

interesting problem since this element is not only capable of existing in a wide range of oxidation states but the most biologically significant of these, vanadium(IV) and vanadium(V), are characterised not by simple cations, but by more complex species [2], commonly described as vanadyl (VO^{2+}) and vanadate (VO_4^{3-}) ions, respectively. Studies have therefore been conducted to delineate the differences between the uptake patterns of vanadium supplied in these different forms. The effects of various physical parameters, notably temperature and pH have been examined and clear differences between the uptake of vanadium in different oxidation states have been demonstrated.

The uptake of vanadium(V), as vanadate, was found to increase with concentration and pH (over the range pH = 3–7) but was unaffected by temperature changes in the range 0–30 °C. For vanadium(IV), as vanadyl ion, uptake again increased with concentration and pH was observed to have an effect, but no significant temperature effect was observed. The uptake of the vanadyl cation was generally greater than that of the vanadate anion (or related polymeric oxoanion) under similar conditions. These effects can all be rationalised in terms of the known chemistry of the vanadium species and the general processes of ion uptake by plant roots.

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The Absorption of Thallium by Plants: A Comparison of the Uptake of Thallium(I) and Thallium(III) by Excised Barley Roots (*Hordeum Vulgare* c.v. *Maris Mink.*)

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In an aqueous environment thallium exhibits two common oxidation states, thallium(I) and thallium(III) [1]. The Tl^+ cation has a similar ionic radius to K^+ and it is known to mimic it in biological systems [2], however relatively little is known about the biological significance of Tl^{3+} . Accordingly the uptake of thallium supplied initially in both of these

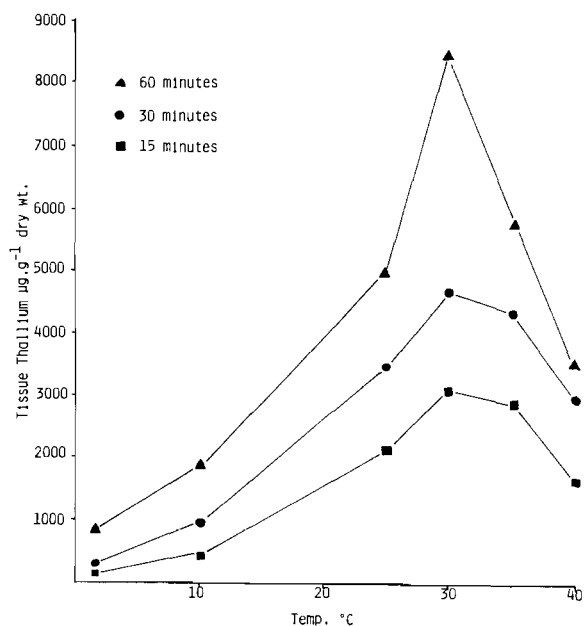


Fig. 1. Uptake of thallium(I) with time at various different uptake temperatures.

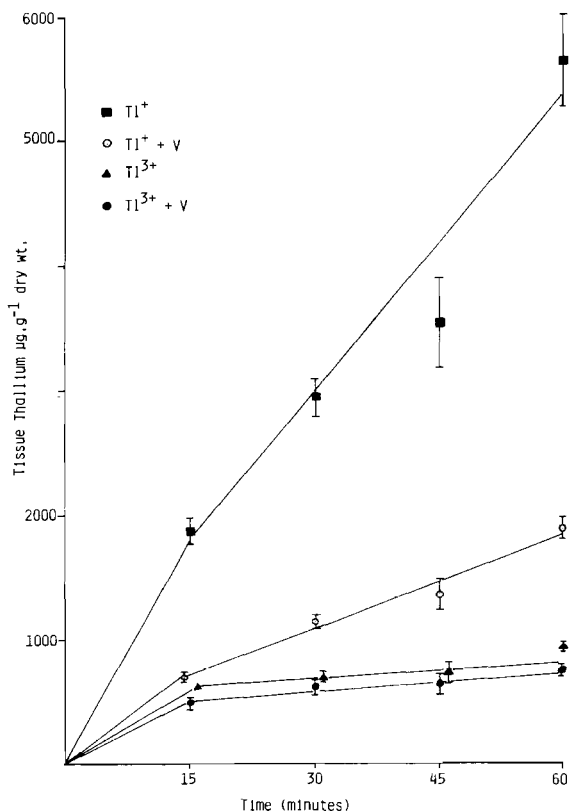


Fig. 2. Uptake of thallium with time in the presence of vanadate.

oxidation states to excised roots [3] has been investigated.

