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Preface

In Comprehensive Analytical Chemistry the aim is to provide a work which, in many instances, should be a self-sufficient reference work; but where this is not possible, it should at least be a starting point for any analytical investigation.

It is hoped to include the widest selection of analytical topics that is possible within the compass of the work, and to give material in sufficient detail to allow it to be used directly, not only by professional analytical chemists, but also by those workers whose use of analytical methods is incidental to their work rather than continual. Where it is not possible to give details of methods, full reference to the pertinent original literature is given.

The present volume is devoted entirely to ultraviolet and visible spectrophotometry. The subject being large and diverse, four authors joined forces to produce the text. They all come from Polish scientific institutions. Some aspects of spectrophotometry, especially instrumentation, have already been dealt with in Volume IV. Further applications in inorganic and nuclear chemistry will be published soon in another volume of the series.

Dr. C. L. Graham of the University of Birmingham, England, assisted in the production of the present volume; his contribution is acknowledged with many thanks.

January 1986 *G. Svehla*

Chapter 1

Introduction

This book is essentially designed for analysts, but it may sometimes fall into the hands of chemists in other fields who want to use the spectrophotometric method in their research, or even into the hands of non-chemists. The authors, therefore, have found it advisable to include an introduction not only in the domain of molecular spectrophotometry, but also in general problems of chemical analysis.

Analytical chemistry, like any branch of science, has its underlying philosophy. The interest in general foundations of analytical chemistry, as well as in the determination of its role in science and society, has grown considerably in the analytical community in recent years [1—11]. This is perhaps because it is still underestimated by specialists of other branches of science, including non-analytical chemists [2, 3, 9, 10], in spite of the spectacular development of analytical chemistry in the 20th century [12]. This situation persists worldwide. In the Centenary lecture delivered by Professor Irving on the centennial of the British Society for Analytical Chemistry, the speaker emphasized several times the omission of analytical chemistry in individual reports on the development of chemistry [13]. This is all the more surprising when one considers that currently an estimated one-third of all work conducted in industrial chemical laboratories is of analytical character, even if the chemists are actually unaware of it [5].

Formerly, the importance of analytical chemistry was even greater. The roots of analytical chemistry reach back to fairly remote times. In principle, all ancient chemistry was originally analytical as man endeavoured to learn what the world consisted of. Alchemists attempted to produce new substances; once the new materials had been made, they had to find out what they had actually obtained; in consequence, one way or another, they analysed this material [9].

The term "analysis" was coined by the Hon. Robert Boyle as early as 1661 in his book "The Sceptical Chymist".

A lack of understanding of analytical chemistry and its underestimation is perhaps due to the fact that it is so "old". For many years chemical analysis largely depended on empirical precipitation and gravimetric methods, supplemented later by volumetric techniques. The rapid progress of the last 50 years has not always been able to change long held attitudes. This may also be due to insufficient teaching of analytical chemistry in many countries [14].

Nowadays the number of methods used in analytical chemistry is vast, and the methods are often based on physical or physicochemical phenomena. Present-day analytical chemistry is of an interdisciplinary nature, it is used by both chemists and physicists alike with indispensable assistance from electronic engineers and mathematicians.

Even new terms and expressions are suggested. For instance, the Division of Analytical Chemistry at the Atomic Energy Establishment at Harwell (U.K.) has been renamed the Division of Analytical Science, so that analytical chemists henceforth will perhaps be called analytical scientists [15]. In the German language today, the term "Analytik" is given preference over the hitherto used "analytische Chemie" [5—7]. Professor Kaiser [5] translates "Analytik" into English as "chemical analytics" (literally, "as something like chemical analytics"), but this translation loses the original meaning, i.e., to drop the attributive "chemical" or "chemistry".

The impression of these authors, however, is that the attempts to escape from "chemistry" are unjustifiable, as the tasks of analytical chemistry are, after all, the same as they used to be. It would perhaps be more correct to say that the tasks of chemical analysis remained the same in their very principle. There is no generally accepted definition for either of the terms mentioned. One of the definitions of chemical analysis goes as follows: "Chemical analysis constitutes such investigations of a material which are aimed at establishing its elemental or phase, qualitative and/or quantitative composition". This definition may well be applied to present-day chemical analysis, although its tasks have greatly expanded in relation to its former ones, and the basis for analytical determinations is conscious activity theoretically based, rather than empirically obtained procedures.

