

Analytical atomic spectrometry in Japan over the last 25 years

Hiroki Haraguchi^a and Naoki Furuta^{*b}

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1. Introduction

This review paper is dedicated to the celebration of the 25th Anniversary of the Journal of Analytical Atomic Spectrometry (JAAS) published by the Royal Society of Chemistry (RSC). This means, of course, that the publication of JAAS started in 1985. On this occasion, we give our sincere congratulations to the past and present editorial board members of JAAS as well as to the editorial staff of the RSC for their efforts in maintaining the highest standards of the journal. We were asked to write our review paper introducing the history of analytical atomic spectrometry in Japan over the last 25 years to the present editorial board. Thus, this review will cover mostly the history of analytical atomic spectrometry in Japan after 1985. As for the historical aspects of spectrochemical analysis in Japan before 1985, it is recommended to refer to the following review paper by K. Fuwa and

H. Kamada; "Brief history of spectrochemical analysis in Japan".¹

We would like to commence this review with the memorial event in 1985 in Japan. At the end of March, 1985, Keiichiro Fuwa, who was a great leader in spectrochemical analysis in Japan, retired from the University of Tokyo, and was promoted to the vice-director of the National Institute for Environmental Studies (NIES) (he became the director of NIES in 1987). The photo of K. Fuwa is shown in Fig. 1, which was taken on the memorial occasion of his retirement ceremony. As is well known, he made a great contribution to the progress of analytical atomic spectrometry not only in Japan but also in the world. One of the most famous works of Fuwa concerned the development of the long tube burner (often called "Fuwa-Vallee tube") for flame atomic absorption spectrometry (AAS), which was developed during his stay in the USA. He stayed from 1955 to 1978 in the Medical School of Harvard University with Bert L. Vallee. Vallee was one of the pioneers to establish the biochemistry of metalloenzymes, especially concerned with zinc enzymes and metallothionein. The long-tube burner AAS of Fuwa provided very high sensitivities for Zn and Cd, enabling detection

of key elements in metalloproteins. Thus, the long-tube AAS contributed to the progress of the early research on metalloenzymes.

After coming back to Japan from the USA, Fuwa was appointed first to the Department of Agricultural Chemistry, and then the Department of Chemistry at the University of Tokyo. In 1981, the Japan Society for Analytical Chemistry (JSAC) organized the XXII Colloquium Internationale Spectroscopicum (CSI), which was held for the first time in an Asian country. In this CSI, Fuwa served as the secretary general, and the conference was successful. It should be noticed here that Velmer A. Fassel gave his plenary lecture in XXII CSI, with a topic on Inductively Coupled Plasma Mass Spectrometry (ICP-MS) as a newly developed analytical method. This lecture took us by surprise, because, as will be described later, Japan was still in the early stage of Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) at that time. A lot of young scientists including Furuta were stimulated by the great chance to meet many prominent scientists at XXII CSI.

2. The era of AAS

Before starting to describe the history after 1985, we should briefly introduce the era of AAS in Japan. In 1965–1967, Hitachi and Shimadzu—the biggest two instrument manufacturers in Japan even now—produced the commercially available proto-type AAS instruments, although these AAS instruments were constructed as the combination of the flame-burner system for flame atomic emission spectrometry and the monochromator-detection system for spectrophotometry. In the late 1960s, Hitachi constructed the AAS model 270 as the first genuine AAS instrument, which was an especially well designed AAS instrument

^aAssociation of International Research Initiatives for Environmental Studies, 1-4-4, Ueno, Taito-ku, Tokyo, 144-0001, Japan. E-mail: haraguch@airies.or.jp

^bFaculty of Science and Engineering, Department of Applied Chemistry, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo, 112-8551, Japan. E-mail: nforuta@chem.chuo-u.ac.jp



Hiroki Haraguchi



Naoki Furuta



Keiichiro Fuwa

Fig. 1 Photo of K. Fuwa on the occasion of his retirement ceremony in 1985.

ning of the 1980s only about 50 ICP-OES instruments were working in the universities and companies' research laboratories. In 1977, the first ICP-OES was installed at Tsukuba University, and in 1978 the second at NIES, and in 1979 the third at the University of Tokyo. We were involved in the installation of the second and third units. All these ICP-OES instruments were imported from Jarrell Ash, USA, since the Japanese scientific instrument companies had only started the construction of their own ICP-OES instruments. In those days, we learned through the literature that the ICP-OES instruments had excellent analytical feasibilities, and then many spectroscopists working in the field of analytical atomic spectrometry were enthusiastically expecting the coming of the new era of plasma spectrometry.

