



Technical Note: An Unexpected Aspect of EDTA Partial Digest Extractions

by Roger Fidler, Mark McGeough and Keith Hannan

As a result of our own difficulties with the use of EDTA, we have no trouble sympathising with several contributors to the discussion of the role of carbonate and pH in partial leach extractions. As has been regularly shown, there are a large number of complications that may be associated with partial leaches, but we have come across an effect with which we were not familiar and that may have relevance to aspects of the discussion.

Our work has been concerned with mineral exploration using copper and zinc complexes of EDTA. It had been our expectation that while elements may compete more or less successfully for a given complexing agent, the optimum conditions for the formation of a particular complex would be relatively constant and independent of the presence of other elements. We now have reason to review this assumption.

Knowing the conditions under which the various complexes were stable has been basic to the project and the computer programs HYDRA and MEDUSA were used to produce speciation models for any particular circumstance. For example, the estimated, relative proportions of EDTA species occurring in the presence of a 20% surplus of EDTA at various pHs for 10 μ M copper (Figure 1) or 10 μ M zinc (Figure 2 - see page 2).

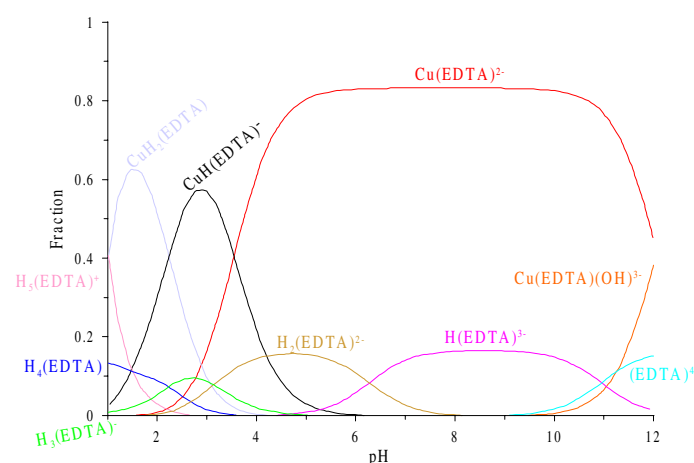


Figure 1. Modelled proportions of EDTA species in the presence of 20% excess of EDTA over that required to complex 10 μ M copper

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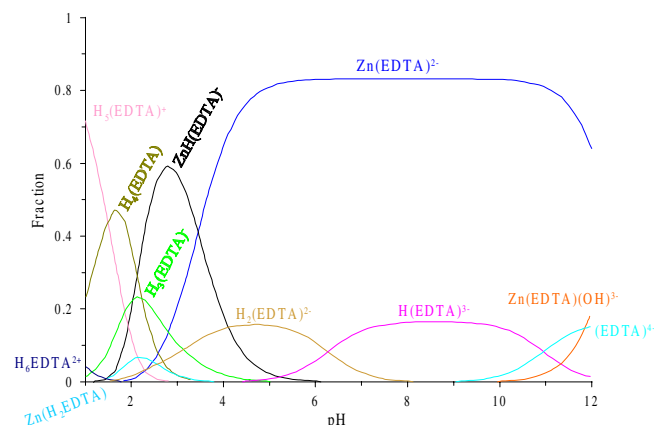


Figure 2. Modelled proportions of EDTA species in the presence of 20% excess of EDTA over that required to complex 10 μM zinc.

A rather large number of species are anticipated and even though the diagrams show a superficial similarity, they differ in detail. However, the important feature as far as this discussion is concerned is that in isolation, Cu(EDTA)^{2+} (red) and Zn(EDTA)^{2+} (blue) are predicted to be the dominant and stable species for the respective elements, between about pH 4.5 and pH 10, the range where geochemical extraction commonly takes place.

As the copper-EDTA complex has a higher stability constant than its zinc counterpart, in circumstances where

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both elements are present and there is insufficient EDTA to form the complexes of both metals, it might be expected that the copper-EDTA complex would be formed, preferentially. If we consider the situation where there is only 80% of the EDTA required to complex both metals, the curves for Cu(EDTA)^{2+} and Zn(EDTA)^{2+} (Figure 3) show that this is exactly what happens. The pH range of either complex is little altered but most EDTA is complexed by copper with zinc only able to form a complex with that which is left over.

