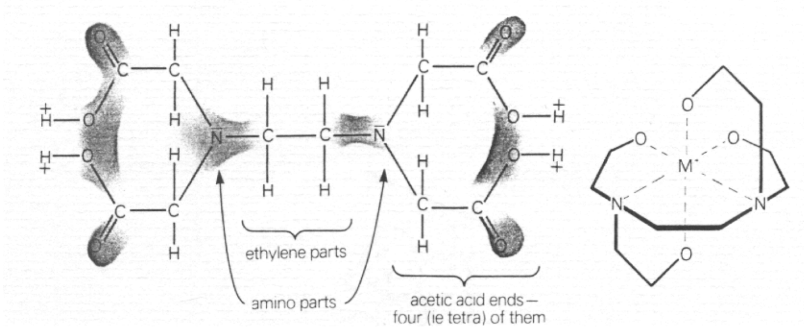
CHELATING AGENTS: their structure and properties

Chelating agents can be defined as organic compounds which complex or sequester metal ions[i]. The word *chelate* derives from the Greek root "chela" meaning the claw of a lobster. The chelating agent removes a metallic ion from a solid salt and holds it in solution. By forming a soluble complex from an insoluble compound it is possible to remove unwanted material, washing it away with water.

Figure 1 shows the structure of a commonly used chelating agent in conservation: ethylene diamino tetra acetic acid (EDTA).



EDTA (ethylene diamino tetra acetic acid) contains six donor atoms capable of co-ordination to a single metal ion and is therefore sexadentate: two basic groups (amino parts) and four acidic groups (acetic ends). EDTA forms very stable complexes with most metals, including the alkaline earth cations calcium and magnesium, and some non-metals.

The chelating agent or ligand must have at least two functional groups, bidentate, capable of bonding to the metal atom. In this bond the ligand is an electron-pair donor and the metal an electron-pair acceptor, this is known as co-ordination bonding. The functional groups can be acidic or basic. An acidic group loses a proton and co-ordinates with a metal atom. Since the loss of a proton is pH dependant, so is the ability of a particular acid to act as an effective chelating agent. A basic group contains an atom carrying a lone pair of electrons which may interact with the metal ion, these basic groups are called *co-ordination groups*.

The functional groups must be so located in the ligand that the formation of a ring including the metal atom is possible. The process of ring formation is known as *chelation*. The word *chelate* describes the ring. Chelation changes, often profoundly, the chemical and physical characteristics of the constituent metal ion and ligand and has far reaching consequences in the realms of chemistry and biology[ii]. The consequences of these changes for artefacts have not been mentioned in literature, though this seems relevant information for the conservator.

In general, for a chelating ligand which contains *Z* donor atoms all capable of co-ordination to a single metal ion, *Z-1* chelate rings will be formed and the larger the value of *Z* the greater the stability of the resulting complex[iii]. The enhanced stability associated with chelation is called *the chelate effect*. The size of the ring can also effect the stability of the chelate complex. The rings usually have five or more sides, smaller rings are possible only on rare occasions.

The properties of metal ions also affect chelate formation. The metal ions vary in their number of co-ordination sites. The major determining factors are the oxidation state (or valence) of the metal atom, the charge of the metal atom and the number of available bonding orbitals[iv].

Stambolov[v] gives a few guidelines in the use of chelating agents:

1 Degreasing of the stained areas prior to treatment is essential.

2 Hot solutions increase the rate of chemical reactions involved in stain removal and intensify diffusion of the reaction products.
3 Repeated prolonged weak solutions are more effective than one drastic treatment.
4 Contact between the stain and the cleaning solution is better and the durability of action on the stain is longer if, instead of a pure solution of the stain remover, the latter is mixed with absorbent matter (starch, chalk, talc, corn meal, flour, magnesia, magnesium silicate, asbestos, cotton-wool, cotton textile etc.) and then spread on the stain as a thick layer.
5 Rinsing with distilled water before and after each treatment is indispensable.

Chelating reactions work fastest when both the chelating agent and the metal to be chelated are present in solution[vi]. A good method of using chelating agents is to combine them with a reducing agent[vii]. The reducing agent will transform the coloured, insoluble ferric iron, Fe(III), into the more soluble, colourless ferrous iron, Fe(II). A good reducing agent is sodium dithionite, also known as sodium hydrosulphite. EDTA would be a suitable chelating agent to use with sodium dithionite.