Thus in January, 1980, the Discussion Group of Plasma Spectrochemistry was established, in which Fuwa was elected as the president of the Group and Hiroki Haraguchi served as the secretary general. Kazuo Yasuda (Hitachi), Kenjiro Tohyama (Shimadzu), Masatoshi Morita (NIES), Taketoshi Nakahara (Osaka Prefectural University) and many other analytical and spectrochemical scientists joined as steering committee members. Since then, this Discussion Group has been continuously taking leadership in the progress of AAS, and contributing to the propagation of the instruments as well as the establishment of analytical methods for various samples. After Haraguchi moved from the University of Tokyo to Nagoya University in Dec., 1988, the activity of the Discussion Group stopped for five years. Taking the opportunity of Furuta's movement from NIES to Chuo University in 1994, the Discussion Group resumed. The following scientists have been the presidents of the Discussion Group; Keiichiro Fuwa, Hiroki Haraguchi, Taketoshi Nakahara, Naoki Furuta, and presently Koichi Chiba (National Metrology Institute of Japan, AIST).

It is worthwhile to introduce the management doctrine of the Discussion Group, which was agreed with the steering committee at the beginning; (1) it covers the whole area of analytical atomic spectrometry, (2) it is independent from any academic societies, (3) the steering committee of the Group is composed of the fundamental researchers (from the universities and national institutes), customers

which had good sensitivity and was easy to operate, and thus it had a great reputation with many customers in Japan. Kazuo Yasuda, an engineer at Hitachi, made a great contribution to the manufacture of the AAS model 270. In the 1970s, various types of AAS instruments were manufactured by many domestic and foreign companies, and they had a significantly big market share because of serious environmental problems such as Minamata-disease (Hg) and Aichi-aichi disease (Cd). Shimadzu constructed a double-beam type AAS-650, Japan Jarrell Ash made an electrothermal graphite furnace AAS, and Seiko Instruments did an electrothermal metal-boat atomizer AAS. A fond memory is that we used the Shimadzu AAS-650 for exploitation of the multielement analysis by continuous source AAS.² In the early 1980s, Hitachi manufactured the famous Zeeman-type AAS Z-8100 available for both flame and graphite furnace, which allowed us to perform the automatic background correction of molecular absorptions caused by inorganic salts and some organics. We express our respect to Hideaki Koizumi, also an engineer at Hitachi, for his excellent and smart work to produce the Zeeman-type AAS. According to the statistics, about 15,000 AAS instruments were extensively used in the world in

the 1970s. Then, many Japanese analytical chemists such as Tsugio Takeuchi, Juryo Ikeda, Shigeru Shimomura, K. Fuwa *et al.* involved trace analysis by AAS, and they also instituted the Discussion Group of AAS under the support of JSAC. It is, however, our sad memory that Takeuchi passed away during XXI CSI held in Cambridge, UK, in 1979.

One more thing should be added to our history on this occasion. Cameron W. McLeod visited Japan as a postdoctoral fellow in Fuwa's laboratory at the University of Tokyo, but he preferred life in rural Japan and thus he was mostly at NIES located in the newly constructed science city, Tsukuba, where he worked with Naoki Furuta. We were so grateful that McLeod stayed in Japan for 3 years and gave us great stimulation in the development of AAS. According to the statistics in 2008, Hitachi High-Technologies (former Hitachi) shared 36% and Shimadzu 30% out of approximately 450 AAS instruments annually sold in Japan.

3. Discussion group for plasma spectrochemistry in Japan

As mentioned above, in the 1970s, AAS was most extensively utilized as the powerful method for trace analysis, but at the begin-

(users) and representatives from all instrument manufacturers. The Discussion Group has been organizing 3 or 4 meetings per year, including one seminar (so-called "Tsukaba Seminar") as the annual event, and keeping the number of registered members over 350.

