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Development of a LC/MS method to analyze simple sugars: an approach to investigate ribose formations on the early Earth

Mana Horiuchi[1*], Furukawa Yoshihiro[1], Otake Tsubasa[1], Kakegawa Takeshi[1]

[1]Earth and Planetary Materials Science, G

Ribose is considered to be one of the difficult molecules to synthesize on the early Earth. Formose reactions with either boric or phosphoric acids have been reported as reactions to produce ribose. However, those reaction pathway and necessary conditions are still uncertainbecause analytical methods of products from the formose reaction are unavailable. Therefore, in this study, we have developed a method to analyze polymerization products of formaldehyde and their complex with borate ion using liquid chromatography-mass spectrometry (LC/MS). Small sugars (glyceraldehyde (C3), erythrose (C4), and D-ribose (C5)) and a complex of D-ribose and boric acid were used as representatives of polymerization products of formaldehyde. In order to increase the ionization efficiency of these samples, a mixture of chloroform and methanol was added as an ionization agent into the mobile phase between the LC and the MS. Tow negative modes, electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI), were adopted for the ionization of these samples. In addition, two types of hydrophilic interaction chromatography (HILIC) columns and a ligand exchange column were used in the LC for the separation of these sugars and ribose-borate complex.

The ionization efficiencies of these sugars and ribose-borate complex were increased by adding the ionization agent in most cases. These sugars ionization modes were not determined either ESI or APCI. Among these three columns, the ligand exchange column was most effective for the separation of the sugars. However, the separation between ribose and ribose-borate complex could not achieve by the column.

Using these methods, we analyzed the polymerization products of glyceraldehyde reacted each other under highly alkaline conditions with or without sodium borate. The method was successful for the analysis of the residual glyceraldehyde. The results showed that decomposition of glyceraldehyde were more significant in the sample free from borate. This result suggests that borate ion improves the stability of glyceraldehydes. On the other hand, the peaks of other sugars were not apparent because of their low yields and the high background counts. All results indicate the usefulness of the newly developed method for studies of prebiotic ribose formation.

Keywords: LC/MS, Ribose, Formose reaction, Borate