Factors that influence the preference of a chelating agent for one ion over another, such as pH and stability of the formed complex, are taken into account in a number called *Conditional Stability Constant.* This is a practical expression of the chelate strength for a certain metal ion with a certain chelating agent.

The chelating agent prefers to chelate metal ions with the highest conditional stability constant, which form a more stable complex. However, any excess of chelating agent will chelate the next favourable metal ion. The conservator must be aware of this process, and control the amount of chelating agent used.

Since the conditional stability constant is pH dependent, pH can be used as a means of increasing the selectivity of a solution for one ion over another.

Chelating agents can be used in a poultice. This will keep their influence restricted to a limited area, and minimise any residue after treatment.

Recent research has shown the effectiveness of some chelating agents (triammonium citrate for example) to remove certain types of dirt or deposits from paint and varnish surfaces[viii]. The ability of chelating agents to dissolve surface dirt deposits is difficult to explain, since the major components are often organic. The chelating agents would not generally be expected to act on these non-polar fractions of dirt. It is possible that the chelating agents, in this situation, are partly acting as surfactants[ix] [x]. This research proves that our existing knowledge about the mechanism of chelation may not be complete yet.

EDTA

The most commonly used chelating agent in conservation is EDTA. EDTA is non ion-selective and has therefore been used for various treatments, such as rust removal, removal of basic lead carbonate, chemical stripping of bronzes, salt removal from mural paintings and frescoes, iron and copper stain removal from leather and textiles and the removal of various accretions from archaeological ceramics and glass.
To improve the efficiency of chemical reactions, to reduce non-productive side-reactions and to minimise damaging secondary effects, the *selectivity* of reagents for metal ions must be high. Furthermore, the chelating agent must be thermally and chemically stable and must have high ion binding energies.

According to Chartier[xi] the deficiency of EDTA is due to the fact that EDTA experiences two parallel and complex acid-base equilibria. One is associated with the deprotonation of the ligand binding sites and the other is the equilibrium of the metal ion and the ligand[xii]. Chartier says that this leads to a very complicated situation that does not favour a high degree of selectivity or control over the overall complexation. The situation would be simplified in a more selective chelate system, especially one that does not require deprotonation before complex formation[xiii].

In her thesis about cleaning rust from riveted faience, Merlin[xiv] tested hydrochloric acid, orthophosphoric acid, thioglycolic acid, EDTA, sodium citrate and sodium oxalate. She found that the acids caused structural deterioration. EDTA resulted in the least deterioration but was not very efficient.

Thorn[xv], however, found in his research for the impact of disodium EDTA on stone that EDTA is quite an aggressive reagent for calcite, has limited effect on gypsum and no effect on kaolinite. Contrary to his expectations the EDTA had little effect on rust, but had clearly etched marble.

Burgess mentions EDTA as a suitable chelating agent to combine with the reducing agent sodium dithionite.

[i] Helen Burgess, 'The use of chelating agents in conservation treatments', The Paper Conservator, 15 (1991), pp 36-44
[ii] Colin F. Bell, 'Principles and applications of metal chelation', Oxford 1977
[iii] Colin F. Bell
[iv] Helen Burgess
[v] T. Stambolov, 'Notes on the removal of iron stains from calcareous stone', Studies in Conservation 13 (1968), pp 45-47
[vi] Helen Burgess
[vii] Helen Burgess
[viii] Alan Phenix and Aviva Burnstock, 'The removal of surface dirt on paintings with chelating agents', The Conservator 16 (1992) pp28-38
[ix] Alan Phenix and Aviva Burnstock
[x] Surfactants reduce the surface tension to allow wetting and bring water and fat, oil or grease into an emulsion.
[xi] Duane Chartier, "Cation-selective reagents for conservation treatments", Materials Issues in Art and Archaeology II, Materials Research Society, Pittsburgh 1991
[xii] Duane Chartier
[xiii] Duane Chartier
[xiv] Christine Merlin, 'Le nettoyage de la rouille sur des faïences agrafés au XIX siècle', Paris 1984
[xv] Andrew Thorn, 'The impact of disodium EDTA on stone', ICOM 10th meeting 1993 pp 357-363

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