The uptake of both forms of thallium increased as expected with both time and applied concentration, but a significant difference was noted in the overall levels of accumulation with Tl^+ concentrations in the root tissue reaching ten times those found for Tl^{3+} under similar conditions.

The uptake of Tl^+ was found to be affected by temperature, with the uptake increasing with temperature over the range 0–30 °C, but showed inhibition thereafter. The uptake of Tl^{3+} was unaffected by changes in temperature. Figure 1.

The uptake of Tl^+ was severely diminished by several common metabolic inhibitors, particularly by vanadate which is recognised as an inhibitor of the Na^+/K^+ ATPases. Tl^{3+} uptake was unaffected.

Desorption studies showed that Tl^+ could not be removed from the root tissue, suggesting that it had entered the cell, but Tl^{3+} was easily removed by cation exchange, suggesting that it was confined to the extracellular space.

Overall the results suggest a process of active uptake for Tl^+ but passive uptake for Te^{3+} .

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Aluminum-Induced Inhibition of Calmodulin-Regulated Phosphodiesterase Activity: Enzymatic and Optical Studies

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Calmodulin, a highly conserved, endogenous calcium-binding protein, plays a major role in coordinating the effects of second messengers in response to cellular stimulation. Calcium is bound to four specific sites on calmodulin which has a molecular weight of about 17 000 [1]. Calmodulin also seems to participate in regulating the polymerization of brain microtubules whose assembly depends in part on the local level of cyclic 3':5'-nucleotide phosphodiesterase [2]. Results presented in this communication show that aluminum binds stoichiometrically to calmodulin thereby changing its conformation which, in turn, leads to an inhibition of the calmodulin- and calcium-dependent phosphodiesterase activity.

Calmodulin was prepared from bovine brain acetone powder by affinity chromatography [3] with 500 mM NaCl in the elution buffers to enhance the purity of the material. All buffers and assay solutions

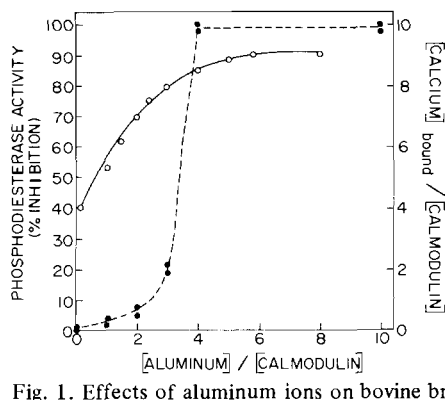


Fig. 1. Effects of aluminum ions on bovine brain calmodulin as monitored by calcium binding (o) and inhibition of calcium-calmodulin stimulated cyclic 3':5'-nucleotide phosphodiesterase activity (●). The enzymatic assay was conducted in the presence of 25 μM $CaCl_2$ and 5 μM calmodulin, at pH 6.5, Tris buffer 10 mM, with reaction times varying between 15 and 30 min.

were free from contaminating metals as analyzed on a Varian atomic absorption spectrophotometer, model 1475. Calcium binding was measured under equilibrium dialysis conditions. The enzymatic activity was assayed as described [4].

The addition of increasing aluminum concentrations to calmodulin- and calcium-dependent phosphodiesterase produces a distinctive inhibition of the enzymatic activity (Fig. 1). In the absence of aluminum, 0 percent inhibition corresponds to 0.6 nmol/ml·min cyclic GMP hydrolyzed. 50 percent inhibition of the enzymatic activity occurs at a molar ratio of 3:1 [aluminum]/[calmodulin]. The metal-induced inhibition does not appear to result simply from a displacement of calcium from its specific sites on calmodulin, as demonstrated by measuring the calcium content with atomic absorption (Fig. 1). Rather, application of aluminum causes a larger hydrophobic surface exposure of the protein as compared to that generated by calcium, as evidenced by fluorescent, hydrophobic probes. These results are in accord with those from circular dichroism experiments indicating that aluminum induces helix-coil transitions in calmodulin at stoichiometric ratios [5]. These kinds of changes in the protein may explain why the aluminum-calmodulin complex cannot interface properly with the enzymatic protein and lost at least part of its regulatory character; formation of this complex may thus be a key lesion in aluminum toxicity.

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