4. Development of ICP-OES in Japan

For ICP-OES instrumentation, a direct-reading polychromator with many photomultipliers and a slew-scanning monochromator with a single photomultiplier were competing each other from the 1970s to the 1980s. As domestic manufacturers, Shimadzu, Seiko Instruments, Nippon Jarrell Ash, Hitachi and Kyoto Koken were selling ICP-OES instruments inside Japan. At that time the present authors developed a slew-scanning monochromator with a silicon intensified target (SIT) detector.³ At present Horiba-Jobin Yvon adapts the combination of a slew-scanning monochromator and a CCD detector, and it is now commercially available as the ACTIVIA model. In the 1980s, a slew-scanning monochromator with a single photomultiplier was popular in Japan. However, after Echelle monochromators with a solid-state detector were commercially available from Perkin Elmer and Jarrell Ash, in 1992 to 1993, multichannel-type

ICP-OES instruments were getting more popular at the expense of resolution (10–15 pm). As international companies such as Thermo-Fisher Scientific, Perkin Elmer, and Varian succeed to penetrate the Japanese market and sell their multi-channel-type ICP-OES instruments, the market for slew-scanning type ICP-OES instruments, which were sold from Japanese manufactures became small. Shimadzu started to sell an Echelle spectrometer with a CCD detector in Japan in 2005. Seiko Instruments started to sell an Echelle spectrometer with a CCD detector as an OEM of Varian. However, when high resolution is required (2–3 pm) for the analysis of semi-conductor materials, a slew-scanning monochromator with a photomultiplier is still used. At present, such an instrument is commercially available from Shimadzu and Seiko Instruments. According to the statistics in 2008, Seiko Instruments and Shimadzu shared 30% each out of approximately 500 ICP-OES instruments annually sold in Japan. ICP-OES is presently used for routine work but the amount of research is becoming small.

5. Development of ICP-MS in Japan

Since SCIEX and VG started to sell quadrupole ICP-MS (ICP-QMS) instruments in 1983–1984, the usefulness of

ICP-MS instrumentation was recognized in Japan but Japanese manufactures were struggling to develop the instruments. Yokogawa Analytical Systems (PMS 100), Seiko Instruments (SPQ 6100) and Shimadzu (PIMS-3000) started to sell ICP-QMS in 1987. At that time the Japanese government requested Japanese institutions, including universities, to buy foreign instruments to reduce the trade surplus. It was in 1987 that NIES bought the Plasma Quad ICP-MS from VG, and the National Institute of Agro-Environmental Sciences (NIAES) ordered a high resolution ICP-MS instrument to VG. This order by Shin-ichi Yamazaki in NIAES triggered the development of a double focus ICP-MS instrument by VG. The double focus ICP-MS instrument was commercially available from VG in 1989. I remember S. Yamazaki, Takafumi Hirata, Naoko Nonose, Yuichi Takaku and Koki Tanaka including Furuta attending the Durham Conference in 1992 (see Fig. 2) and on the way back to London, we stopped by VG company (Winsford, Cheshire). We saw a multi-collector ICP-MS (Plasma 54) there. Since the multi-collector ICP-MS was launched in 1992, precise isotope ratio measurements were applied in the field of geological science.

Hitachi started to sell a high power N₂-Microwave Induced Plasma (MIP)-MS in 1990, and ICP-ion trap MS in 1997. Hitachi instruments were commercially



Fig. 2 Photo taken on the occasion of Durham Conference in 1992. From left to right; K. Tanaka, N. Furuta, S. Yamazaki, N. Nonose, and Y. Takaku.

available only inside Japan. They did not sell the instrument outside Japan because of maintenance problems. Scientists actively involved in the development of ICP-MS instruments at Hitachi were Konosuke Oishi, Toyoharu Okumoto, Yasushi Terui *et al.*⁴ At present Hitachi High-Technologies have stopped selling both ICP-OES and ICP-MS instruments, and only deal with the sale of a solid-phase extraction resin, so called NOBIAS, for sample pre-concentration. Yokogawa Analytical Systems succeeded in selling their instruments abroad in cooperation with international companies. Yokogawa Analytical Systems launched HP 4500 ICP-MS to the world market in 1994 in cooperation with Hewlett-Packard. The instrument was of a smaller size and easy to operate, and the detection capability was improved by one order of magnitude. In order to respond to the request of further sensitivity improvement from semi-conductor industries in Japan, Yokogawa Analytical Systems developed a shield torch and cool plasma ICP-MS in 1995–1996. Scientists actively involved in the development of such an instrument at Yokogawa Analytical Systems were Kenichi Sakata, Katsuhiko Kawabata *et al.*⁵ From 1996 to 1999 a collision-reaction cell was developed to alleviate spectral interferences in the ICP-QMS instrument using a hot plasma, and Agilent 7500 was launched in 2000. A collision cell for the Agilent 7500 proved very effective at reducing spectral interferences due to poly-atomic ions and the S/N improvement was also achieved. Noriyuki Yamada, Junichi Takahashi *et al.* were deeply involved in the development of the Agilent 7500. The semiconductor industry is one of the important industries in Japan, so that high resolution ICP-MS is used widely for analysis of ultra-pure materials and reagents. According to a reference in 1999,⁶ the number of high-resolution ICP-MS instruments installed in Japan was 57, and this amounted to one fourth of the total number of instruments (227) worldwide. According to the statistics in 2008, the market share of Agilent Technologies was 55%, and Perkin Elmer 22%, out of approximately 200 ICP-QMS instruments annually sold in Japan.

