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普通高等教育化学类专业规划教材
国家级双语教学示范课程配套教材

化学计量学基础

梁逸曾　易伦朝　◎编著

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前　言

化学计量学(chemometrics)由瑞典科学家 Svante Wold 提出，自其 20 世纪 70 年代问世以来，在国际上得到普遍认同，现已被欧盟分析化学专业委员会列为分析化学的四大支柱学科(波谱与光谱、色谱技术、化学生物传感和化学计量学)之一。化学计量学在化学量测中的采样理论与实验设计、化学数据处理、分析信号解析与分辨、化学分类决策与预报等方面，解决了大量传统的化学研究方法难以解决的复杂问题，显示了其强大的生命力，已受到化学尤其是分析化学工作者的极大关注。

近年来，国际国内一些院校的化学及其相关专业已将化学计量学作为必修课或选修课纳入本科生或研究生的教学计划中。由于化学计量学是一门新兴交叉学科，大量重要文献都是英文给出，英文基础对学好此课程亦十分重要。其实，教育部历来对英语教育就十分重视，相应的英语四、六级的考试也在督促学生在大学期间的英语学习。但是，大学本科的英语教育效果确实不够理想。学生在学习期间花了不少时间，学到的是一些英语的基本语法和基本词汇，但英语学习与知识或专业的学习是分离的，所学到的英语知识基本难以得到应用的机会，致使英语作为语言交流工具的基本功能难以实现。所以，学生在大学学业完成后，还很难与国外同行进行学术交流。一种语言的学习应该与其经常的应用结合起来方能真正学好。教育部近年来力主教授(其中特别是知名教授)要上本科课堂，还特别对“双语教学”进行强力推崇，其初衷可能也在于此。

现今的社会是一个竞争的社会，我们国家急需一大批能与国际科研界平等对话和平等竞争的人才，没有这样一大批的人才，绝无实现“中华崛起”梦想之可能。直接采用英文来进行知识或专业教育，对培养能与国际科研界平等对话和平等竞争的人才的确很重要。记得本人在研究生的学习中，导师俞汝勤院士就采用英语为我们上化学计量学课，教材就是本专业中的一些重要文献(英语原文论文)。我虽没有参加任何专门的如 TOFFE 或 GRE 之类的英语考试和培训，但当我完成了博士期间的学习在 20 世纪 90 年代到挪威继续做博士后研究时，基本就没感到学术交流过程中有语言障碍的困难。这些课使我受益匪浅，令我终生难忘。所以，通过进行双语教学，以缩短学生从课程学习快速过渡到科学研究的准备过程，提高学生的国际竞争能力，力争达到既学好了课程又提高了英语的作用。

我校对化学计量学课程进行双语教学始于 2002 年，2008 年该课程成为教育部双语教学示范课程。在进行双语教学的过程中，我们体会到学生对双语教学是欢迎的，其中尤其是一些基础较好的学生，他们认为双语教学对他们是一种挑战，使他们兴奋，积极性很高。他们在学习过程中，不但学习了专业知识，英语也在交流过程中得以提高。但是，对于如何在教学过程中同时也考虑到一些英语基础较差的学生，使他们也能在双语教学中获益，还是双语教学中应注意的一个问题。

一般说来，双语教学的困难有两点，一为知识难点的化解，另一为语言难点与知识难点的混杂。如采用英文原版教材，可要求学生预习英文原版教材，再根据难点进行重点讲解以解决上述困难。然而，英文原版教材一般售价较高，且大多内容偏多，与我国本科和研究生教学的实际情

况有一定差距(一般课时不够)。这些都导致有部分学生不愿或不能购买原版教材,使双语教学难以达到理想的效果。另外,双语教学的首要目的毕竟不是英文学习,而主要是掌握专业知识,如何在双语教学的过程中,同时也要兼顾部分英文程度不高的学生。但如何保证"兼顾"而不是"姑息",如何体现"促进"而不是"为难",这些仍是双语教学中需进一步探讨的重要问题。值得提出的是,这些问题在化学计量学的双语教学中还显得特别重要。

