Quantitative Chemical Analysis

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PREFACE

This text brings together the individuals and the desire to develop a text for undergraduate students who have English as a second language. Our initial focus was undergraduate students with chemistry major in the College of Chemistry and Molecular Engineering, Peking University, Beijing, China, but now we hope and expect that other undergraduate students may be able to learn more easily with this text as they cope with the English language and the essentials of analytical chemistry.

Lecture Series Leading to Text:

The one semester course in analytical chemistry in English for undergraduate students was initiated by Professor Li Ke'an in February 2005 with Dr. Li Na as the presenter of one 2 hour lecture each week for 15 weeks. The size of the lecture room limited the number of students to 50.

Each year the students prepare presentations of their science project reports. The audience of their peers grades the oral presentations of those students who volunteered and were selected to give oral presentations. Competition for being included among the oral presenters has been impressive. Student discussion, grading of the presenters and the presentations bring forth a profound bonding. Each of us in the lecture room feels the shoes worn by another.

As we introduced different examples and illustrations to the lecture series, these quickly became ideas for the coming analytical chemistry text. In Chapter 1, the Human Genome Project was used to show the power and success possible when analytical chemists join forces to bring the minds and resources of the academic community to focus on a goal. The project is indeed a road map of problem solving using new and different technologies plus automation to resolve analytical road blocks to meet the time constraints of the Genome Project thus opening research opportunities for decades. A global environmental need brought together another group of scientists in the concluding Chapter 10 to address the ever present need to monitor drinking water contamination throughout the world. We selected arsenic as one example of the world-wide need for simple, sensitive, cost effective analytical methods to monitor drinking water. Again, we tried to show the rationale dictating

the path taken by scientists to deal with the specifics of water treatment analysis. Fundamental to analytical chemistry are the problem solving tools that scientific minds select for each set of circumstances. This analytical chemistry text lists many of the scientific minds of analytical chemistry from Berthelot and Jungfleisch in 1872 to those of 2009 who have provided the best tool for the situation.

Peking University Lecture Team:

This text has been assembled and is based upon more than a quarter of century of teaching analytical chemistry at Peking University. Many examples and illustrative problems in this text have been taken from previous textbooks in Chinese written by the Peking University Team Teaching Program. This text was written by Dr. Li Na and edited by Professor John Hefferren with the guidance of Professor Li Ke'an. Some of the Chinese teaching style has been used in the text to maintain ties to the Chinese traditions; however, references and terminology of established analytical chemistry books published in the world have also been used. It is hoped that this blend of perspective is helpful and interesting to all readers.

Authors:

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We gratefully acknowledge the influence of those that we consider our chemistry colleagues who have written the texts of the world. It is our profound hope that each of you will join us in continuing to nurture the rich tradition of analytical chemistry.

Li Na, Ph. D.
John J. Hefferren, Ph. D.
Li Ke'an, professor

CONTENTS

CHAPTER 1

INTRODUCTION OF ANALYTICAL CHEMISTRY

This chapter deals with the basis of analytical chemistry including the definition of analytical chemistry, steps of developing an analytical method, classification of the analytical methods, and introduction of volumetric analysis.

1.1 WHAT IS ANALYTICAL CHEMISTRY

Analytical chemistry is a measurement science, responsible for characterizing the composition of natural and artificial materials, both qualitatively (what is present) and quantitatively (how much is present). With the advancement of science, the current definition of analytical chemistry would be "analytical chemistry is the science of inventing and applying the concepts, principles, and strategies for measuring the characteristics of chemical systems and species" (Murray R W. Anal Chem, 1991, 63: 271A). Analytical chemistry widely applies the knowledge of all the other chemical disciplines, physics, biology, information theory and many other technical fields to the development of analytical methods for all the sciences and human activities with information on the character and amount of chemical species and their distribution in space and time. In return, analytical chemistry is of fundamental importance to academia and industry of almost all disciplines, naming a few: biological sciences, engineering, medicine, public health, and the environment, as well as homeland and food safety.

The human genome project (HGP) is one of the best examples to demonstrate how analytical chemistry came to the rescue to solve the human genome mysteries. The human genome project started in 1990 and was scheduled to finish in 2005. There are approximately 20000～25000 genes in human DNA which is composed of 3 billion base pairs (http://www.ornl.gov/sci/tech resources/Human_Genome/project/).

