

超高分解能質量分析計「MULTUM」を用いた希ガス(Ne)のオンサイト測定法の開発

Development of on-site neon measurement system using a portable ultra-high resolution mass spectrometer (MULTUM)

*中山 典子¹、古谷 浩志²、角野 浩史³、豊田 岐聡⁴

*Noriko Nakayama¹, Hiroshi Furutani², Hirochika Sumino³, Michisato Toyoda⁴

1.東大・大海研、2.阪大・院・理学研究科(現 阪大科学機器リノベーション・工作支援センター)、3.東大・院・総合文化研究科、4.阪大・院・理学研究科

1.Atmosphere and Ocean Research Institute, University of Tokyo, 2.Graduate School of Science, Osaka University (Now at Center for Scientific Instrument Renovation and Manufacturing Support, Osaka University), 3.Department of Basic Science, Graduate School of Arts and Sciences, University of Tokyo, 4.Graduate School of Science, Osaka University

Dissolved noble gases (He, Ne, Ar, Kr, and Xe) in seawater are chemically inert and their variations are thus solely responsible for physical processes such as temperature change, diapycnal mixing, and mixing of water masses. Since different noble gases have different temperature dependence on diffusivity and solubility, the noble gases show different responses even to the same physical forcing, which make us possible to quantitatively estimate how much physical processes the water mass experienced in the past through the simultaneous measurements and subsequent comparison of the observed noble gas concentrations.

Present measurement of dissolved noble gases requires a comprehensive purification and separation of each noble gases from sample gases extracted from seawater (*e.g.*, Sano and Takahata, 2005, Stanley, et al., 2009) to avoid that residual atmospheric gases interfere subsequent mass spectrometric quantification of the target trace noble gases using a quadruple mass spectrometer (QMS) with a low mass resolution. The pretreatment system is quite large and complicate for its field operation and it is practically impossible to conduct the purification and quantification on-site along with seawater sampling. Water samples, then need to be brought back to a land-based laboratory. The taking seawater samples back to the land-based laboratory without suffering contamination of highly permeable atmospheric noble gases requires to store the samples in copper tubes with the both ends fully squashed and completely sealed, which is quite cumbersome and requires man power. Such time-consuming and labor-intensive sampling and pretreatment in both field and laboratory have limited available number of samplings and measurements, and subsequently resulted in a quite limited number of observed data of noble gases in water environments.

Here we introduce a new method for the direct measurement of atmospheric neon concentration without cumbersome pretreatment and sampling treatment by combining multi-turn time of flight mass spectrometer (MULTUM) and a simple cryo-gas trap as a preliminary stage of the development for the online analysis of dissolved noble gases. The ultra-high mass resolution of the MULTUM (10000~30000) compared to that of ordinary QMS (100~500) allows our Ne⁺ (m/z 19.9919) ion detection to be free from interference ions, such as H₂¹⁸O⁺ and HF⁺ (m/z 20.0057 and 20.0151, respectively) which have close m/z to that of Ne⁺ (Fig. 1) and cannot be detected separately with commonly used QMS. Prior to the ultra-high resolution mass spectrometric analysis, most of the major atmospheric gases (*e.g.*, N₂, O₂, Ar and CO₂) were removed by a cryo-gas trapping to avoid a saturation effect during ionization in the mass spectrometer and further optimize the mass spectrometer for the detection of trace Ne⁺ ion. Such a simple and compact pretreatment system, compared to the ordinary large and complicated one, enables us to bring the pretreatment system to the field and conduct on-site analysis of Ne.

As a test case, atmospheric Ne was analyzed by directly injecting 0.5~5 cm³ of atmospheric air

into the developed system. Atmospheric Ne (18 ppmv) was successfully measured in every 10 minutes by simply injecting sample atmospheric air into the system (Fig. 1-2). An obtained good linearity between injected air volume and Ne^+ ion peak (Fig. 2) shows that the simple cryo-gas trap also can work as a pre-concentrator, which is another advantage for trace gas analysis. The preliminary result shows that the developed method can be applied for the continuous and direct measurement of dissolved Ne and other noble gases with further modification.

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Keywords: MULTUM, dissolved noble gas, on-site measurement, ultra-high resolution mass spectrometry

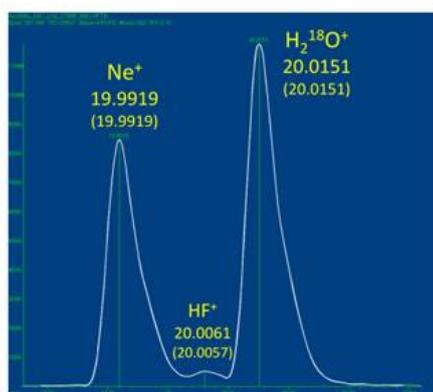


Fig. 1. The high resolution mass spectrum of an atmospheric air sample (m/z 19.19 ~ 21.19) obtained derived from obtained mass chromatogram using MULTUM. The high mass resolution ensured separate detection of Ne^+ (m/z 19.9919) ion from interference ions, such as HF^+ (m/z 20.0057) and $\text{H}_2^{18}\text{O}^+$ (m/z 20.0151).

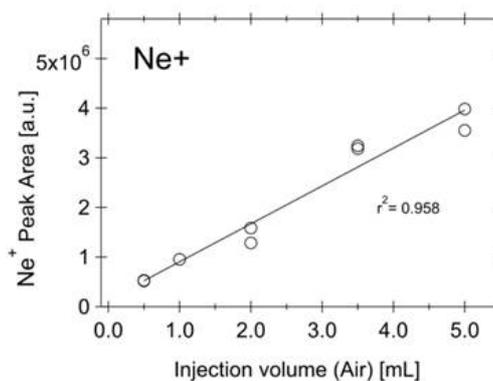


Fig. 2. The relationship between injected volume of atmospheric air samples and the Ne^+ ion peak area obtained using a simple cryo-gas trapping system. A good linear relationship was obtained between the analytical ion peak and injection volume over a range of 0.5–5mL ($r^2 = 0.958$).