化学计量学是化学量测的基础理论与方法学,是以近代计算技术为基础的一门新兴交叉学科,所用的方法大都是基于矩阵运算,对于数学基础学得不够的化学专业的学生来说,本身就有很大难度。如按常规教学方法(即依靠 BASIC、FORTRAN 等经典高级语言为工具,以讲算法为内容)来进行的话,不但需要很多学时甚至很难组织好它的教学,只会使学生感到该课程支离破碎,不成系统。然而,化学计量学虽的确是以近代计算技术为其基础,但它是有其深刻的化学内涵的;而且,如果化学计量学离开了它得以生长的土壤——化学学科,就失去了它存在的必要性。所以,我们认为,进行化学计量学研究的首先必须是化学家,研究者所关心的问题应是化学问题,而不是计算机和数学问题。首先应正视以下问题:如何从化学的角度来介绍化学计量学,怎样将化学计量学的全貌介绍给学生,使他们通过学习这门课程,充分理解化学计量学是一门什么样的化学分支,它为化学家们提供了什么样的新思路,可以解决什么样的化学问题,只有这样才会使化学学科的本科生和研究生认识到这门课程的重要性,才会激起化学学科的学生对这门新兴学科的学习热情。为此,我们在实际的教学过程中通过多种教学手段的应用,以达到提升教学质量的目的。本书的出现就是为达此目的的一种尝试。

本书以化学计量学的基础知识为其主线,在讲述数学基础时就试图与其化学应用直接相连,始终注意到讲解这些知识可为化学家们提供了什么样的新思路,可以解决什么样的化学问题。本书虽用英文编写,但文中出现的一些非常用英文单词皆给出中文提示,以节省学生查阅字典的时间;凡是在书中出现重要知识点的地方,本书尽量佐以问题进行提示,以引起学生的足够注意;另外,本书在必要时还尽量给出中文注释和评述,对所授知识进一步进行解释和阐述,以提高学生的认识和降低阅读的难度。

本书是一种尝试,实际也是我们近年来进行化学计量学双语教学经验的一个总结,今天得以付梓,且已入选"十一五"国家重点图书出版规划。本书虽已出版,但其中不足之处定还不少,希望得到化学计量学同行的不吝赐教和批评指正,使它逐步趋于完善,为我国化学计量学教学步入国际先进行列尽我们的绵薄之力。

梁逸曾

2010 年 10 月,岳麓山

内容提要

本书以双语形式(英语+汉语)介绍化学计量学的必备基础知识:Chemical Experiment Design,Processing of Analytic Signals,Multivariate Calibration and Multivariate Resolution,Pattern Recognition and Pattern Analysis for Chemical Analytical Data,阐述化学计量学中的基本概念和化学计量学方法的基本思路,对一些方法的数学推导均以矩阵运算的形式给出。为了便于读者学习,在介绍化学计量学的同时,专门开辟章节介绍必要的有关矩阵运算的基础知识及其重要数学概念的物理化学意义。

本书适合化学、应用化学及其相关专业本科生选作教材,同时也可作为分析化学计量专业研究人员的参考书和工具书。

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目　录

Chapter 1
Introduction and Necessary Fundamental Knowledge of Mathematics

Chapter 1 Introduction and Necessary Fundamental Knowledge of Mathematics

1.1 Chemometrics: Definition and Its Brief History

The term *chemometrics* was first introduced by Svante Wold in the early 1970s when he applied a scientific project from Swedish government. Terms like *biometrics and econometrics* were also introduced into the fields of biological science and economics. Afterward, the International Chemometrics Society was established when Svante Wold and Bruce R. Kowalski met in 1974 [1-1]. Since then, chemometrics has been developing and is now widely applied to different fields of chemistry, especially analytical chemistry in view of the numbers of papers published, conferences and workshops being organized, and related activities.

