ANALYTICAL CHEMISTRY IN JAPAN

T. SOMIYA

Department of Industrial Chemistry, Faculty of Engineering, University of Tokyo, Bunkyo-ku, Tokyo, Japan

ABSTRACT

The International Congress on Analytical Chemistry was held in Japan, under the sponsorship of IUPAC and the Science Council of Japan in April 1972. This is a report on the progress of analytical chemistry in Japan which I gave as the opening lecture of the Congress, in commemoration of the 20th anniversary of the Japan Society for Analytical Chemistry.

Analytical chemistry courses were first established in Japan in 1911 by Professor Emeritus Matsusuke Kobayashi of the Faculty of Science of Tohoku University; then in 1921 by Professor Emeritus Yuji Shibata of the Faculty of Science of the University of Tokyo, who has served as president of this International Congress and who is a former president of the Japan Academy. In the following year, 1922, Professor Emeritus Motooki Matsui established the course in the Faculty of Science at Kyoto University. In this year the author also established a course in the Faculty of Engineering at the University of Tokyo. Sixty years have gone by since these beginnings.

In 1952 the Japan Society for Analytical Chemistry was established by people from various fields, i.e. from science, engineering, medicine, pharmaceutical science, and agriculture as well as from various industries.

Professor Emeritus Shibata, with Professor Emeritus Kenjiro Kimura, of the University of Tokyo (the president of the Japan Society for Analytical Chemistry) and his group, is well known for his contribution to the spectrophotometrical study of complexes[1]. This research was fundamental to the chemistry of coordination compounds. Its application to analytical chemistry, one of the largest research fields, was later developed by members of the Organic Reagent Research Committee, composed of Professor Kazuo Yamazaki of Nagoya University, Professor Nobuyuki Tanaka of Tohoku University, Professor Keihei Ueno of Kyushu University and Professor Motoharu Tanaka of Nagoya University. In addition to the spectrophotometrical study of complexes, Professor Emeritus Shibata began the study of rare earth elements[2] and geochemistry in Japan and in other parts of the Orient[3]. These studies have been continued by many of his successors, including Professor Emeritus Kimura, Professor Emeritus Eiichi Minami of the University of Tokyo and Professor Kozo Nagashima of Tokyo Kyoiku University. The techniques of chemical analysis developed in the course of these studies helped form the basis of analytical chemistry in Japan.

Professor Emeritus Kimura, together with Professors Hiroshi Hamaguchi, Nobufusa Saito and Masatake Honda of the University of Tokyo and many others, also investigated radiochemical analysis, using ultramicro samples. For example, radioactive materials in hot springs and the radioactive materials in the 5th Fukuryu-maru and its crew, which was irradiated by a nuclear explosion in the Pacific, were analysed[4]. From this, microchemical analysis and ion-exchange analysis were founded.

In Kyoto University, Professor Emeritus Masayoshi Ishibashi, chairman of the organizing committee for this congress, and his group started oceanochemistry and analytical chemistry. In the Faculty of Agriculture, Professor Masuzo Shikata developed and automated a polarograph with Professor Heyrovsky in 1923[5]—as is well known amongst those concerned with analytical chemistry. Research on polarography has been continued under the leadership of Kyoto University and Professor Emeritus Ishibashi's group[6] has developed inorganic polarography with Professor Mutsuaki Shinagawa of Osaka University, and Professor Taichiro Fujinaga of Kyoto University, the general secretary of the organizing committee of this conference. Professor Emeritus Isamu Tachi and his group in the Faculty of Agriculture have developed organic polarography[7]. At the University of Tokyo, Professor Emeritus Takeo Takahashi, Professor Eiji Niki and Professor Giichi Muto have investigated AC polarography[8] and electrochemical analysis. The results of these investigations are highly esteemed all over the world. In 1966, an International Congress of Polarography[9] under the leadership of Professor Isamu Tachi and Professor Mitsugi Senda was held at the International Conference Hall. It can certainly be said that the developments and improvements in the polarograph were driving forces for the development of many analytical instruments.

At Tohoku University, Professor Emeritus Matsusuke Kobayashi with his group developed a mercury amalgam as a reductant in 1921[10]. This approach was truly remarkable and can be regarded as a complete pattern, for research in analytical chemistry. Under his expert tutelage, Professor Emeritus Takio Kato, Professor Hidehiro Goto who is famous for analysis of metals, Professor Soichiro Musha of Osaka Prefectural University, and other well-known chemists who were earnest for education and to study analytical chemistry, emerged. Later, Professor Toshiyasu Kiba of Kanazawa University, who is from Professor Kobayashi's group, investigated the application of strong phosphoric acid as a reaction medium[11]. This study is most highly regarded.

