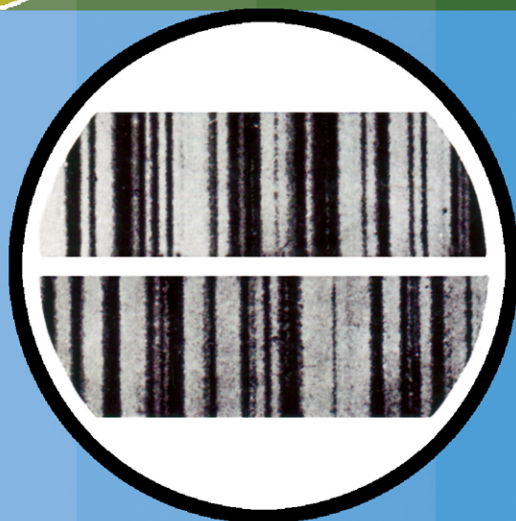


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Organic Reagents in Metal Analysis

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by

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PREFACE

THE tremendous scientific and technical development during the past twenty years has led to increased demands with regard to the production and quality control of highly pure materials. Research continues to uncover the increasingly important role of trace contaminants in more and more fields, ranging from industrial technology to living organisms. This advance imposes continuously growing requirements on the analyst. More and more new analytical procedures need to be developed for the selective or even specific determination of very minute amounts of various substances. In the field of metal analysis, the possibility of simple accomplishment of such tasks is offered primarily by organic complex forming reagents. These reagents form coordination compounds with metals, some particular characteristics of which permit their application in micro-analysis.

The considerable development of coordination chemistry during the past two decades has made possible, *inter alia*, the recognition of the factors determining the analytical selectivity of complexation reactions. In the light of modern chemical knowledge, more and more analytical problems can be solved via complexation reactions.

For further progress in this field it is important that analytical chemists possess a coordination chemical view and apply this in their work. This is why the first part of this book deals with a coordination chemical treatment of analytical reactions based on complexation.

The second part of the book provides tried and time-honoured analytical procedures for the accomplishment of many metal analytical tasks. An effort has been made to present examples covering a wide range of applications in such a manner as to provide assistance in further problems not detailed here. The number of analytically applied organic reagents is so vast, and still rapidly increasing, that I could not aim at completeness in this respect. Instead, those methods are presented of which I myself have experience.

At the end of the book tabulated data facilitate experimental work in the field of metal analysis.

I sincerely hope that this book will provide useful aid both to those researchers engaged with further development in this field of analytical chemistry and to practical analysts busy with routine metal analyses.

The Hungarian edition of this book appeared early in 1969. The English edition has been supplemented by several newer procedures and further literary references.

I should like to express my sincere gratitude to Professor R. Belcher and Professor H. Freiser, Editors of this series of monographs, who initiated the edition of this book in English.

I thank Dr. Tivadar Mohácsy for translation of the text, Dr. D. Durham for stylistic revision of the translation and Miss Judit Temesi for her extensive technical assistance in preparation of this edition.

Finally I express my thanks to Mrs. E. K. Kállay for her thorough and conscientious editorial work.

KÁLMÁN BURGER

INTRODUCTION

THE main trends in the development of analytical chemistry are determined by the demands of technical progress in the rapidly advancing old and the newly emerging branches of industry. This is why the determination of trace impurities in highly pure materials has become one of the central problems in analytical chemistry in this age of nuclear reactors and space vehicles, transistors and telecommunication satellites. The requirement is a double one: the *selective* determination of *very minute amounts of impurities* in the presence of several hundred or even thousand times as much of the main component. This duality is reflected in the two main directions of progress in analytical chemistry during the past twenty years: the development of instrumental methods and new analytical instruments which have increased the sensitivity of analytical procedures to an almost unbelievable degree; and the application, or the extension of the application, of selective and specific, highly sensitive organic reagents and reactions. These reagents^(108, 258, 339, 473) (a) form the basis of selective analytical procedures, (b) make possible the combined separation and enrichment of trace constituents, and (c) may be employed as masking auxiliary complexing agents in analytical procedures.

The high sensitivity of organic reagents may be illustrated by the following examples: palladium(II) ions can be detected with *p*-dimethylaminobenzylidene-rhodanine in a dilution of as great as 1:12,500,000. With the same reagent 0.02 γ silver can be detected in a dilution of 1:2,500,000. Similar sensitivity is found in the determination of copper with rubeanic acid (0.006 γ in a dilution of 1:2,500,000), or of lead with dithizone (0.04 γ , 1:1,250,000), and in a number of similar estimations using organic reagents. If one notes that under optimum conditions the above reactions are also more or less specific, the paramount importance of organic reagents in the analysis of metals appears evident.

The great majority of the analytical reactions of organic reagents are based on complexation. A thorough examination and evaluation of these reactions has been made possible only by the recent developments in coordination chemistry. This is the reason that though sixty and eighty years have elapsed since the introduction of the first selective organic reagents: α -nitroso- β -naphthol⁽²⁰⁷⁾ and dimethylglyoxime,⁽⁴⁵⁸⁾ respectively, the physicochemical examination of the reactions utilized in analytical chemistry started as late as twenty years ago, while their evaluation has been made possible only by recent results.

The early investigations were mainly devoted to determining the stoichiometry and the quantitative course of reactions. In the next stage, the extent of the selectivity of reactions was determined by empirical "tests"; from many data the selectivity was held to be a property of the various functional groups and no attempts were made to find more fundamental explanations. The most outstanding representative of this era is Feigl.⁽¹⁵⁸⁾

Contributions by coordination chemists,^(226, 262, 283, 415, 453, 479, 483) opened up new vistas in research. Empirical tests were replaced by the exact physicochemical determination of stability constants and the thorough physical examination of the reaction products.

