Heat changes measured are actually heats of displacement, the water being gradually replaced by the solute [3]. The trend of the enthalpies of displacement in Fig. 1 considering the influence of the thermal treatment shows that the MDS exhibit at every surface coverage a higher enthalpy of displacement; this fact is interpreted by supposing that the thermal treatment favours the exhibition at the surface of chemical and polar groups capable of strong interaction with the Cu(II) ions. This fact could be interpreted as due to an increase in the electrical potential of the Stern Gouy diffuse layer [5] with a consequent more difficult diffusion of Cu(II) ions toward the polar surface: analogous results have been obtained on an oxide surface [6]. From the analysis of calorimetric peaks, relative to DS and MDS samples, we can deduce that the thermokinetic trend is somewhat different, the MDS showing an apparently smaller reaction rate.

Starting from the hypothesis that the rate determining step is the diffusion of the solute, we have tried to apply a semiempirical treatment assuming a time dependence of the diffusion equation [8].

In Fig. 2 we have reported the function:

$$F(t) = \log P + 3/2 \log t$$

where $P \cong KW$ is the instantaneous deviation of the calorimeter *vs.* the reciprocal of time. The linearity of the curves in Fig. 2 is satisfactory enough both for DS and MDS samples.

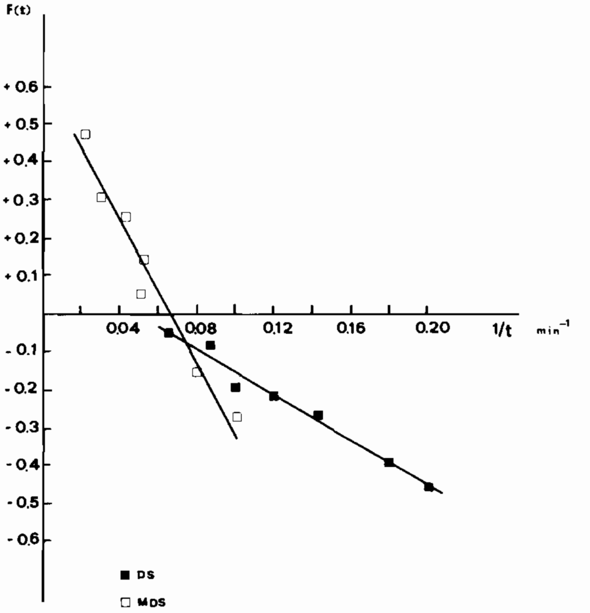


Fig. 2. The function: $F(t) = \log P + 3/2 \log t$.

The MDS samples show a greater slope, that means a smaller diffusion coefficient; that would correspond to a more dense Gouy layer; in other words, the MDS sample that exhibits a greater number of polar and ionic groups would have a higher repulsive potential field in the diffuse layer. We may conclude that kinetic [1] and thermokinetic studies are in agreement and show that the initial uptake rate is smaller on MDS than DS; but the limiting adsorption quantities are higher for the former. This situation could be interpreted by assuming that the determining step is the diffusion of the ions through the double layer which should be characterized by a higher electrical potential in the case of MDS.

1 C. Sarzanini, *Sep. Sci. and Technol., 18,* 1 (1982).
2 J. F. Wilkinson, *Bacteriol. Rev., 22,* 46 (1958).
3 G. Della Gatta, L. Stradella and G. Venturello, *Zeit. für Phys. Chemie, Neue Folge, 106,* 95 (1977).
4 G. Della Gatta, L. Stradella and P. Venturello, *J. Solution Chem., 10,* 209 (1981).
5 H. B. Abramson, M. J. Jaycock and R. H. Ottewill, *J. Chem. Soc.,* 5041, 5034 (1964).
6 M. H. Kubatov, G. B. Wood and J. D. Kubatov, *J. Phys. Chem., 55,* 1170 (1951).
7 C. Sarzanini and L. Stradella, *Entropie,* to be published.
8 R. E. Weston, Jr. and H. A. Scwarz, *Chemical Kinetics, N. J.,* 162 (1972).

---

## S18

## New Approach for the Determination of Stability Constants of Metal Ions–Soil Organic Matter

Y. BIZRI, M. CROMER and J. P. SCHARFF*

*Laboratoire de Chimie Minérale, Université Claude Bernard Lyon I, 69622 Villeurbanne, France*

The binding of metal ions to organic materials in soil and water is an area of considerable interest. A better understanding of the equilibria that determine the behaviour of the chemical elements in the superficial environment is clearly essential for effective geochemical research. Naturally occurring organic compounds are an integral part of soils and aquatic systems. These substances play a major role in the retention and deactivation of anthropogenic organic and mineral chemicals and are involved in the geotransport of metals.

Humic substances make up the bulk of organic matter and they probably control the abundance and distribution of trace metals in the environment by complexation or chelation processes through functional groups including carboxylic, phenolic, alcoholic and enolic OH, carbonyl and $NH_2$ sites at which binding may occur [1].

