Analytical Measurement and Information

Advances in the information theoretic approach to chemical analyses

K. Eckschlager
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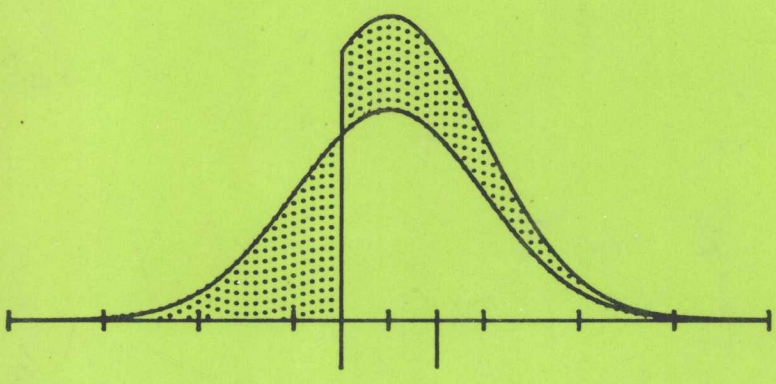

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To the memory of our fathers

Editorial Preface

Since the introduction of the mathematical formalisations of information theory some decades ago, they have found application in many diverse fields of science and technology. They have proved to be particularly powerful when used to give quantitative expression for the information provided by a technique or apparatus of measurement. This monograph deals with such an application, in the field of analytical chemistry. The authors have been at the forefront of research in this area, and have already written a standard text, of which this monograph may be considered a continuation. The application of information theory to analytical chemistry is a topic likely to increase in importance in the future, and it is to be hoped that this monograph will inspire interest by analytical chemists in general, as well as those already involved in work in this area.

David Bawden
Sandwich, July 1984.

Preface

The aim of this monograph is to comprehensively summarize recent results achieved in the development of the information theory approach to the evaluation of methods, procedures and results in chemical analysis. Since we have published a fundamental treatise on this subject in our monograph 1979 (Information theory as applied to chemical analysis, Wiley-Interscience, New York) this new publication collects and discusses almost exclusively those results that have been obtained by us as well as by other scientists after that date. Knowledge of basic concepts of probability theory and of information theory are prerequisite for the readers or may be drawn from the quoted monograph, to which also the text of this publication refers in many places. Nevertheless a considerable extention of the theoretical apparatus appears in this book as a tool for treating new analytical problems.

The introductory chapter presents a survey of the development of information theory applied to analytical chemistry. It is followed by Chapter 1 in which the principles of obtaining analytical information are outlined. In Chapter 2 some information measures are briefly recalled, other ones are newly introduced and they are all discussed and compared. A broader theoretical framework has been transferred to the Appendix. Next,

Chapter 3 brings together results concerning information properties and values of information quantities obtained in various analytical procedures. It is divided into sections reflecting different types of chemical analyses and requiring different approaches to the evaluation. Chapter 4 deals with models of analytical systems and their impact upon information theoretic evaluation. Here sources of uncertainty are investigated and among them attention is paid to the calibration and to the effect of sampling techniques. A reader wishing to gain a deeper insight into the philosophy of measuring information and into the ties between various information measures adopted in this book is referred especially to Appendix A.4. References are given at the end of each chapter in alphabetical sequence.

We wish to thank the editor of the Chemometrics series Dr Bawden from Central Research, Pfizer Limited, Sandwich for his initiative with which he encouraged the writing of this book and for his reading the text in the preparatory period. Our thanks belong also to our colleagues A.Petřina, K.Baše, and J.Fusek for attention in typing the manuscript and assistance in conducting the illustrative material.

Prague, March 1984

K.Eckschlager
V.Štěpánek

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Introduction

Although at the beginning of this century analytical chemistry was taken for a part of experimental chemistry and understood as a set of analytical methods and procedures based on chemical reactions, it has been developing, in recent decades, towards the utilization of various, mainly physical phenomena for analytical purposes. At the same time laboratory (instrumental and computing) technique continues its rapid advance. The analytical process accepts smaller quantities of material, it is possible to discriminate substances formerly undistinguishable and we can establish, by the means of local analysis, heterogenity of materials formerly treated as entirely homogeneous, etc. There occurs such conspicuous methodic differentiation of analytical chemistry that today individual methodologies develop altogether independently: they have their own "theoretical background", working methods, their own terminologies or at least laboratory slangs, and "methods" papers from different fields are published in closely specialized journals. Yet this differentiation, which greatly accelerated the development of analytical methods, narrows down the domain of interest of the analysts, sometimes to such an extent that they lose "the analytical approach" to problems to be solved.

Therefore the search for generally valid analytical points of view appears as a counterbalance to this differentiation: a major factor in these integration efforts has been the use of information theory in analytical chemistry.

Information theory has been developed since the end of World War II, first as a part of probability theory and today rather independently. Since information theory deals with the measurement of uncertainty, which is studied by the apparatus of the probability theory, this theory becomes fundamental for it. Information theory is pure mathematics, for it does not originate from empirical facts but from abstract definitions alone. Therefore, the statements of information theory apply everywhere in handling mathematical expressions of the same kind and its formulae do not depend implicitly on any empirical context.

