to meet our needs for:

-practical use

-environmental, health & safety concerns

-economic responsibility

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AFTERNOON SESSION: EXPERIMENTING WITH pH, CONDUCTIVITY, & CHELATING AGENTS

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Thank you for your attention.

Questions? Contact:
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