In the field of pharmacy, a medical analysis course was first established in 1942 with the help of Professor Emeritus Yasuhiko Asahina at the University of Tokyo. This course was given by Professor Emeritus Morizo Ishidate[12], who is well known for his invention 'Vitacamphor'. The course made a great contribution to medical analysis, particularly in the use of the spot test, paper chromatography and polarography. In addition, his successor, Professor Zenzo Tamura[12] of the University of Tokyo has investigated the analysis of biological materials, developing clinical tests which have contributed to medical treatment.

Research on azotometry by Professor Emeritus Ken Iwasaki[13] of Kanazawa University, made one of the great contributions in establishing a

system for the submicroanalysis of biochemical problems, as did the work of the research committee on organic microanalysis under the leadership of Professor Tetsuo Mitsui of Kyoto University.

In the field of engineering, I started industrial analytical chemistry in 1922, as was stated earlier. In those days, the chemical industry had just taken root in our country. People in industry brought many practical problems to us to be solved. These problems were frequently the sources of ideas for fundamental studies. For example, when we wanted to examine the analysis of the acetylation bath of cellulose, reaction heats from titration prevented us from carrying this out. But a new idea for thermal titration in non-aqueous solutions[14] was found in 1924, using these reaction heats. This was the beginning of what we now call thermal analysis. In 1930, I described an apparatus for photometric titrations[15], utilizing the photoelectric effect of a neon-glimlamp and a phototube to detect colour changes of indicators. This apparatus was improved by Professors Shizo Hirano and Hitoshi Kamada of the University of Tokyo. This was one basis for the development of instrumental analysis in our country.

Since 1934, studies with steel have been carried out by the 19th committee of the Japan Society for the Promotion of Science. Universities and industries have collaborated in these studies. We used a high-vacuum technique to analyse the hydrogen in steel, and developed vacuum fusion to analyse the oxygen in steel[16]. Dr. Sasaburo Kobayashi, President of Nippon Steel Co. and a former president of the Japan Society for Analytical Chemistry, and the author, supervised the work of the 19th committee, which contributed much to the iron and steel industry. With the research group at Tokyo Shibaura Electric Company, I have exploited a 14 MeV neutron activation analyser[17], which is currently used to rapidly analyse the oxygen in steel for process control in many Japanese factories at an earlier stage than in steelworks of other countries. With this device, it takes about 4 minutes to carry out the analysis, including sample preparation. Another rapid analysis[18], developed by the 19th committee, is based on measuring the electromotive force of the oxygen concentration cell, in which an oxygen ion conductor is used as the electrolyte. This method takes only about 20 seconds and is in wide use in the steel industry, and has greatly elevated Japanese productivity.

Since 1940, the 19th Committee has been investigating rapid chemical analysis methods for quality control analysis in the production processes of iron and steel[19], with the help of those working in the analysis sections of Japanese steelworks. We have been able to develop many methods which we consider to be the most rapid chemical analyses, making it possible to analyse steel within 15 minutes. Therefore, the achievements of the 19th Committee are highly commendable. In addition, this Committee provided opportunities for the education of analysts in factories and created the basis of the Japan Society for Analytical Chemistry.

Thus, looking back on the history of analytical chemistry, one can say that research in analytical chemistry has resulted in the development of the field of instrumental analysis in Japan. In 1949, with Professor Tsuguo Takeuchi of Nagoya University I helped develop the area of organic analysis, using an infrared spectrometer from the United States. At that time, the infrared spectrometer cost about 8 million yen, which is equivalent to 40

or 50 million yen today. But now we can buy better ones made in Japan for only 2 million yen, and infrared spectrometers are found in most organic chemistry laboratories. The efforts made by technical research companies deserve admiration. Growth in the number and quality of analytical apparatuses is remarkable in this country, and many excellent models are being exported. We are particularly proud of having developed a 3 million volt electron microscope and a scanning electron microscope.

On a world-wide basis, investigation in analytical chemistry is changing from elementary analysis to analysis of the molecular structure, state analysis and the measurement of material functions, e.g. catalytic activity. Objectives are also changing from the analyses of natural and industrial products to the analyses of biological materials and to the problems of human environment. With this change, analysts must turn their attention to developing new methods of analysis, new analytical instruments, and to the application of computer systems.