From 2000 to 2010, ICP-MS instruments were installed in many universities, national institutes and industries, and were applied to environmental and geological sciences; biological, clinical and pharma-

ceutical; industrial materials; high purity materials including semiconductors; food, agriculture and nutrition; and nuclear. Some recent activities in Japan will be introduced further here. Akitoshi Okino (Tokyo Institute of Technology) is developing an alternative plasma source which is operated by a pulse mode using gases other than Ar such as He, N₂, CO₂ and Air. Takafumi Hirata (Kyoto University) is conducting precise isotope ratio measurements of geological samples and recently, biological samples, too, using a laser ablation system combined with a multi-collector ICP-MS instrument. Furuta is monitoring concentrations of trace elements in size-classified airborne particulate matter and is investigating the role of selenium in biological samples by using selenium speciation analysis. Koichi Chiba (AIST) is developing certified reference materials of industrial and environmental samples. Yuichi Takaku (Institute for Environmental Sciences) is investigating environmental cycles of actinide elements, strontium, cesium and iodine, which have the possibility of being released from a nuclear reprocessing plant, located at Rokkasho village in Japan. These active scientists are the current steering committee members of the above mentioned Discussion Group for Plasma Spectrochemistry in Japan and are contributing to dissemination and development of plasma spectrochemistry in Japan. Young scientist participation is growing steadily. Intensive discussion is taking place in the atomic spectroscopy sessions at annual meetings (twice in a year, in spring and in autumn) organized by JSAC. The Discussion Group for Plasma Spectrochemistry organized the Third Asia-Pacific Plasma Winter Conference in 2008 (2008 APWC) and invited many prominent scientists from abroad. Young scientists attending the conference were stimulated and will contribute to the future development of atomic spectrochemistry in Japan.

6. Chemical speciation—development of hyphenated analytical systems

According to the development of various atomic spectrometric methods such as ICP-OES and ICP-MS, the analytical sensitivities for various metallic elements including metalloids (As, Se, Te) have

been significantly improved down to the ppt or sub-ppt level. In addition, ICP-OES and ICP-MS have excellent feasibilities such as simultaneous multielement detection and wide dynamic range. These analytical characteristics of plasma spectrometric methods leads us to expect further developments and progress in analytical methods for all-elements analysis of a single biological cell in the future.

After the development in sensitivity by analytical atomic spectrometry, a new trend from total analysis to speciation analysis was initiated in the late 1970s. As is well known, the biological functions or toxicities of the elements mostly depend on the chemical forms (species), not on their total contents. Then, species analysis, *i.e.*, chemical speciation, became a hot topic in analytical atomic spectrometry since the early 1980s. The review paper by T.M. Florence and G.E. Batley, entitled “Chemical speciation in natural waters”, provided great impact on the establishment of the concept of chemical speciation.⁷ In chemical speciation analysis, analytical atomic spectrometric methods such as AAS, ICP-OES and ICP-MS, which are highly-sensitive and element-selective detection methods, are generally combined with various separation methods such as GC (Gas Chromatography), LC (Liquid Chromatography), CE (Capillary Electrophoresis) *etc.* Since no more details about chemical speciation are described here, it is recommended to refer to some important references^{8,9} about the fundamentals and application in chemical speciation.

