Detection and assignment of inorganic aqueous polymers relevant to environmental nanogeoscience by direct infusion electrospray ionization mass spectrometry

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Inorganic polymers in aqueous solutions are being proposed as essential components in new theories concerning nonclassical nucleation and growth of nanominerals relevant to environmental nanogeosciences. The study of those complex natural processes requires multi-technique analytical approaches able to characterize the solutions and their constituents (solutes, oligomers, polymers, clusters and nanominerals) from atomic to micrometric scales. A novel analytical approach involving an electrospray ionization source (ESI) coupled to time-of-flight mass spectrometry (TOF/MS) was developed to identify inorganic polymers in aqueous solution. To this end, the presence of initial Al oligomers and their polymerization processes was studied during a nanomineral aqueous synthesis (hydrobasaluminte, Al4SO4(OH)10·12-36H2O). Ensuring the feasibility and robustness of the methodology as well as the stability of the polymers under study (avoiding undesirable fragmentation), a meticulous study of the ESI-TOF MS working conditions was performed. Precision of the methodology was evaluated obtaining relative standard deviations below 3.3%. For the first time in the study of inorganic polymers in the earth sciences, the mass accuracy error (ppm) has been reported and the use of significant decimal figures of the m/z signal has been taken into account. Complementary to this, a four-step polymer assignment methodology and a database with the Al? and Al-SO42? polymers assigned were created. Several polymers have been assigned for the first time, including Al (SO4)+·H2O, Al2O(SO4)2+·H2O, Al5O4(OH)52+·2H2O, and

Al3O5(OH)2?·4H2O, among others. The results obtained in the present study help create a foundation to include mass spectrometry as a routine analytical technique to study mineral formation in aqueous solution.