SEPARATION OF TRACE ELEMENTS FROM OTOLITHS BY COPRECIPITATION APPROACH FOR DETERMINATION BY ICPMS

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Abstract: Otoliths of a fish contain trace elements that are mainly derived from the fish’s habitat, and act as chemical markers to elucidate the life-history of the fish. Excluding few trace elements (Ba, Sr, Mg), the concentrations of most elements in otoliths are very low, ranging from ng/g to low sub-µg/g. Additionally, the predominant calcium matrix deteriorates the accurate measurements by inductively coupled plasma mass spectrometry (ICP-MS). The objective of this study was to develop a coprecipitation method to separate the trace elements from the otolith’s calcium matrix to achieve accurate determination by ICP-MS. Sodium hydroxide (NaOH) and ammonium hydroxide (NH₄OH) were used to precipitate trace elements simultaneously with trace amounts of calcium hydroxide. Several variables, including calcium concentration, volume of bases, volume of solution, and precipitation time were investigated to optimize the precipitation of trace elements and effective elimination calcium matrix. The acidity of the sample solutions were adjusted to 0.1% HNO₃ before addition of the base. NaOH performed better in precipitation of the elements than NH₄OH. Only few elements, including Mn, Pb and Fe coprecipitated when NH₄OH was added to synthetic otolith solutions acidified to 0.1% HNO₃. When NaOH was used as precipitation agent, a series of elements, including Ag, As, Bi, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn were quantitatively coprecipitated with calcium hydroxide matrix. Optimum volume of 1.0 mol/L NaOH was around 100-110 µL. Visible precipitation were detected upon addition of NaOH solution. In the case of NH₄OH, no visible precipitation observed. The solutions were filtered through 0.45 µm PTFE filters to recover precipitates that were redissolved in 2 mL of 5% HNO₃ for ICP-MS analysis. For successful coprecipitation, calcium concentration in solution should be above 5 mg/mL. The volume of sample solution did not significantly affect the coprecipitation efficiency, but was found to be advantageous to reduce the concentration of calcium in solution. The calcium concentration in analysis solutions was around 500, 350, 180 and 120 µg/mL when precipitation was performed in 1, 2, 3, and 4 mL. Under same conditions, the recoveries of the elements ranged from 92-99%. Although most elements coprecipitated instantaneously with calcium hydroxide, Ag, Co, Ni, Pb and Zn exhibited low recoveries for short-period of precipitation time (2 h). These elements were quantitatively recovered when precipitation was carried out overnight. The method was validated by analysis of otoliths reference material and applied to analysis of otoliths of pacific halibut (hippoglossus stenolepis).

Keywords: Otolith, coprecipitation, trace element, calcium matrix, ICP-MS

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