As far as the term of "analytical chemistry" is concerned, the definition due to Jones [2] may be invoked here, viz.: "Analytical chemistry is a science of chemical analysis". This definition embodies the whole interdisciplinary character of present-day analytical chemistry.

A modern analyst (or perhaps the analytical scientist) has a vast number of methods and techniques from which to choose. Which of these techniques is to be used depends on what is to be determined, and in which material. A method which affords excellent results in one case may not work in another, even though determination of the same element is involved, sometimes even in the same material. To be more specific, determination of europium in lanthanum can be made by one of the following methods: a direct spectrophotometric method (content $\geq 0.3\%$); an indirect spectrophotometric method by determination of Fe(II) formed as a result of the Eu(II) reduction (content 10^{-2}—$5 \times 10^{-1}\%$); emission spectroscopy (10^{-4}—$10^{-1}\%$), and finally by neutron activation analysis (10^{-7}—$10^{-4}\%$). The methods just mentioned are not the only suitable techniques; others include atomic absorption spectroscopy or mass spectroscopy, which also have preferred application ranges.

The logic sequence typically occurring during analytical work may be illustrated by the scheme shown in Fig. 1. The solid line encircles the operations in the charge of the analyst, the dashed line delineates stages that belong to the analysis customer. All the steps shown in the scheme form an integral whole and the final result of the work depends on all the intermediate stages. Nonetheless, the upper part of the scheme concerning stages prior to an analyst's work is quite often neglected as unimportant.

The final analytical answer depends on the question asked and on the analytical sample obtained. Unfortunately, the passage from the stage of material under analysis to the stage of analytical sample often lies in incompetent hands, and the sample received by the analyst no longer corresponds to the material supplied, or else the way in which it has been prepared may make the task impracticable. To give an example, if a zone-refined mono-crystal is to be analysed (material under study — a mono-crystal) the sample should be taken differently, depending on whether it is the average amount of a specific impurity, or the purification efficiency (single samples from within various mono-crystal zones) that is required; the sampling should be effected in yet another manner if contamination of the sample with the crucible material is of interest. Therefore, the mutual understanding of the analyst with the analysis customer can never be overestimated.

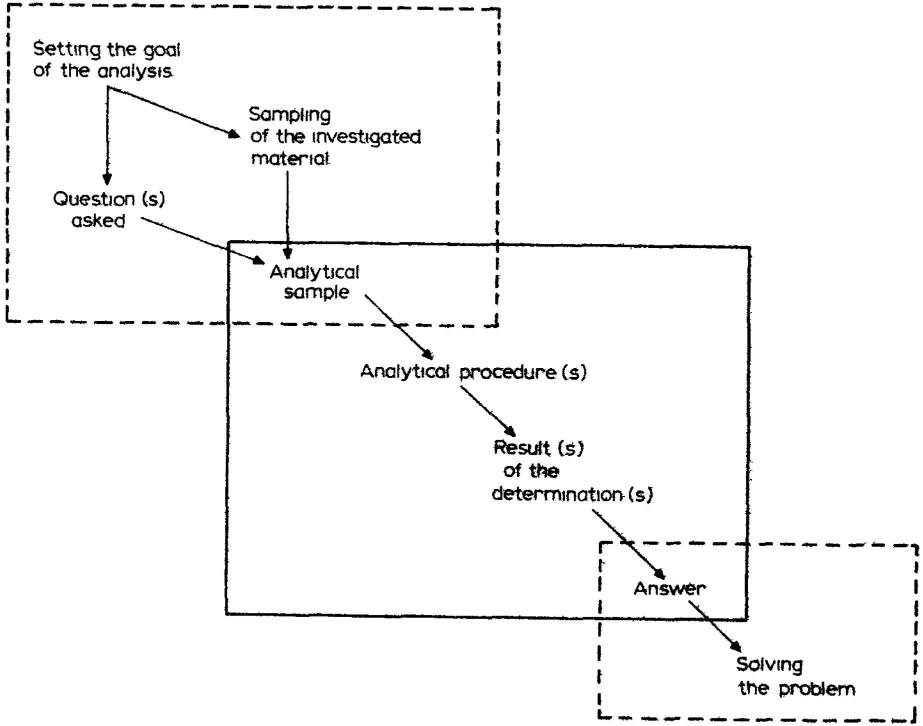

Fig. 1. The logic sequence typically occurring during analytical work