SCIENTIFIC INSTRUMENT NEWS

Special Edition | Interview

Developer's thoughts, their succession and innovation

INTERVIEW

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In January 2016, Hitachi shipped its 10,000th Hitachi Polarized Zeeman Atomic Absorption Spectrophotometer, the first in the world at the time of its release in 1974. Repeated improvements have been made in the 42 years since its release, and the current ZA3000 Series product is the eleventh series. How has the Hitachi Polarized Zeeman Atomic Absorption Spectrophotometer has remained so popular for all these years? We talked to Hitachi Fellow Hideaki Koizumi, and to Akira Yonetani of Hitachi High-Tech Science, who were involved in the development of applications, about the principles and the behind-the scenes stories of the development, and we spoke to Hayato Tobe of Hitachi High-Tech Science, who is currently working to further develop the technology.

Commemorating the 10,000th sale of
a polarized Zeeman atomic absorption spectrophotometer

Hitachi Measurement Technology: Evolving Within the Social Sciences

Akira YONETANI

Hitachi High-Tech Science Corporation
Optics Design Department, Naka Office
Applied Technology Development Group

Hayato TOBE

Hitachi High-Tech Science Corporation
Optics Design Department, Naka Office
Director

Hideaki KOIZUMI

Fellow, Hitachi, Ltd.

1. What made it possible to deliver 10,000 units?

What impact do you think selling 10,000 Hitachi Polarized Zeeman Atomic Absorption Spectrophotometers will have? Some people must be wondering about this. If it were a household appliance selling for several hundred dollars, selling 10,000 would not be a big deal. But we are talking about a measurement apparatus that sells for at least several million yen each. When you consider that the Polarized Zeeman Atomic Absorption Spectrophotometer is relatively expensive for a measuring apparatus, you realize just how frequently it is used.

It is no surprise that the Hitachi Polarized Zeeman Atomic Absorption Spectrophotometer has been used in such a variety of scenarios since it was first released in 1974. Units are now being supplied to 25 countries around the world and are widely used in various industrial fields, especially for environmental analyses of materials including tap water, sewage, and soil, and also for metals, chemicals, food products and drugs. Hayato Tobe of Hitachi High-Tech Science, who is involved in the technological development of the Polarized Zeeman Atomic Absorption Spectrophotometer, told us about its previous uses. "During the period of high economic growth in the 1970s, this measuring device made a big contribution to the identification of pollution-causing metals and to shedding light on the mechanisms by which pollution-related diseases occurred. In the 1980s, environmental problems began to be seen as global problems beyond national and local concerns, and the device proved useful for research into the behavior of metallic elements in the sea, air, and soil. From the 1990s until the early 2000s, measuring techniques were widely reviewed against the backdrop of tightened regulations for water quality and environmental standards etc., and the use of the device expanded greatly from research into general analysis. Later, in 2003, it was a potent force in the analysis of arsenic in pollution with organoarsenic compounds in the city of Kamisu in Ibaraki Prefecture and in analyses of harmful substances such as lead and cadmium under the European RoHS Directive[*1], which went into effect in 2006, and the revised Food Sanitation Law of 2008".

Atomic absorption spectrophotometers are used for measuring numerous elements, especially metallic elements, in solutions at concentrations from mg/L (ppm, 1/1 million) to µg/L (ppb, 1/1 billion). Forty years of ongoing technological development has produced improvements in the sensitivity of the Hitachi Polarized Zeeman Atomic Absorption Spectrophotometer, which is now sensitive enough to measure elements, particularly arsenic, at concentrations of 1 µg/L, 1/10 of the standard value for tap water. Meanwhile, in response to increasing needs for rapid analysis of multiple elements, other measuring technologies such as ICP optical analysis and ICP/MS have rapidly come into widespread use.

Hideaki KOIZUMI

Fellow, Hitachi, Ltd.

"The fact that the Polarized Zeeman Atomic Absorption Spectrophotometer has been popular for such a long time is thanks to its versatility, which enables this measuring device to be used in a wide range of fields, and ultimately to its great reliability and accuracy (accuracy and precision)," says Tobe.