Here, we will briefly introduce the early contribution to chemical speciation by Japanese scientists. In 1980, K.T. Suzuki published the paper entitled “Direct connection of high speed liquid chromatography equipped with gel permeation column to atomic absorption spectrophotometer for metalloprotein analysis: metallothionein”.¹⁰ In this work, the hyphenated system of HPLC and AAS was used to identify the isomers of metallothionein containing Cd, Cu and Zn. It can be noted that this paper by Suzuki is a sort of classical paper in speciation of metallothionein and so often cited even now. After the pioneering work, Suzuki made a great contribution to the development of chemical speciation of metals and metalloids.¹¹ His work on the metabolisms of arsenic and selenium elucidated several

unknown metabolites of arsenic and selenium in human and animals. Sadly, Suzuki passed away on July 15, 2008. It was soon after his retirement from Chiba University. He was formerly based at NIES, Tsukuba.

Morita and his co-workers at NIES developed speciation methods of arsenic compounds in various biological samples such as seaweeds, fish and shellfish, where they used LC/ICP-OES¹² and LC/ICP-MS.¹³ These works by Morita *et al.* provided a kind of classical standard method for speciation of arsenic compounds. In addition, Hiroaki Tao (AIST) developed speciation methods using GC/ICP-MS, which was successfully applied to speciation of mercury and tin compounds in environmental samples at the femtogram level.¹⁴

7. Organization of the international conference/symposium in Japan

In recent years, a variety of international conferences and symposiums related to analytical chemistry have been held not only in Japan, but also in other Asian countries. Here, the international conferences/symposiums concerned with analytical atomic spectrometry or related fields, held in Japan over the last 25 years are listed:

- International Conference on Analytical Chemistry 1991 (ICAS 1991), Maku-hari, Japan, August 25–31, 1991. The 1st Asian Conference on Analytical Chemistry (Asianalysis I) was co-organized.
- International Conference on Analytical Chemistry 2001 (ICAS 2001), Tokyo, Japan, August 6–10, 2001. Asianalysis VI was co-organized.
- International Symposium on Bio-Trace Elements 2002 (BITREL 2002), Wako, Japan, October 28–November 1, 2002.
- The 11th International Symposium on Biological and Environmental Reference Materials (BERM 11), Tsukuba, Japan, October 29–November 2, 2007.
- International Symposium on Metallomics 2007 (ISM 2007), Nagoya, Japan, November 28–December 1, 2007.
- 2008 Third Asia-Pacific Winter Conference on Plasma Spectrochemistry (2008 APWC), Tsukuba, Japan, November 16–21, 2008.

In addition to the above conferences held in Japan, several international conferences related to analytical atomic spectrometry have been held in Asian countries. Some of them are as follows;

- (1) 2005 First Asia-Pacific Winter Conference on Plasma Spectrochemistry, 2005 (2005 APWC), Chiang Mai, Thailand, April 25–30, 2005.
- (2) 2006 Second Asia-Pacific Winter Conference on Plasma Spectrochemistry (2006 APWC), Bangkok, Thailand, November 27–December 2, 2006.
- (3) XXXV Colloquium Spectroscopicum Internationale (XXXV CSI), Xiamen, China, September 23–27, 2007.
- (4) The 9th Asian Conference on Analytical Chemistry (Asianalysis IX), Jeju Island, Korea, November 4–8, 2007.
- (5) The 10th Asian Conference on Analytical Chemistry (Asianalysis X), Kuala Lumpur, Malaysia, August 11–13, 2009.

8. Proposal of the new scientific field “Metallomics”

In 2004, Haraguchi coined “Metallomics” as a new scientific field by publishing his paper entitled “Metallomics: Integrated biometal science” in JAAS.¹⁵ Before 2004, however, he had already delivered some lectures concerning metallomics at the domestic symposium in 2002. Those lectures are not known well, and so we take an opportunity to introduce the summaries of those lectures here.

The first lecture was given at the Tokushima Seminar on Chemical Engineering, June 14, 2002, Tokushima, Japan. In this lecture, he hopefully proposed the establishment of a new scientific world “metallomics” for the first time, based on the progress of analytical atomic spectrometry, as follows.

A challenge to pico-world and metallomics: A new frontier of trace element chemistry

In recent years, the analytical detection sensitivities have been increasingly improved down to the pico gram or sub-ppt (10^{-12} g/ml) level, according to the development of ICP-MS. As a result, now we have a good chance to make a contribution to pico-technology or pico-science, which may be called “Pico-World in Science”. Such progress of analytical

atomic spectrometry will make it possible to explore new interesting and important research on bio-trace elements in biological systems including “human beings”, because all-elements might be contained in all biological systems. This concept is referred to as “Extended All Present Theory of the Elements”. Furthermore, various trace elements play various important roles in biological systems, as the components of metalloproteins and metalloenzymes. Now is thus a good time to challenge trace element biochemistry to open our new scientific world “metallomics”. In the 1960s, Fuwa and Vallee investigated the function of zinc enzymes, but nowadays we can expand the research to all metalloproteins and metalloenzymes.