The determination of stability constants of metal–humic and fulvic acid complexes permits the prediction of the chemical speciation of many metals and the elucidation of their dispersion cycles.

The present work deals with the interactions of lead(II), cadmium(II) and copper(II) ions with water soluble soil organic matter. Cu(II) like Zn(II), Mn(II) ..., is a metal which is essential to plants while Cd(II) and Pb(II) are without known function in plants but are of considerable interest in view of their toxicity and accumulation in the environment. A variety of methods have been applied for determining stability constants of metal–humate complexes, as reviewed by Stevenson [1]. Considerable progress has been made, but agreement has not yet been reached as to how the data can best be analyzed and interpreted. One of the most popular methods is base titration, which uses the competition of metal ions and protons for complexing sites on the ligand. It is such a modified approach that has been developed in this work.

Humic substance samples (in this context, this term will be used to designate a system of organic water soluble compounds including polymers) were recovered by percolating rain-water through a A2 horizon of a podzolic soil and purified by filtration, ultracentrifugation, and treatment by passage through ion exchange resins [2]. Stock solutions of metallic perchlorates were prepared from commercial products and standardized against EDTA.

Samples containing constant quantities of humic substances and perchloric acid were titrated by sodium hydroxide in the absence and in the presence of metal ion. Protometric measurements were performed at 25 °C in 0.1 $NaClO_4$ medium under nitrogen atmosphere. An automatic titrator 'Tacussel TT Processor' fitted with extension glass and calomel electrodes was used for recording direct and differential titration curves; pH readings were combined with determinations of free metal ion concentrations by means of ion selective electrodes (ISE).

### *Titration and Protonation Constants of Humic Samples*

For humic substances which contain COOH and OH groups of various acid strengths we shall define the ligand concentration in terms of titratable acidity. The total acidity content was resolved into a strong, weak and very weak acidity by applying linear titration plots derived by McCallum and Midgley [3] in combination with Gran's plots as previously used by Takamatsu and Yoshida [4].

In order to obtain $pK_a$ values for each of the two weak acidities, the so-called extended Henderson–Hasselbalch equation was used

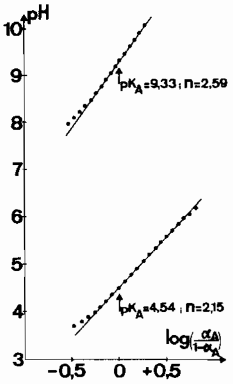
$$pH = pK_a + n \log \alpha/(1 - \alpha)$$

During the alkali titration, the dissociation of humic samples was characterized by a coefficient that may be determined from titration curves of perchloric acid alone and in the presence of humic substances, according to a procedure derived from Irving–Rossotti's method [5]. Figure 1 shows typical Henderson–Hasselbalch plots leading for instance to results such as:

– strong acidity: 0.32 meq $l^{-1}$

– weak acidity groups (COOH): 0.33 meq $l^{-1}$; $pK_a = 4.54$; n = 2.15.

– very weak acidity groups (OH): 0.34 meq $l^{-1}$; $pK_a = 9.33$; n = 2.59.



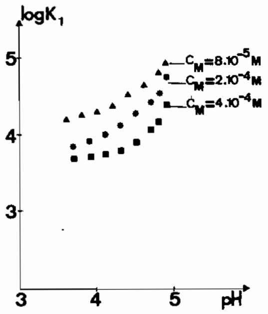


Fig. 1. Henderson–Hasselbalch plots. Humic substances sample; ionic strength 0.1 *M* ($NaClO_4$), temperature 25 °C.

Fig. 2. Variations in overall stability constant for PbA complexes with changing pH and total concentrations of lead(II).

### *Stability Constants of Metal–Humate Complexes (HA)*

Three different methods have been investigated in the acidic range:

– an approach closely related to that of Gregor *et al.* [6] but the experimental values of [HA] and [$A^-$] are determined using an original derivation of equations resulting from the application of Irving and Rossotti's concepts [5].

– direct estimation of the free metal ion concentrations from ISE measurements.

– application of Marinsky's method [7] accounting for complications arising from the electric field at the surface of the polyelectrolyte which determines the effective concentration [$A^-$].

Reasonable agreement is observed. The existence of mono-complexes MA is expected for the three metal ions, while bis-complexes $MA_2$ are detected with Pb(II) and Cu(II) ions. Stability of the complexes followed the order $Cu > Pb \gg Cd$. An increase in stability constant was observed with increase in pH and also with decrease in total metal ion concentration (at constant pH), as exemplified by Fig. 2.

*Acknowledgements.* We would like to thank B. Guillet and J. Rouiller for providing aqueous soil extracts and for many helpful discussions. This work was supported by the French Scientific Research National Center (CNRS).