From a knowledge of the equilibrium constants of complex formation it is now possible in many cases to predict by simple calculation which metal ion or which ligand will interfere with a given complexation reaction,^(378, 453) which ligand is suitable for masking a given metal ion in a given complexation reaction, and how this masking can be terminated later.^(115, 379)

From a knowledge of the regularities of complex formation and the factors which determine the stability, solubility and the spectrum of a complex, it has become increasingly possible to design new organic reagents and to specify the scope and limitations of long-known reagents.^(86, 96) Thus the study of the analytical application of organic reagents has emerged from the era of empirical data collection. More and more empirically elaborated analytical procedures become interpretable on a physicochemical basis and this greatly stimulates the development of new analytical procedures.

It should be mentioned, however, that though a knowledge of theoretical relationships considerably facilitates the design of the optimum conditions for analytical experiments and reduces the number of unsuccessful attempts, *it never substitutes for experimental work*. It holds true in analytical chemistry, too, that experiment is the criterion of theory. The results of research work carried out in this respect clearly indicate to analysts the importance of the contribution of coordination chemical investigations. On the other hand, it has frequently been proven that a thorough, detailed physicochemical study of reactions well known from an analytical viewpoint can result in the elucidation of complex chemical and bonding theory relationships.

Almost all organic reagents utilized in the analysis of metals are complex-forming agents. They give complexes with the metal ion to be determined or to be identified. The properties of the metal complex formed determine whether the organic ligand is suitable for application in gravimetry, volumetric analysis, spectrophotometry, polarography or in some other field of chemical analysis, and whether it should be used for the *enrichment* of the metal ion to be determined, the *masking* of interfering metal ions or the direct *determination* of the metal ion in question.

The reactions of organic reagents are *selective* if they react with a certain group of metals only, or if one or some of the complexes they give with various metal ions possess some particular physical or chemical properties. By means of selective reactions certain metals can be determined or detected in the presence of several other accompanying metal ions.

A selective reaction is termed *specific* provided it is characteristic of a single metal. However, although reactions considered as selective are usually common for many cations, by appropriate choice of the reaction conditions the selectivity can be enhanced in many cases, and under optimum conditions the reaction may even be made specific.

For many years Feigl and his co-workers⁽¹⁵⁸⁾ investigated how various organic compounds react with metal ions, and the nature of the relationship between the structure of an organic molecule and its reaction with metal ions. Their work

resulted in a great number of new, more or less selective analytical reagents. After Feigl, many analysts^(258, 329, 474) considered from an empirical viewpoint that the analytical selectivity of organic reagents is associated with the various functional groups they contain, but they usually did not look for more fundamental reasons.

The relationship between the basic strength of the ligand and complex stability and its analytical importance was first pointed out by Calvin^(109a) in connection with the stabilities of cupric chelates of a number of enolic substances. The papers of Freiser⁽¹⁷⁵⁾ and Irving and Williams⁽²²⁸⁾ presented at the First International Congress on Analytical Chemistry (Oxford, 1952) represent attempts to interpret analytical selectivity on a coordination chemical basis. Both papers emphasized the importance of the knowledge of the stability constants of complexes. They stated that by systematic variation of the factors affecting the stability of complexes, complex formation can be made selective or under optimum conditions even specific. Of these factors, both papers considered steric effects as the most promising from an analytical point of view. Irving stressed the role of orbital stabilization[†] and the effect of the basicity of the donor atom. In a continuation of Irving's work, Williams⁽⁴⁷⁹⁾ called attention to the analytical significance of the thermodynamic relations of complex formation, and dealt with the role of the oxidation state and changes in the oxidation state of metals.

Szabó and Beck⁽⁴⁵³⁾ provided a classical example for the application of the stability constants of complex formation and the acidic dissociation constants of the ligand in analytical chemistry. They demonstrated the possibility of calculating from such data those reaction conditions under which a given complex formation reaction is selective. During the last decade, Ringbom *et al.*⁽³⁷⁷⁻⁸⁰⁾ have dealt with the introduction of such calculation methods using the results and ideas of several complex chemistry research centres. It is due to their work that this approach is gaining more and more ground.

Erdey⁽¹⁴⁸⁾ interpreted the stability of complexes utilized for analytical purposes on the basis of the Lewis theory of acids and bases. He explained the Lewis acid strength of the central atom partly by electrostatic factors (ion potential, electronegativity) and partly on a quantum-chemical basis (bond types).

Bayer⁽³⁵⁾ pointed out the relationship between possible conjugation within the chelate ring and analytical selectivity.

The publications dealing with the problem illustrate the reasons for selectivity, with concrete examples (Irving:⁽²²⁸⁾ the copper(I) complex of 2,9-dimethyl-1,10-phenanthroline; Bayer:⁽³⁵⁾ glyoxal-bis-(2-hydroxyanil) complexes, etc.).

Burger *et al.*⁽⁸⁶⁾ examined the reasons for the selectivity of dioximes, considered the most selective reagent group. Using equilibrium measurements,^(35, 89, 94, 95, 148, 175, 377, 380) infrared,⁽⁹⁸⁾ ultraviolet and Mössbauer spectrometric analyses,⁽⁹²⁾ they established why dimethylglyoxime is specific for nickel(II) and palladium(II) ions.

These publications and those cited above clearly demonstrate that the question of the analytical selectivity of complex formation can be answered only by thorough coordination chemical examination of the individual systems. Since selectivity may be caused by different factors in the case of various complexes, the general

[†] By orbital stabilization is meant here the enhancement of stability due to electron pairing under the effect of strong-field ligands.