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## S19

## Fluorescence EXAFS of Biological Systems at SRS

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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*

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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  $\text{CuSO}_4$  solution and washed with distilled water the spectrum 1a is observed (Fig. 1).

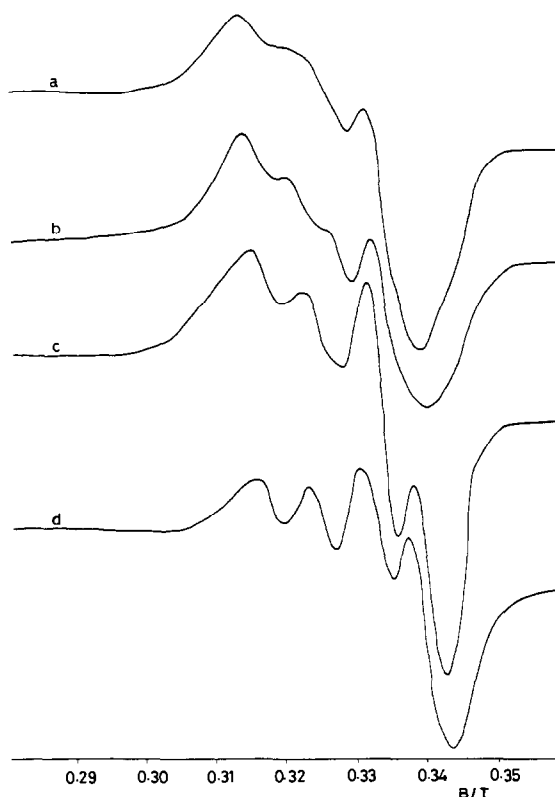


Fig. 1. ESR spectra of plant roots of genus *Alyssum* after immersion for 1' in  $10^{-4}$  M  $\text{CuSO}_4$  solution followed by immersion in distilled water for (a) 30 s, (b) 1 h, (c) 6 h, (d) 24 h.

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

immersed in distilled water after the treatment with  $\text{CuSO}_4$ , the spectrum 1a changes with time (1b, 1c, 1d) showing the progressive formation of a copper(II) complex with low molecular weight.

The spectrum 1d is also found in the leaves indicating that this is the medium through which copper(II) is transported across the plant. The  $g_{\text{iso}} = 2.13$  and  $A_{\text{iso}} = 80 \times 10^{-4} \text{ cm}^{-1}$  values are consistent with the presence of nitrogen atoms among the donors. This complex is fairly stable as it is also found in crude extracts of the plant and this might provide a possible way for its isolation. Preliminary experiments indicated that this complex does not migrate under electrophoresis. This complex could represent a 1:2 copper(II) amino acid complex. Studies are in progress in order to isolate and characterize this species (or mixture of species).

We also studied the absorption of other metal ions by these plants and we found that the uptake follows the order Cu Zn Ni Co Mn Cr. All these metals behave competitively toward Ni(II) indicating a common uptake pathway at least at the level of the roots (Fig. 2).

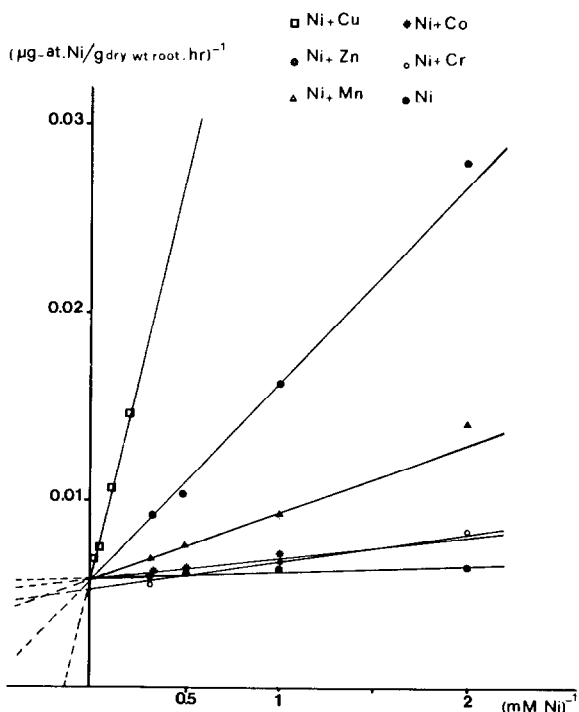


Fig. 2. Double reciprocal plot of uptake for nickel in the absence and presence respectively of 1.0 mM  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cr}^{3+}$ .

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## S21

### Trace Metals in Human Milk

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Analytical data regarding the metal content of human milk are rather scanty [1], although heavy metals represent one of the most common polluting agents. For this reason we investigated the composition of samples of human milk with respect to six metals (Cd, Cu, Cr, Ni, Pb, Zn).

The data refer to 28 analyzed samples, collected between the 20th and 60th days post partum.

The metals, after a wet mineralization, were detected by flameless atomic absorption spectrometry with a heated graphite furnace and deuterium background corrector, except for Zn which was detected by normal flame atomic absorption spectrometry.

The results are reported here:

– Cd: for 93% of samples the content of this metal is lower than 0.01 ppm, two samples containing 0.012 and 0.015 ppm respectively.

– Cu: this element is present at concentrations between 0.20–1.00 ppm in 96% of samples (mean 0.6 ppm). One sample shows a concentration of 1.65 ppm; this value is anomalous even when compared with those seen in the literature [1–4].

– Ni: 50% of samples show values lower than 0.10 ppm. 35% of values are between 0.10 and 0.20 ppm, while the remaining samples contain between 0.20 and 0.41 ppm.

– Cr: 96% of samples show values between 0 and 0.32 ppm (32% lower than 0.10 ppm and 64% between 0.10 and 0.32 ppm). One sample shows an anomalous value of 0.75 ppm.

– Zn: the samples show values of this metal between 1.60 and 4.50 ppm (89% of samples). The remaining samples have higher values of up to 8.30 ppm. Other authors have also pointed out the existence of such a large range [1–4], which seems to be correlated with the lactation time. However we cannot exclude the possibility that the highest values are due to the widespread use of zinc derivate pesticides.

– Pb: 28% of the samples show values below 0.10 ppm. 54% are between 0.10 and 0.30 ppm. The remaining values are remarkably higher (up to 1.62 ppm). In our opinion this may be due to lead contamination by fuel pollution.