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Micro-Analysis for Sea Water by Freeze Concentration and X-Ray Fluorescence Method

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Summary

Concentration rate in freeze concentration depends on type of solute and the temperature of sample ice, that is, the concentration rate can be arbitrarily determined by adjusting these. Although the freeze concentration method is useful, it has rarely been used as a pretreatment method of analytical methods so far. The reason is that the liquid phase is dispersed throughout the doped ice. In this study, X-ray fluorescence (XRF) method using synchrotron radiation was adopted as a means for performing high sensitivity measurement by freezing concentration, in order to apply the freeze concentration method to trace element analysis. The freeze-concentrated liquid phase, which was not taken out from doped ice, was directly and simultaneously multi-element-detected by synchrotron-XRF method. Sodium chloride was used as a main solute in sample solutions. In addition to NaCl, the several μM transition metal nitrates (Mn, Co, Cu and Zn) were included in solutions. The aqueous solution was frozen to prepare doped ice with a hole prepared using a capillary. Liquid phase in doped ice flows into the hole in doped ice, whereby the dispersed liquid phase was collected in the hole. Synchrotron-XRF measurement was performed at beamline BL-4A and BL-15A1, Photon Factory, High Energy Accelerator Research Organization, Tsukuba. When the hole in doped ice at -8 ℃ was observed using confocal fluorescence microscopy, the hole (Ø420 mm) was filled with solution. The observed fluorescence X-ray intensity weakened as the size of the hole increased. This result indicates that the amount of the collected aqueous phase in the sample ice was smaller than the hole size or the neighboring aqueous solution moved to the hole. As a result, the hole size to be made on doped ice was set to 400 μm or less. 68mM NaCl doped ice with some transition metal nitrates was observed by Synchrotron-XRF measurements at -1 ℃. The hole size in the doped ice was Ø150 mm. The distributions of fluorescence X-ray intensities for Mn, Co, Cu and Zn were almost agreement with that for Cl. It could be regarded that these metal ions moved to the hole with the aqueous solutions at the grain boundaries. That is, we were able to collect aqueous solutions dispersed in the doped ice and detect it by Synchrotron-XRF measurement.