So how has it been possible to maintain such reliability and accuracy? The answer will be obvious once you know about the development and principles of this device. First let's look at the development process.

*1 RoHS Directive
A directive that restricts the use of specific harmful substances in electronic and electrical equipment in the EU

2. Developing a measuring device that would quickly be useful

The development of the Hitachi Polarized Zeeman Atomic Absorption Spectrophotometer was sparked by pollution problems that occurred during the period of high economic growth in Japan. The initial need in particular was to contribute to the detection of the methylmercury compounds responsible for Minamata disease, which had begun to cause widespread harm in the 1960s.

Hideaki Koizumi, who had just joined the company at the time, was asked to develop it.

Reflecting on that time, Koizumi says "Back in those days, articles about Minamata disease were appearing in the newspapers almost every day and I was given the task of creating a measuring device that would quickly be useful. I had already been working on some design drawings at the time I joined the company, and that is why Shigeki Ozawa, the Director of the Optical Instrument Design Department (and later the President of Hitachi Electronics Co.,Ltd.), asked me to take on the work of development. I then began to learn about measuring devices using the mercury isotope[*2] Zeeman effect[*3] (hyperfine structure) from Dr. Tetsuo Hadeishi of the Lawrence Berkeley National Laboratory at the University of California after being introduced by Dr. Kazuo Yasuda (the Deputy Chief Engineer at Naka Plant at the time). I am very grateful to have been given the opportunity in spite of being an inexperienced new employee.

Dr. Hadeishi had been a pupil of Dr. Hans Bethe, the winner of the 1967 Nobel Prize for Physics, and he was an authority on physics. Koizumi received close guidance from Dr. Hadeishi.

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Hitachi High-Tech Science Corporation
Optics Design Department, Naka Office
Applied Technology Development Group

Hayato TOBE

Hitachi High-Tech Science Corporation
Optics Design Department, Naka Office
Director

However, at the time, mercury isotopes were not widely produced and were very expensive, so product development stalled. It seemed that development would be abandoned.

Koizumi explains that "It occurred to me that skillful use of polarization and the Zeeman effect might make isotope use unnecessary. I picked up an old-fashioned device for generating microwaves called a magnetron, which was used in plasma research, from a junkyard, removed the coil, and made a magnet that generated a strong magnetic field of 2 tesla to see whether the characteristic Zeeman effect of naturally occurring mercury could be used. At the time, the magnet gap was just 5 mm, so I wondered what to do. In the end, we decided to use the small light bulb used for bicycle lights to embed an atomizing furnace in this tiny space. The sample was dissolved in water and a drop of that water was applied to the tungsten filament of this small bulb. Electric current was applied and argon gas was blown in. This approach succeeded in generating atomic vapor at the very high temperature of 3,000°C."

Atomic absorption spectrophotometers provide a quantitative analysis of elements by applying light to a sample transformed into atomic vapor by being heated to high temperatures and examining atomic absorption,*4 the property by which atoms quantitatively absorb light at a specific wavelength. "Background correction" at this time is vital for accurate measurement. Background, as the word suggests, refers to factors present in the environment that affect the results of analysis due to absorption or scattering of light by atoms or molecules other than the target atom. It is essential to remove the background when measuring trace amounts of atoms. Koizumi used the characteristic Zeeman effect of naturally occurring mercury rather than an isotope for this background correction.

Koizumi recalls, "We were fortunate enough to find optimal conditions under which light was absorbed by a particular polarized component and under which light was not absorbed by a particular polarized component, in spite of complex Zeeman effects. This was very lucky."

In this way, Koizumi and the product development team invented the world's first Zeeman Mercury Analyzer, the Hitachi 501. The development of this revolutionary analytical device, which enabled the direct analysis of solids such as hair and fish without preprocessing, attracted considerable attention.

*2 Isotopes
Atoms or atomic nuclei with the same atomic number but different mass numbers.