The second lecture concerned with metallomics was given in the International Symposium on Bio-Trace Elements 2002 (BITREL 2002), October 28–November 2, 2002, Saitama and Yamana-nashi, Japan, which was organized by Shuichi Enomoto in RIKEN (Institute of Physics and Chemistry). In this lecture, Haraguchi formally proposed metallomics as a new scientific field in order to integrate the research fields related to bio-trace metals, with emphasis on the importance of chemical speciation analysis.¹⁶

Trace element speciation for metallomics

In the paper, “metallomics” is newly proposed as a new scientific field in order to integrate the research fields related to bio-trace metals. Metallomics is the scientific field of post-genomics and post-proteomics, where metal-containing compounds are defined as metallome, in a similar manner to genome in genomics and proteome in proteomics. Since the elucidation of the biological or physiological functions of metal-containing species in the biological systems is the main research target of metallomics, elemental speciation is important as one analytical technology to promote metallomics.

In the BITREL 2002, Ryszard Lobinski from France was one of the invited lecturers. He noticed this proposal and strongly recommended to write a paper in the special issue about “Metals in Biology” in JAAS, in which he was



Fig. 3 Photo taken on the occasion of ISM 2007 (from left to right). First row: K. Tsunoda, J. Takahashi, Mrs. Suzuki, H. Haraguchi, C.W. McLeod, Second row: K. Chiba, K. Okamoto, Third row: H. Tao, K. T. Suzuki, Mrs. Haraguchi.

planning to publish at that time. Then, the first paper on this topic was published in JAAS in 2004. At the same time, Bibudhendra Sarkar from Canada was also there, and he enthusiastically encouraged Haraguchi to organize the International Conference on Metallomics. Accordingly, Haraguchi organized the first ISM 2007 in Nagoya through November 28–December 1, 2007 (see Fig. 3). Thus, it can be said that BITREL 2007 was an epoch-making symposium for the establishment of metallomics.

As is well known, the Royal Society of Chemistry (RSC) launched the journal “Metallomics” in January, 2009, and the second ISM (ISM 2009) was held in Cincinnati, USA, in 2009, under the organization of Joseph A. Caruso, Gary M. Hieftje and David W. Koppenaal. The third ISM will be held in Munster, Germany, in 2011. In addition, recently the IUPAC guideline for terminology in metallomics was published by the effort of Lobinski *et al.*¹⁷

Metallomics has been receiving great attention among Japanese scientists, and several domestic symposiums have been organized in the various academic societies of chemistry, pharmacy and

bio-medicine. In 2008, the Metallomics Research Forum was instituted, and it was agreed by the participants that this forum will be held every 2 years.

“Many events and great attention oriented to metallomics since 2004 are much more than I expected and everything is so surprising to me.” This is Haraguchi’s impression at the current time, but he is still expecting further progress of metallomics, in symbiosis with genomics, proteomics and other *omics*-science.

9. Future perspective of analytical atomic spectrometry

Finally, we would like to mention briefly our opinions on future prospects for analytical atomic spectrometry. In this review, the progress of analytical atomic spectrometry we have experienced over the last 25 years was described. Compared to the progress before 1985, the progress of this field after 1985 has been rapid and dynamic, reflecting the transition from absorption to emission as well as from optical detection to ion detection. These dynamic changes have been ground-

breaking resulting in the development of new and powerful and sophisticated analytical technologies.

In Table 1, the requirements for ideal spectrochemical analysis is summarized, which was proposed by Haraguchi in 1980 on the occasion of the first seminar of the Discussion Group for Plasma Spectrochemistry in Japan. If the table is carefully inspected, one can reflect “what has changed?”, “how much progress?”, “what is still a problem?” and so forth. It seems that various instrumentation and analytical techniques/methods have been explored to fulfil the research targets listed in Table 1 owing to the efforts by many scientists and instrument companies over the last 30 years, although we do not give concrete examples here.