For example, in iron and steel analysis, fractional state analysis for matrices, precipitates and non-metallic inclusions have been adopted, and investigations using chemical shifts[20], i.e. x-ray spectroscopy and photoelectron spectroscopy, have been advanced by members of the x-ray analysis research committee. Analysis of compound states using e.s.r. is also being pursued by Professor Fujiwara and others[21].

High-resolution mass spectrometers and high-resolution n.m.r. and ^{13}C-n.m.r. to analyse molecular structure, and computer systems for automatic structural analysis[22] in combination with m.s., n.m.r., ^{13}C-n.m.r. and i.r., have been developed by Professor Shinichi Sasaki of Miyagi Kyoiku University.

The research committee for polymer analysis, under the leadership of Professor Fujiwara of the University of Tokyo, is studying not only composition analysis but also the functional analysis of polymers[23], using all sorts of instruments.

Gas chromatography, invented by Professor Martin who attended this International Congress, has been investigated in our country under the leadership of Professor Takeuchi of Ngoya University, Professor Shun Araki of Tokyo Metropolitan University, Professor Wataru Funasaka of Kyoto University and Dr. Yoichiro Mashiko, president of the Government Institute of Chemical Industries, Tokyo. The g.c.–m.s. system has greatly contributed to the development of organic chemistry in Japan.

A time-resolved spectrometer system[24] to analyse free radicals, unstable chemical species and excited molecules by observing a few microseconds or few nanoseconds of transient phenomena, is being developed by Professor Hitoshi Kamada of the University of Tokyo.

Also, analytical instruments such as the x-ray microanalyser, ion microanalyser, the Auger electron spectrometer and e.s.c.a., all used to investigate characterization on solid surfaces, i.e. catalytic activity, are being developed by technical research departments of analytical instruments. Laboratory automation using computers is also remarkable.

However, public hazards, such as air and water pollution and health hazards, are world-wide problems of human environment. In Japan, we take them very seriously and regard them as important social problems.

Analytical chemistry has come to play an important role here. With the Smon disease, for example, Professor Tamura of the University of Tokyo has succeeded, through analytical investigations, in discovering that Quinoform, a drug for controlling intestinal functions, is a major contributor to the cause of Smon[25].

Working with air pollution, Professor Araki of Tokyo Metropolitan University, and Professor Saburo Yanagisawa of Keio University are developing an automatic analyser for sulphur dioxide and carbon monoxide, and an exhaust-gas analysis method with members of the Air Pollution Analysis Research Committee. Therefore, the plenary lecture by Professor West impressed us greatly.

The thesis 'Analytical Chemistry and Automation' published by Professor Malissa (*Pure and Appl. Chem.* **18**, 17 (1968)) is very stimulating and interesting. As stated in this report, the development of new subjects for analysis and new analytical methods, as mentioned earlier, will be greatly influenced by ideas coming from information science, i.e. information theory, automatic control theory, system engineering and pattern recognition theory, and the pattern dynamics[26] originated by Professor Emeritus Shoji Makishima of the University of Tokyo.

In the Section for Industrial Analytical Chemistry, the Faculty of Engineering, of the University of Tokyo's research committee on information science and its applications to analytical chemistry, has begun to function.

Our society is changing from an industrial age, which emphasizes material, to an informational age, which emphasizes information. In this sense, analytical chemistry will be basically changed during the next 10 years. This means that analytical chemistry will be in a position to produce information production in the information period, corresponding to its material production in the industrial period. We must recognize that analytical methods are needed in such social problems as public hazards, medical hazards and poisoned food, apart from the materials themselves, and that analytical chemistry will find itself in a different situation from where it has been historically.

This is a rough explanation of the movement of analytical chemistry in Japan. We have produced many theses, i.r. data and gas chromatograph data. The processing of so many theses is a difficult problem in all countries. We are sure that this kind of thing should be done on a world-wide scale, though we are now going to have an Information Processing Committee, under the leadership of Professor Fujiwara of the University of Tokyo.

Thus, the development of analytical chemistry owes much to the development of technology and industry. However, good analytical chemistry education under a good educational system also helped. We now have about 180 analytical chemistry courses available in Japan, and there are many students who major in this field in their senior year. In Japan, specialists who have majored in analytical chemistry are now in much demand. This will strengthen the analytical chemistry field in Japan.

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