*3 Zeeman effect
A phenomenon discovered in 1896 by the Dutch physicist Pieter Zeeman, who was awarded the Nobel Prize for Physics in 1902. It is the effect of splitting the electromagnetic field of a single wavelength (spectral line) emitted by an atom in the absence of a magnet into several spectral lines when the atom is placed in a magnet.

*4 Atomic absorption
Atoms in a ground state absorb light at a specific wavelength and enter an excited state. This phenomenon of light absorption by elements is called atomic absorption.

3. The Zeeman effect is the key to accuracy

It should be specifically noted that it is the use of the Zeeman effect that ensures the accuracy of the device. To understand why, you need to delve into the principles involved, but Koizumi has some surprising words to say on the subject.

"Actually I don’t fully understand the principles of the device myself. Through experimentation I learned that this is the best method, but to understand the essential principles, you need to understand the basic properties of light.

As you know, light moves at a constant speed and never stops for a moment. It is neither positively nor negatively charged and is virtually weightless. Nevertheless, it interacts with electrons and its trajectory is bent by strong gravitational force. Light certainly has some very unique characteristics. To understand these properties of light, you need to be familiar with various cutting-edge fields including Einstein's general theory of relativity, astrophysics, quantum mechanics, and quantum electrodynamics."

Another phenomenon related to the properties of light are the gravitational waves reportedly detected directly for the first time in 2016, 100 years after Einstein first predicted their existence. This demonstrates how the properties of light are still being revealed and are not fully understood. Still, Koizumi says that the most important principle in the Polarized Zeeman Atomic Absorption Spectrophotometer is "the fact that the photons that make up light have only two basic degrees of freedom."

It is to be emphasized that the polarized Zeeman method was a new measuring technique and not a mere background correction. This is also a fundamental difference from the principle of atomic absorption using isotopes.

The degree of freedom of the photon is expressed by the term "spin," but spin can only take one of two states, +1 and -1. The device examined differences in the spin state of photons of a single wavelength. This is called zero point measurement, but it is the same as for a so-called balance. Since there are only two states, it is possible to measure very accurately in a state close to the limit like for a balance," explains Koizumi.

4. The significance of making observations using one wavelength rather than two

The Polarized Zeeman Atomic Absorption Spectrophotometer applies a magnetic field to a sample converted into atomic vapor to alter the behavior of electrons in the sample. It measures the two states of 1) being able to interact with light and 2) not being able to interact with light in the same way as a measurement with a balance. When measurements are made using polarized components parallel to the magnetic field, the combination of the atomic absorption and background absorption is detected. However, when measurements are made using polarized components perpendicular to the magnetic field, there is no atomic absorption spectrum at the measuring wavelength and only the background absorption is measured. This difference can be used to find the atomic absorption of the sample measured, enabling measurement of elements.

Says Koizumi, "The role of isotopes is to shift the wavelength due to differences in the properties of the atomic nucleus in the isotope. In other words, a dual wavelength is used to find the difference between the different wavelengths. The mercury analyzers first developed were an extension of this dual wavelength approach and this method could not fully exploit the property of photon spin that I mentioned earlier. To use the property of spin as is, it is essential to create two states by polarization at a single wavelength. It occurred to me that doing this might result in a close to ideal balance."

The Koizumi team developed the Hitachi 170-70 Polarized Zeeman Atomic Absorption Spectrophotometer using a single wavelength polarized Zeeman method. It became commercially available in 1976. This product enabled the high-sensitivity analysis of more than 50 elements, including cadmium, lead, and iron as well as mercury.

Akira Yonetani of Hitachi High-Tech Science was involved for many years in the development of applications for the Polarized Zeeman Atomic Absorption Spectrophotometer. He has this to say about its merits.

"Until then, measurements of metals had typically involved adding reagents to produce a color change and measuring this using a spectrophotometer, but this method required time for preprocessing. But with the Polarized Zeeman Atomic Absorption Spectrophotometer, it is possible to get results without the need for any such preprocessing. Also, since only a single wavelength is used for measurement, the baseline is stable and accurate measurement is possible. Another big advantage is that the background correction range covers the full spectrum."