DNA, as shown in Figure 1.1, is a polymer with the monomer units called nucleotides. Each nucleotide consists of a pentacarbon sugar (deoxyribose), a nitrogen containing base attached to the sugar, and a phosphate group. There are four different types of nucleotides found in DNA, differing only in the nitrogenous base, adenine (A), thymine (T), guanine (G), and cytosine (C). DNA is a normally double stranded macromolecule. Within the DNA double helix, A forms two hydrogen bonds with T on the opposite strand, and G forms three hydrogen bonds with C on the opposite strand. A DNA sequence or genetic sequence is a succession of letters (A,T,G, and C) representing the primary structure of a real or

hypothetical DNA molecule or strand, with the capacity to carry information as described by the central dogma of molecular biology.

At the early stage, human DNA was sequenced by the Sanger method which used gel electrophoresis with radioactive labeled dideoxynucleotides (ddNTPs) to produce fragments terminated at each of the four bases in separate lanes. This method was time consuming, labor intensive, and expensive. It is hard to imagine that HGP can be accomplished in time using this traditional method.

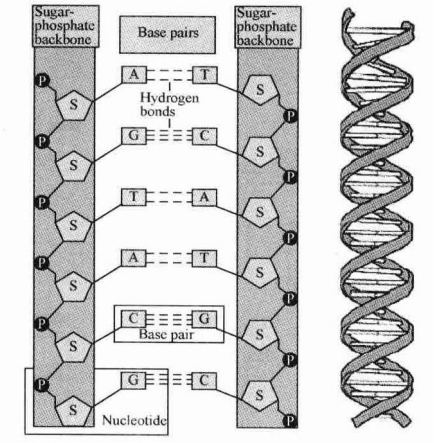

Figure 1.1 Illustration diagram for DNA structure.

Fortunately, analytical chemists worked together to make this happen. Professor Lloyd Smith at the University of Wisconsin-Madison developed the strategy of four-color DNA sequencing which made it possible to run the entire sequencing reaction in one lane rather than keeping the A, G, C, T bases in separate channels (Figure 1.2). Laser was induced to ensure a high sensitivity of this technique. Professor Barry Karger of Northwestern University developed a modified linear polyacrylamide matrix (LPA) DNA separation in a capillary. This polymer provided high-resolution separation performance that was easy to reload the capillaries by simply blowing out the polymer solution. Many analytical chemists worked on developing capillary arrays for high throughput assays. In 1992, Professor Rich Mathies and his colleagues at the University of California-Berkeley developed a 25-capillary array system with scanning detection (Figure 1.3). The confocal microscope set-up together with laser induced fluorescence detection provided very high spatial resolution and sensitivity, arming this system with higher

throughput. The capillary electrophoresis combined with laser induced fluorescence detection by labeling four bases with different fluorescent dyes, and made it possible to run the sequencing in one lane or channel (Elizabeth Zubritsky. How analytical chemists saved the human genome project... or at least gave it a helping hand. Anal Chem, 2002, 74 (1): 22 A-26 A).

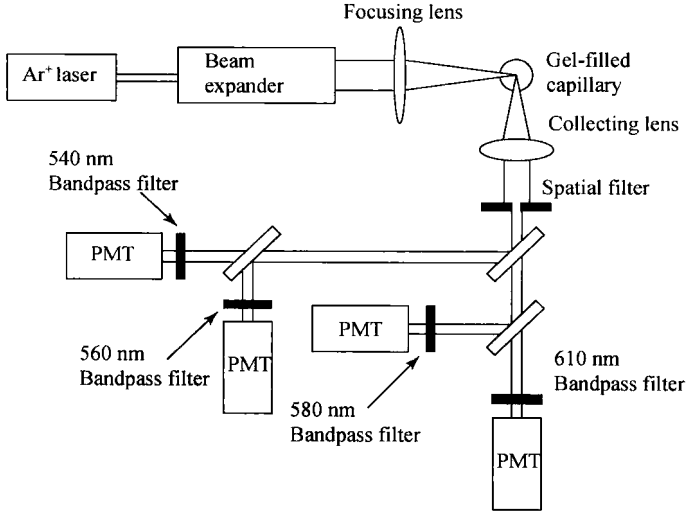

Figure 1. 2 Optical system employed for multiple wavelength fluorescence detection in capillary electrophoresis of DNA. From Luckey J A, Drossman H, Kostichka A J, et al. High-speed DNA sequencing by capillary electrophoresis. Nucleic Acids Res, 1990,18(15): 4417-4421.

The human genome project was completed in 2003, two years ahead of the projected deadline, which is best demonstration of how analytical chemists contributed by improving the throughput, speed, sensitivity, reproducibility of the analytical method for DNA sequencing, and an appropriate way (in this author's eyes) to commemorate the 50th anniversary of the discovery of DNA-helix structure in 1953 by James Watson and Francis Crick who shared the 1962 Nobel Prize.