"A reasonable definition of chemometrics remains as how do we get chemical relevant information out of measured chemical data, how do we represent and display this information, and how do we get such information into data?" as mentioned by Wold [1-1]. Both the academic and industrial sectors have benefited greatly in employing this new tool in different areas. As pointed out by Professor Yu Ruqin [1-2], a renowned analytical chemist and also a member of Chinese academy, "Chemometrics with the use of statistics and related mathematical techniques forms a new area in chemistry. According to D. L. Massart, its targets are to design or select optimal measurement procedures and experiments as well as to extract a maximum of information from chemical data. With these unique features and applications, some believe that chemometrics provides an important theoretical background for analytical chemistry".

According to the International Chemometrics Society, chemometrics can be defined as "chemometrics is a new chemical discipline that uses the theory and methods from mathematics, statistics, computer science and other related disciplines to optimize the procedure of chemical measurement, and to extract chemical information as much as possible from chemical data."

Howery and Hirsch [1-3] in the early 1980s classified the development of the chemometrics discipline into different stages. The first stage is before 1970. A number of mathematical methodologies were developed and standardized in different fields of mathematics, behavioral science, and engineering sciences. In this period, chemists limited themselves mainly to data analysis, including computation of statistical parameters such as the mean, standard deviation, and level of confidence. Howery and Hirsch, in particular, appreciated the research on correlating vast amounts of chemical data to relevant molecular properties. These pioneering works form the basis of an important area of the quantitative structure-activity relationship (QSAR) developed more recently.

The second stage of chemometrics falls in the 1970s, when the term *chemometrics* was coined. This new discipline of chemistry (or subdiscipline of analytical chemistry by some) caught the attention of chemists, especially analytical chemists, who not only applied the methods available for data analysis but also developed new methodologies to meet their needs. There are two main reasons why chemometrics developed so rapidly at that time: (1) large piles

of data not available before could be acquired from advanced chemical instruments (for the first time, chemists faced bottlenecks similar to those encountered by social scientists or economists years before on how to obtain useful information from these large amounts of data) and (2) advancements in microelectronics technology within that period. The abilities of chemists in signal processing and data interpretation were enhanced with the increasing computer power.

The future evolution of chemometrics was also predicted by Howery and Hirsch in their article [1-3] and later by Brown [1-1]. Starting from the early 1980s, chemometrics was amalgamated into chemistry courses for graduates and postgraduates in American and European universities. In addition, it became a common tool to chemists. Since the early 1980s, development of the discipline of chemometrics verified the original predictions. Chemometrics has become a mainstay of chemistry in many universities of America and Europe and some in China and other countries. Workshops and courses related to chemometrics are held regularly at conferences such as the National Meetings of American Chemical Society (ACS) and the Gordon Conferences, as well as at symposia and meetings of the Royal Society of Chemistry and International Chemometrics Society. For instance, four courses were offered under the title "Statistics/Experimental Design /Chemometrics" in the 226th ACS National Meeting held in New York in September 2003 [*http://www.acs.org*]. The course titles are "Chemometric Techniques for Qualitative Analysis", "Experimental Design for Combinatorial and High-Througput Materials Development", "Experimental Design for Productivity and Quality in R&D," and "Statistical Analysis of Laboratory Data". Furthermore, chemometrics training courses are held regularly by software companies like such as CAMO [1-4] and PRS [1-5]. In a review article [1-6] on the 25 most frequently cited books in analytical chemistry (1980—1999), four are related to chemometrics: *Factor Analysis in Chemistry* by Malinowski [1-7], *Data Reduction and Error Analysis for the Physical Sciences* by Bevington and Robinson [1-8], *Applied Regression Analysis* by Draper and Smith [1-9], and *Multivariate Calibration* by Martens and Naes [1-10] with rankings of 4, 5, 7 and 16, respectively. The textbook *Chemometrics: Statistics and Computer Applications in Analytical Chemistry* [1-11] by Otto was the second most popular "bestseller" on analytical chemistry according to the Internet source *www.amazon.com* on February 16, 2001. The Internet source *www.chemistry.co.nz* listed "Statistics for Analytical Chemistry" by J. Miller and J. Miller as one of the eight analytical chemistry bestsellers on January 21, 2002 and February 10, 2003. "

More importantly, there were two international journals, named as "Journal of Chemometrics" and "Chemometrics and Intelligent Laboratory Systems" appeared in 1987 from both American and Europe. It is a mark that chemometrics has been growing as a mature chemical discipline in chemistry.

