7 5

Aluminum Speciation in Soil Solution through Differential Kinetic Reactions with Ferron

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^{27}Al-NMR spectroscopy has been required for definitive identification of the $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ polycation (Al_{13} tridecamer), but recent studies suggest that it is equatable to the polynuclear Al fraction that exhibits a moderate reaction rate with the spectrophotometric ferron (8-hydroxy-7-iodo-5-quinoline-sulfonic acid) reagent (Al_b). Our objectives were to further test this correspondence, to critically evaluate the ferron-Al_{13} reaction kinetics, and thus to use this method for identification of Al_{13} tridecamer in natural soil solution. Firstly, partially neutralized solutions were prepared with $[Al]_{Total}$= 10^{-2}~10^{-3} mol L^{-1} after equilibration in different pH conditions, and were quantitatively analyzed using ferron, 8-hydroxyquinoline method for $[Al]_{monomeric}$, and AAS for $[Al]_{Total}$. The results confirmed that the $[Al]_b$ fraction measured with ferron corresponds to $[Al_{13}]$ in the simulated solutions, indicating that they are, if properly evaluated, indeed consistent and predictable, permitting near-certain identification of Al_{13}. Secondly, simulated soil solutions (pH=5.0) were extracted from B horizon of Andisols, Cheju Island, after equilibration for 24 hours with 1mM NaCl (pH=3.0), and were also quantitatively analyzed using ferron. The results showed that at least two different polymeric Al fractions (10^{-4}~10^{-5} mol L^{-1}), possibly including Al_{13}, were identified by the distinct slope changes between reaction time and Al-concentration relation. Proto-imogolite sol might be another possible phase, which is supported by the substantial amounts of Si in soil solution and the result of ferron study for the synthetic proto-imogolite sol. In spite of some uncertainty for the identification of Al_{13} in soil solution, the ferron method offers a simple and inexpensive alternative to ^{27}Al-NMR spectroscopy and allows quantification of Al_{13} at concentrations 10-100 fold lower than presently analyzable by NMR, a concentration range pertinent to natural waters.