Then we need the next research targets which are expected in analytical atomic spectrometry. In the second column of Table 1, the future-oriented analyses are listed in the terminology of modern analytical chemistry in parallel to the requirements proposed in 1980, they are: (1) all-elements analysis, (2) multielement profiling analysis, (3) matrix-free analysis, (4) single particle/liquid analysis, (5)

Table 1 Requirements for ideal spectrochemical analysis proposed in 1980^a and future-oriented analysis

Requirements proposed in 1980	Future-oriented analysis
1. Quantitative and qualitative analysis of all elements are possible	All-elements analysis
2. Simultaneous multielement analysis of the elements at the major, minor, trace and ultratrace concentration levels can be performed	Multielement profiling analysis
3. Inter-element interferences are negligibly small	Matrix-free analysis
4. Applicable to the small volume or amount of sample	Single particle/liquid analysis
5. All states of samples, <i>i.e.</i> , in solid, liquid (solution) and gas, can be analyzed with minimum sample pretreatment	Direct and <i>in-situ</i> analysis
6. Rapid analysis is possible (<i>e.g.</i> , applicable to process control)	Process control analysis
7. Accuracy and precision are guaranteed	Good laboratory analysis
8. Non-destructive analysis is desirable	Chemical speciation and 3D imaging analysis
9. Compact-type of instruments should be designed	Microchip instrumentation
10. Commercial instruments with proper price should be sent to the market	Cost-performance instrumentation

^a This table was presented by H. Haraguchi on the occasion of the first seminar of the Discussion Group for Plasma Spectrochemistry in Japan, held on January 31, 1980 at the University of Tokyo.

direct and *in-situ* analysis, (6) process control analysis, (7) good laboratory analysis, (8) chemical speciation and 3D imaging analysis, (9) microchip instrumentation, and (10) cost-performance instrumentation. We hope that the targets listed in Table 1 will give a good guideline for the future development of analytical atomic spectrometry and various new technologies will be explored not only for analytical chemistry, but also for science of humans and nature.

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References

- 1 K. Fuwa and H. Kamada, *Spectrochim. Acta*, 1981, **36B**(7), 597–602.

- 2 N. Furuta, H. Haraguchi and K. Fuwa, *Anal. Chem.*, 1977, **49**(8), 1263–1265.
- 3 N. Furuta, C. W. McLeod, H. Haraguchi and K. Fuwa, *Appl. Spectrosc.*, 1980, **34**(2), 211–216.
- 4 K. Oishi, T. Okumoto, T. Shirasaki, H. Iino, M. Koga and N. Furuta, *Spectrochim. Acta*, 1994, **49B**(9), 901–914.
- 5 K. Sakata and K. Kawabata, *Spectrochimica Acta*, 1994, **49B**(10), 1027–1038.
- 6 C. B. Douthitt, *ICP Inform. Newsletter*, 1999, **25**(2), 87–120.
- 7 T. M. Florence and G. E. Batley, *Crit. Rev. Anal. Chem.*, 1980, **9**(3), 219–296.
- 8 D. M. Templeton, F. Ariese, R. Cornelis, L. G. Danielsson, H. Muntau, H. P. Van Leeuwen and R. Lobinski, *Pure Appl. Chem.*, 2000, **72**(8), 1453–1470.
- 9 J. Szpunar, *Analyst*, 2005, **130**(4), 442–465.
- 10 K. T. Suzuki, *Anal. Biochem.*, 1980, **102**(1), 31–34.
- 11 K. T. Suzuki, *J. Health Sci.*, 2005, **51**(2), 107–114.
- 12 M. Morita, T. Uehiro and K. Fuwa, *Anal. Chem.*, 1981, **53**(12), 1806–1808.
- 13 Y. Shibata and M. Morita, *Anal. Sci.*, 1989, **5**(1), 107–109.
- 14 H. Tao, T. Murakami, M. Tominaga and A. Miyazaki, *J. Anal. At. Spectrom.*, 1998, **13**(10), 1085–1093.
- 15 H. Haraguchi, *J. Anal. At. Spectrom.*, 2004, **19**(1), 5–14.
- 16 H. Haraguchi and T. Matsuura, *Proceedings of International Conference on Bio-trace Elements 2002 (BITREL 2002)*, ed. S. Enomoto, Published by RIKEN, pp. 3–8.
- 17 R. Lobinski, J. S. Becker, H. Haraguchi and B. Sarkar, *Pure Appl. Chem.*, 2010, **82**(2), 493–504.