Another good example would be the food-borne pathogen detection. The detection of pathogenic bacteria is the key step in prevention and identification of problems related to public health and safety. The most frequently used methods are based on culture and colony counting methods. While this method gives reliable results, it is very time consuming, and usually needs a few days to one week to give a result. Biosensor technology can provide equally reliable results in a much shorter

time period. For detection of *Legionella pneumophila*, the colony count method needs 5～14 days to give a final result, in contrast the polymerase chain reaction (PCR) method and biosensor method need only 1～2 hours. Although the new techniques need to improve their sensitivity to the same level as the traditional method, the new methods provided a faster and more realistic approach for food pathogen detection (Olivier Lazckaa, F Javier Del Campob, and F Xavier Muñoza. Pathogen detection: A perspective of traditional methods and biosensors. Biosensors and Bioelectronics, 2007,22 (7): 1205-1217).

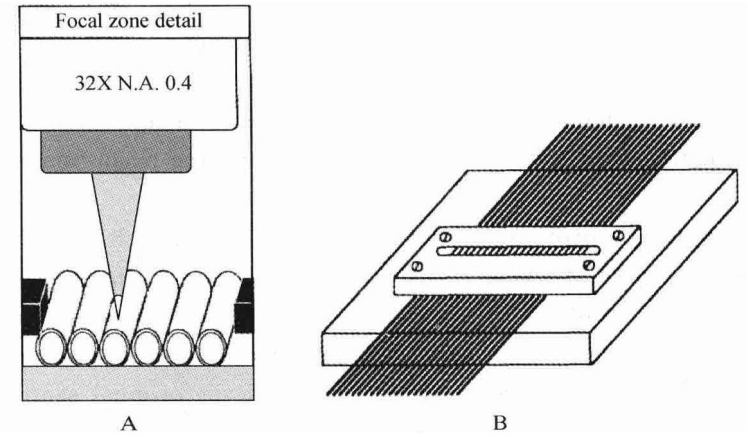

Figure 1.3 The exploded schematic view of focal zone (A) and the capillary array holder (B) of the laser-excited, confocal fluorescence capillary array scanner. From Huang X H C, Quesada M A, and Mathies R A. Capillary array electrophoresis using laser-excited confocal fluorescence detection. Anal Chem, 1992, 64(8): 967-972.

1.2 STEPS IN THE DEVELOPMENT OF AN ANALYTICAL METHOD

An **analyte** is a substance or chemical constituent of a sample that is to be measured by an analytical method. The development of an analytical method for an analyte always starts with a problem encountered, followed by choosing an analytical method, acquiring the sample, processing the sample, eliminating interferences, calibrating and measuring concentrations, calculating results, and evaluating results by estimating their reliability.

Choosing an analytical method is a crucial step. Many factors need to be considered in selecting an analytical method. Accuracy is usually the first factor to be considered. Cost in

labor and time that combine to estimate the real cost often determine the selection of an analytical method. One always selects the method with the lowest real cost providing that the method meets the requirement of accuracy.

It is desirable to obtain a representative sample of less than one gram with the same composition as the bulk sample. Analysis of a non-representative sample will result in false information which in turn will result in wrong decision making.

The general sampling procedure for the solid sample is:

- Take small amount of samples from many sites within the bulk supply.
- Pool the samples together.
- Grind, sieve, and mix the sample to ensure homogeneity.

Sample preparation includes all necessary steps to obtain a final solution ready to be measured: drying, dissolution, eliminating interferences, enrichment and concentration. Sample preparation is usually the most difficult step and the major source of analytical error.

Absorption and desorption of water may occur during each of the sampling and storage steps that result in changes in the chemical composition of the solid sample. It is better that the sample is stored in a container located in an environment with controlled temperature and humidity. To best maintain the water content of the prepared solid sample as close as possible to that of the original sample, drying at selected temperature is usually conducted just before analysis starts.

Most analyses are performed on solutions of the analyte. Therefore, a dissolution step is necessary to dissolve the solid sample into a solution. The conditions of dissolution should be sufficiently mild to avoid loss of the analyte. The solvent should be able to dissolve the analyte rapidly and completely.

Once a sample is dissolved in a suitable solvent, it may be possible to proceed directly to the measurement step. However, in most cases, interferences must be eliminated before measurements. An **interference** is a species that coexists with the analyte and may affect the final measurement by enhancing or attenuating the signal. Few chemical and physical properties of importance in chemical analysis are unique to an individual chemical species, thus masking or separating the interfering chemical species from the analyte will be necessary. Separation methods used for analytical purpose will be introduced in Chapter 9.

Once the interferences are eliminated, the sample is ready for measurement step. After acquiring the sample concentration, a statistical report must be provided to estimate the reliability of the results.