# 学位論文内容の要旨

A water-soluble cationic derivative of porphyrin, which is named as meso-tetrakis(4-N- trimethyl -aminophenyl)porphine(ttmapp), was synthesized in our laboratory in 1981 as a potential ultra sensitive colorimetric reagent for metal analysis due to its intense absorption in visible region. By using the method of acid-separation of the spectra, Soret band of ttmapp was first time utilized in the ultra trace analysis of metal and copper in serum was successfully determined. Since then, Cd(II), Pd(II) and Pb(II) have also been determined with ttmapp at ultra trace level.

Like other derivatives of porphyrins, ttmapp is also inert to form complexes with metal elements and up to now, only five metals of Cd(II), Pd(II), Pb(II) and Cu(II) have been reported to be determined with ttmapp. The aim of this research is to find out more applications of ttmapp in analytical field, focusing on its ultra high molar absorptivity and the rapid catalytic complexation reaction with Cu(II).

This dissertation mainly consists of 3 parts as follows:

a) Post-column substitution methods for the simultaneous determination of some species of amino acids, the simultaneous determination of 14 species of rare earth elements(REE) and the simultaneous determination of 5 species of heavy metals of Cu(II), Zn(II), Ni(II), Co(II) and Cd(II).

b) Kinetic method for the individual determinations of ascorbic acid, glutathione, cysteine and homocysteine on a flow injection analysis (FIA) system.

c) Analytical methods derived from the FIA system developed in part b) for the individual determinations of some oxidative metals and glutathione disulfide.

The basis of these analytical methods is the catalytic complexation reaction of Cu(II) with ttmapp. In part a), the methods can be subdivided into direct substitution method for the determination of amino acids, which can form stable complexes with Cu(II); and indirect substitution method for the determinations of REE and heavy metals, in which EDTA was utilized as a mediate chelating agent to form complexes with both metal elements and Cu(II). The reactions involved in each method should occur consecutively thus the control of the reaction sequence is critical for these substitution methods. A postcolumn FIA system was employed to meet this requirement and achieved the analytical purposes with both efficiency and precision.

In part b), the complexation reaction of Cu(II) with ttmapp was used as the indicator reaction to determine some catalytic substances like ascorbic acid, cysteine and etc.. Instead of the traditional batchwise kinetic procedure, a continuous flow injection system was employed, which automated the reaction procedure thus led to the efficient and precise results.

In part c), the methods for the determination of some oxidative metals or glutathione disulfide were developed. The former is based on the strong reducing ability of ascorbic acid and a reaction system as ascorbic acid-Cu(II)-ttmapp was incorporated into a FIA system. The latter is based on a masking procedure of glutathione with N-ethylmalaimide followed with an enzymatic reduction of glutathione by glutathione reductase in a batchwise experiment, making the selective analysis of both forms of glutathione possible on one system.

# 論文審査結果の要旨

環境科学においても、また生命科学においても、その複雑な質の変化を精密に、定量的に、かつ迅速に把握する方法論の開発は今日的急務である。水溶性陽イオン型ポルフィリンttmapp は現存する最高の吸光感度を持つ化合物として知られているが、Cuイオンとの反応が特異的すぎることから、その応用範囲が限られていた。本研究では近年、そのハードウエアの開発が著しいフローインジェクションアナリシス（FIA）システムをこのCuとポルフィリンの反応システムに応用することにより、これまで考えられなかった種々のアミノ酸や、アスコルビン酸、グルタチオン、ホモシステインといった生体微量物質の迅速・正確なモニタリングや、Cu以外の数多くの重金属を吸光度モニタリングとしては最高レベルの感度で定量を可能にするという目覚しい成果をあげた。これは非常に複雑なCu-ポルフィリン反応システムの熱力学的な特性と触媒反応の速度論的特性を巧みに利用し、従来のマニュアル操作では到底不可能な手法を、自動化したFIAシステムに組み込むことによりはじめて可能とした成果である。

この成果が、今後の環境科学研究および生命科学研究における貴重なツールとして貢献するところは、非常に大きいと言える。

よって、申請者は北見工業大学博士(工学)の学位を授与される資格があるものと認める。