1.2 The Relationship between Analytical Chemistry and Chemometrics

As pointed out by Danzer [1-12], a famous analytical chemist in Germany, analytical chemistry is a problem-solving science. Independent from the concrete analytical method, the course of action, called analytical process, is always very similar. The analytical process starts

with the analytical question on the subject of investigation and forms a closed chain to the answer to the problem. Using a proper sampling technique a test sample is taken that is adequately prepared and then measured. The measured data are evaluated on the basis of a correct calibration and then interpreted with regard to the object under study.

The analytical process in the broader sense is represented in Fig. 1. 1.

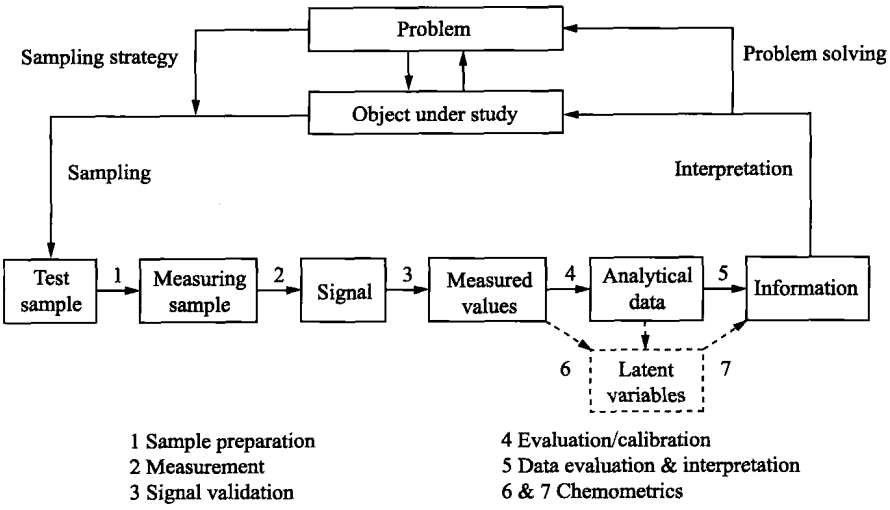

Fig. 1. 1 The analytical process [1-12]

Analytical chemistry possesses today a sound basis of chemical, physical, methodical, metrological, and theoretical fundamentals. The first of these is usually taken as the basis of classical textbooks on analytical chemistry. The others is found in diverse publications in the field of analytical chemistry and chemometrics. It is essential to state that chemometrics is not the theoretical basis of analytical chemistry but it contributes significantly to it. Frequently, analytical chemistry is considered to be a measuring science in chemistry. Therefore, its object is the generation, evaluation, interpretation, and validation of measuring signals as well as the characterization of their uncertainty. With this aim, the analyst needs knowledge of the general analytical process, statistics, optimization, calibration, chemometric data analysis, and performance characteristics.

In recent times, analytical chemistry has stimulated not only chemistry but many fields of science, technology and society. Conversely, analytical chemistry itself has always been heavily influenced by fields like nuclear engineering, materials science, environmental protection, biology, and medicine. Fig. 1. 2 shows by which challenges analytical chemistry has been stimulated to improved performances within the last half century.

Wilhelm Ostwald [1-13], who published the first comprehensive textbook on analytical chemistry, emphasized in it the service function of analytical chemistry. This fact has not changed until now. Interactions with all the fields of application have always had a promoting influence on analytical chemistry.

It can be seen from the figure, with the development of science and technology, demands from social service for analytical chemistry became more and more. Consequently, a lot of new