1 F. J. Stevenson, 'Humus Chemistry', Wiley–Interscience, New York (1982).

2 B. Guillet, J. Rouiller and J. C. Vedy, 'Migrations Organo-Minérales des Sols Tempérés', Ed. CNRS, Paris (1981).
3 C. McCallum and D. Midgley, *Anal. Chim. Acta, 78,* 171 (1975).
4 T. Takamatsu and T. Yoshida, *Soil Sci., 125,* 377 (1977).
5 Y. Bizri, M. Cromer, J. P. Scharff, B. Guillet and J. Rouiller, *Geochim. Cosmochim. Acta,* to be published (1983).
6 H. P. Gregor, L. B. Luttinger and E. M. Loebl, *J. Phys. Chem., 59,* 34 (1955).
7 J. A. Marinsky, *Coord. Chem. Rev., 19,* 125 (1976).

---

## S19

## Fluorescence EXAFS of Biological Systems at SRS

S. S. HASNAIN, G. P. DIAKUN and P. D. QUINN

*Daresbury Laboratory, Science and Engineering Research Council, Warrington, U.K.*

E. M. WARDELL and C. D. GARNER

*Department of Chemistry, University of Manchester, Manchester, U.K.*

N. J. BLACKBURN

*Department of Chemistry, UMIST, Manchester, U.K.*

P. F. KNOWLES

*Department of Biophysics, Leeds University, Leeds, U.K.*

A fluorescence detection system consisting of five scintillation detectors has been commissioned recently on an EXAFS station at the world's first dedicated X-ray synchrotron radiation source (SRS). This facility has been established to measure the X-ray fluorescence excitation spectrum of specimens containing small amounts of metal atoms with absorption edges between 1 Å and 3.1 Å. Results recently obtained on copper containing enzymes are presented.

---

## S20

## Metal Ion Uptake by Plants of Genus Alyssum

R. FIUMANÒ, A. SCOZZAFAVA

*Dipartimento di Chimica, Università di Firenze, Florence, Italy*

R. GABBRIELLI

*Laboratorio di Fisiologia Vegetale, Università di Firenze, Florence, Italy*

Some plants of the genus Alyssum are able to accumulate nickel(II). It has been observed that increase in nickel content is accompanied by an increase in the level of malonic and malic acids in the leaves [1]. Indeed crude extracts obtained from the leaves showed the presence of the nickel salts of the above mentioned acids. However, it has been shown these plants also contain a considerable amount of free amino acids, which in principle should also act as ligands of the nickel(II) ion [2]. R. J. P. Williams has suggested that only the presence of ligands containing nitrogen donors can explain the selective uptake for example of nickel(II) over cobalt(II) [3]. We decided therefore to study the mechanism of uptake, transport and accumulation of metal ions by these plants, using the copper(II) ion as a probe. This is because the copper(II) ion can be studied through ESR, a technique which can be applied directly to whole samples (roots, leaves, plants *etc.*) thus avoiding the formation of artefacts.

When the cut roots of the plant are introduced for 1' into a $10^{-4}$ *M* $CuSO_4$ solution and washed with distilled water the spectrum 1a is observed (Fig. 1).

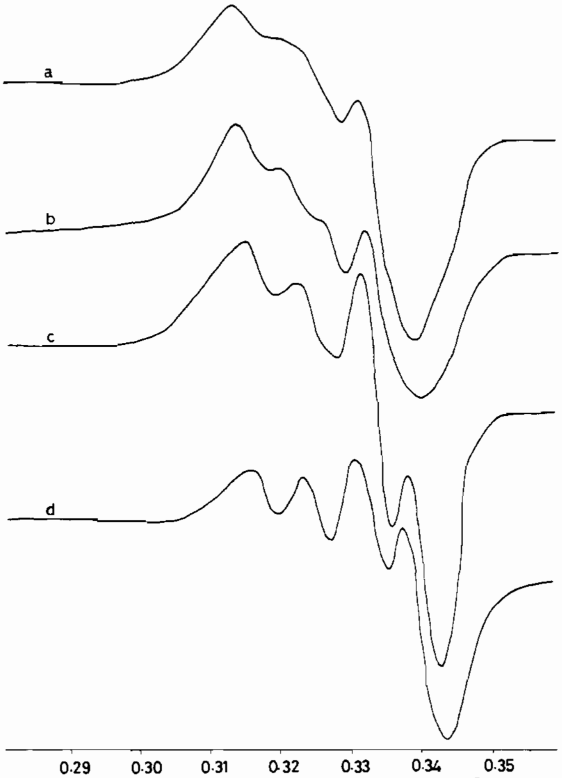


Fig. 1. ESR spectra of plant roots of genus Alyssum after immersion for 1' in $10^{-1}$ *M* $CuSO_4$ solution followed by immersion in distilled water for (a) 30 s, (b) 1 h, (c) 6 h, (d) 24 h.

This spectrum can be interpreted as the superimposition of the isotropic spectrum of freely rotating aqueous copper(II) with an anisotropic spectrum typical of immobilized copper(II) [4]. This spectrum does not change with time even if the roots are kept in water. If however the roots of an entire plant are