The use of information theory in analytical chemistry has been subject, of course, to explicit development. In the first period at the beginning of the 1970s the members of "the Lindau circle" introduced general concepts and definitions from the point of view of system and information theories for the needs of analytical chemistry (Malissa, 1972). They also recognized that analytical chemistry has evolved into an independent scientific discipline dealing with methods obtaining and interpreting information about the chemical composition of material systems (Fresenius, 1977) or of signals bearing this information. Today information quantities are applied rather to evaluating, comparing, and optimizing analytical methods, procedures and devices (Eckschlager and Štěpánek, 1979, 1982; Liteanu and Rica, 1979; Cleij and Dijkstra, 1979; Danzer and Eckschlager, 1978; Danzer, 1973a, b, c, 1974, 1975a, b; Danzer and Marx, 1979; Eckschlager, 1975, 1976;

Frank et al., 1982; Danzer et al., 1982) and besides the "black-box" approach inherent in studies of information systems particular viewpoints are also of use which are conditioned by the chemical or physical substances of an analytical procedure or by properties of the device used. Also important is the application of information theory in decoding analytical signals, e.g., of IR or MS spectra (van Marlen and Dijkstra, 1976; Dupuis and Dijkstra, 1978). Kowalski (1980) classifies the use of information theory in analytical chemistry as a field of chemometrics.

Literature dealing with the use of information theory in analytical chemistry has become voluminous enough: one monograph (Eckschlager and Štěpánek, 1979) is entirely devoted to these problems and in another one (Doerffel and Eckschlager, 1981) we can also find application of information theory in the search for optimum strategy in analytical practice. Review articles (Cleij and Dijkstra, 1979; Eckschlager and Štěpánek, 1982; Frank et al., 1982; Liteanu and Rica, 1979) present surveys of some fields of analytical chemistry and of possibilities to adopt information theory in them. Another more than one hundred original papers can be divided into three groups:

1) Papers mostly originating from the beginning of the seventies, in which the importance of the use of information theory in analytical chemistry has been pointed out and in which some concepts and quantities have been defined by the use of the language and the relationships of information theory or of system theory. These papers have had great significance because they contribute to the modern and inter-disciplinary concept of analytical chemistry as of an independent scientific discipline. From a variety of papers by the members of "the Lindau circle" the Malissas' textbook (1972) is to be commemorated preferably.

2) Papers that introduce information measures and quantities into analytical chemistry and draw attention to their use in analytical practice for the evaluation and optimization of analytical procedures. Originally mainly the Brillouin measure (Eckschlager, 1971; Danzer, 1973a, b, c; Danzer and Eckschlager, 1978; Danzer and Marx, 1979, 1982), more recently measures transferred from Shannon's communication theory have been introduced (Liteanu and Rica, 1979). Cleij and Dijkstra (1979) recommend equivocation and Frank et al. (1982) introduce transinformation for the evaluation of analytical results and methods. The divergence measure, which is a comprehensive measure of information obtained from measurements (Vajda and Eckschlager, 1980) was first adopted in chemical analysis by Eckschlager and Vajda (1974) and later its use was extended and generalized by Eckschlager (1975), Eckschlager and Štěpánek (1979, 1980, 1982).
3) Case studies, in which methods and relationships of information theory are used to evaluate and compare analytical results, methods, procedures and ways of processing analytical data, in choosing and optimizing analytical methods and procedures and in coding and decoding analytical signals (e.g., the spectra): over one hundred such papers have now been published.

Here we will try to summarize the main results of papers belonging to the second group, to classify the somewhat divergent definitions and terminology and to review the mathematical foundations of this domain, which forms today a field of chemometrics. Bonchev (1983) has reviewed the development and the application of information theory in various branches of chemistry in the introduction of his book published in Volume 5 of this Chemometrics Series. We explored some possibilities

of the use of information theory in chemical analysis in our monograph of 1979. However, there exists a difference between chemometrics in analytical chemistry and in other branches of chemistry. Whereas in physical, organic, and inorganic chemistry or in biochemistry we mainly adopt prepared data that are reduced, classified or mutually related, the use of mathematical and statistical methods in analytical chemistry concerns almost exclusively with obtaining data, and therefore with a process of obtaining information about the chemical composition.

We have dealt in our monograph from 1979 as well as in this book only with information measures and possibilities of their practical employment in carrying out analyses or in theoretical analytical chemistry. Nevertheless we think that the aim of adopting chemometrical methods in analytical chemistry should be a simultaneous use of several mathematical methods that would supplement each other and that could be combined. If a specific problem is solved by the use of a number of mathematical methods at the same time, which have different substances and stem from different fundamental ideas we can reach, in favourable cases, a cooperation phenomenon, i.e., a synergetic tendency of individual methods to the given objective. This point of view has not been so far sufficiently pointed out in chemometrical literature, although a possibility to combine statistical methods with those of information theory in analytical practice in the search for optimum strategy has been mentioned in some examples in the monograph by Doerffel and Eckschlager (1981).

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