Trace elements play a very important role in many areas, such as environmental science and technology, industrial applications. Increasing attention has been focused on determination trace metals in environmental samples from the perspective of the pollution of the nature environmental and their roles in the geochemical research. However, analyses are usually difficult owing to the complex nature of samples and the low concentrations involved. On the other hand, to produce high purity materials, rapid determination of trace metals to control of the purity of the materials is rather important.

Atomic spectrometry is widely used in many laboratories, particularly whenever trace element analyses are required. The particular technique used will depend on the sensitivity required, the number of samples to be analyzed. In this paper, analytical methods for the determination of trace elements in high purity materials (high purity iron and steels) and environmental samples (sediment samples and water samples) were established introduced as follows:

1) Effectiveness of Pd/Mg chemical modifier for the accurate direct determination of zinc in marine/lacustrine sediments by graphite furnace atomic absorption spectrometry (GF-AAS) using slurry samples was evaluated. A calibration curve prepared by aqueous zinc standard solution with addition of Pd/Mg chemical modifier is used to determine the zinc concentration in the sediment. The accuracy of the proposed method was confirmed using Certified Reference Materials, NMIJ CRM 7303-a (lacustrine sediment) from National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology, Japan, and MESS-3 (marine sediment) and PACS-2 (marine sediment) from National Research Council, Canada. The analytical results obtained by employing Pd/Mg modifier are in good agreement with the certified values of all the reference sediment materials. Although for NRC MESS-3, an accurate determination of zinc is achieved even without the chemical modifier,

the use of Pd/Mg chemical modifier is recommended as it leads to establishment of a reliable and accurate direct analytical method. One quantitative analysis takes less than 15 minutes after we obtain dried sediment samples, which is several tens of times faster than conventional analytical methods using acid digested sample solutions. The detection limits are 0.13 $\mu g \ g^{-1}$ (213.9 nm) and 16 $\mu g \ g^{-1}$ (307.6 nm), respectively, in sediment samples, when 40 mg of dried powdered samples are suspended in 20 ml of 0.1 mol l^{-1} nitric acid and a 10 μl portion of the slurry sample is measured. The precision of the proposed method is 8-15% (relative standard deviation).

2) The preparation of calibration curves using an aqueous standard solution was studied for the direct determination of trace levels of zinc in high-purity iron and steels by graphite furnace atomic absorption spectrometry (GF-AAS) using solid sampling technique. Certified reference materials of high-purity iron and steel samples were used to confirm the trueness of the proposed methods. The standard addition method for the solid sampling technique that we have proposed gave accurate analytical results. The calibration curve prepared by the standard addition method can be used as a kind of an iron-matrix matching calibration

curve, and it provides rapid and accurate determinations of zinc. The detection limit of zinc in iron and steel samples was 0.86 mg/kg when 15 mg of one sample was measured.

3) This work introduces the development of a novel determination method of trace nickel (ng l^{-1} level) in natural water samples. Nickel in the water samples is liquid-liquid extracted into methyl isobutyl ketone (MIBK) as nickel-diethyldithiocarbamate (DDTC) complex, and isotope dilution-oxygen added nitrogen-microwave induced plasma mass spectrometry (ID-oxygen added nitrogen-MIP-MS) is conducted by direct measurement of the liquid-liquid extracted organic MIBK phase. The accuracy of the proposed method was confirmed by analyzing certified reference materials (NRC NASS-5 seawater, NRC SLRS-3 estuarine water and NRC SLRS-4 river water), and the analytical results obtained were in good agreement with the certified values. The detection limit for nickel is 24 pg l^{-1} when water sample is 50 times concentrated. The precision as RSD is <4%. The proposed method was applied to clarify the concentration-depth vertical profiles of nickel in Lake Mashu, Japan, as the Baseline Station of the United Nations GEMS/Water (Global Environment Monitoring System/Water) Programme.

論文審査結果の要旨

本論文は5章より構成される。第1章は研究全体の序論、第2章は高純度鉄鋼中微量亜鉛直接定量のための検量線作成方法、第3章は海底および湖底堆積物中微量亜鉛の直接定量法、第4章は天然水中超微量ニッケル定量のための抽出分離濃縮/同位体希釈/プラズマ質量分析法、第5章は総括である。

第2章では、迅速なsolid sampling原子吸光分析法の問題点であった検量線作成方法についてマトリックスマッチングによる検量線を用いて迅速かつ真度の高い定量を可能にした。第3章では、試料中微量亜鉛を原子吸光分析装置黒鉛炉内でchemical modifierと化学反応させて原子化効率を統一することによって迅速かつ真度の高い定量を可能にした。第4章では、真度の問題点と感度不足が指摘されていた天然水中超微量ニッケルの定量について、ニッケル錯体をマトリックス成分から分離濃縮し同位体希釈を用いることにより高感度で真度の高い定量を可能にした。本法を国連GEMS/Water programのベースラインステーションである摩周湖水中の超微量ニッケル定量に適用し大気由来ニッケル負荷を考察した。

本論文は、分析目的を明確にし、試料の種類と試料中分析目的元素の状態、使用可能な試料量、分析に許される時間、要求される感度・精度・真度を把握することによって従来の問題点を解決する方法論を確立しており、博士後期課程論文に値すると判断される。