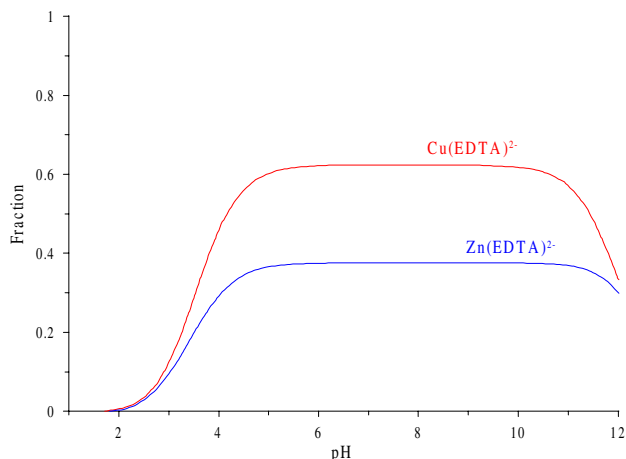


Figure 3. pH stability ranges for Cu(EDTA)^{2+} Zn(EDTA)^{2+} with a deficiency of 20% EDTA

However, the nature of the model is quite different when the amount of EDTA is much lower. For instance, with only 5% of the EDTA necessary to complex all metal, the proportions of the complexes are no longer constant over the pH range and instead, the prediction is that the copper-EDTA complex, alone, will form at low pH and at higher pH, the EDTA will be shared more evenly, such as shown in Figure 4.

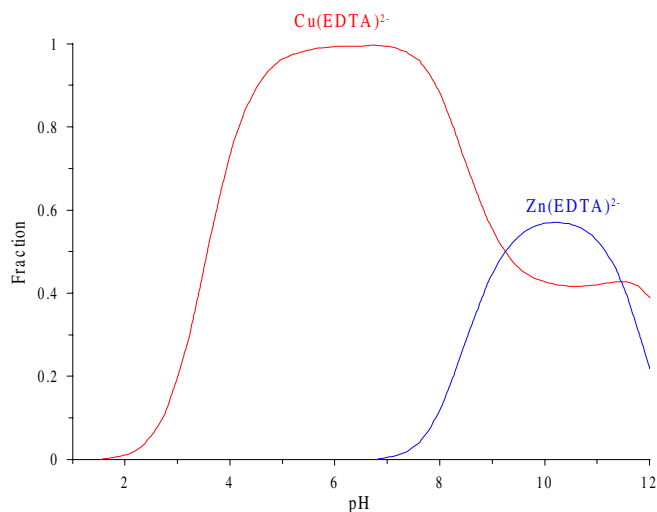


Figure 4. pH stability ranges for Cu(EDTA)^{2+} Zn(EDTA)^{2+} with a deficiency of 95% EDTA

This is a computer simulation of only one aspect of an extraction and not a laboratory measurement but the practical implication is that for an extraction dependent on EDTA complexation, the optimum extraction pH for a particular element is not necessarily independent of other metals present when the ratio of EDTA to metal is low. However, it does have some laboratory support.

One of several peculiar aspects of the survey that triggered this investigation was that high zinc results came from samples giving high, final pHs (>pH8) when our expectation, based on Dronseika and Evers careful, experimental work, was the opposite. Conversely, the high copper results all came from samples giving low final pHs (<5). As a consequence, even though copper and zinc are thought to have a common source, no sample was anomalous for both copper and zinc. A number of explanations can be devised but few have the advantage of those involving this modelled pH effect of simultaneously accounting for all.

Models of other element pairs suggest that this should not be unique. Lead should interact with the zinc-EDTA complex in a similar fashion to copper, as would, ferric, bismuth, some rare earth elements and many others. Cobalt, however, should do the opposite and push the zinc optimum to a lower pH. The elements mentioned are also predicted to have a geochemically-noticeable effect on the pH range of each other. Common metals such as aluminium and iron III are of particular interest, not only because they are ubiquitous and abundant, but also because some have chemically stable EDTA complexes (but may be limited by the solubility of the minerals in which they occur).

The use of low-concentration EDTA extractants is widespread but since a low EDTA to metal ratio is necessary for this particular problem to arise, one remedy (within limits) would seem straightforward. The use of buffers has been suggested as a means of limiting pH-related extraction problems. Although a varying pH is not beneficial to extraction, limiting pH change would not

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seem an adequate defence from problems arising in this fashion as the optimum pH for a specific element could vary with the composition of the sample and in a manner which might differ from element to element. Forcing a low, constant pH could conceivably even be counterproductive in that it could result in an increase in the level of diverse cations to battle for available ligand, thereby worsening the EDTA to metal ratio.

Though problems of this nature can be prevented in future, their recognition in existing data sets is both a challenge and an opportunity. Some of the unusual results which led to the current hypothesis may thus be of interest to those reviewing existing data and to that end, a

more comprehensive communication is being prepared.
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References

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- The programs HYDRA and MEDUSA were written by Ignasi Puigdomenech of the Royal Institute of Technology, Stockholm.