The basic patent was disputed all the way to the supreme court, and the decisive factor in the approval of the patent was the fact that the Hitachi Polarized Zeeman Atomic Absorption Spectrophotometer used a novel single wavelength approach. The first 170-70 Polarized Zeeman Atomic Absorption Spectrophotometer was purchased by PerkinElmer. It was later exhibited in the company museum as the world's first polarized Zeeman atomic absorption spectrophotometer. In 2013 it received Analytical and Scientific Instrument Heritage Certification from the Japan Analytical Instruments Manufacturers' Association (JAIMA).

5. Relentless improvements to precision

Although the Polarized Zeeman Atomic Absorption Spectrophotometer had come into mainstream use as a device for measuring minute quantities of metallic elements, its history continued with the addition of various improvements to equip it with cutting edge technology and functionality to improve precision. About the development efforts, Koizumi reflects,

"We were told to somehow 'develop a product quickly, even if it is a bit rough and ready,' and we developed and released the first Zeeman mercury analyzer in a short space of time. So we encountered some unexpected situations when it went on the market. At the time, there were no other devices for rapid measurement, so in many cases the device was being operated 24 hours a day. Under such hard use, the device deteriorated in no time and worn out parts were discovered. Against this backdrop, inspection staff at Hitachi who normally expected developers to rigorously investigate failures remarked that "We'll sort it out ourselves. When you do your development work, just focus on the future." I really appreciated that. When I think about that, it brings tears to my eyes."

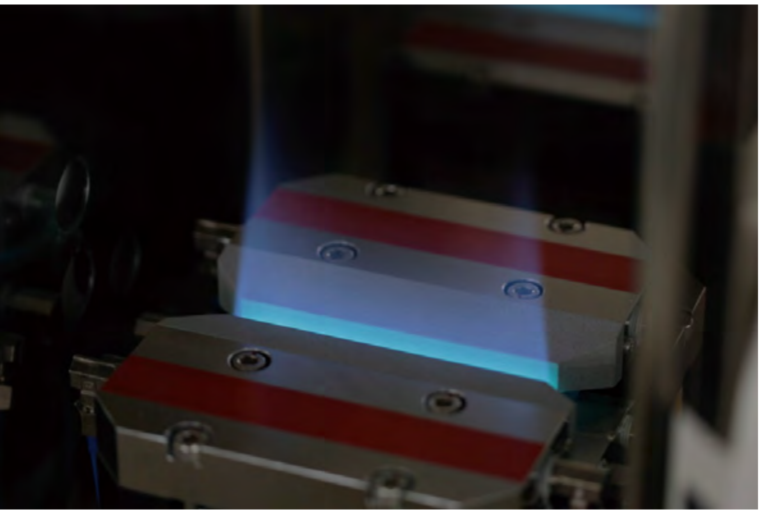
Koizumi's efforts paid off with the production of a sharply separating highly polarizing prism that could be used from part of the vacuum ultraviolet region to the near infrared region. At this time, work was being done on a method for cutting blocks from artificial crystals grown from seeds in such a way that the crystal axes intersected, polishing the cut surface to the greatest extent possible, and pasting them.

Koizumi explains, "When two surfaces that had been polished perfectly to the point where no interference fringe was produced were joined, molecules were attracted to each other and formed a rigid bond. This is called optical adhesion. However, since the intersecting crystal axes of two blocks have different coefficients of thermal expansion, a powerful force acts to separate them from one another when the temperature varies. I was really curious about how to achieve perfect optical adhesion that would prevent things coming apart even in the low temperatures of the cargo hold of a jet flying in the stratosphere or the hot temperatures of the tropics." Koizumi laughs, "People are still carrying on with the secret methods that I discovered."

Another project was to improve and regularize the S/N ratio (signal to noise ratio) of the photoelectric surface of the photomultiplier tube used as the light detector. Koizumi recalls, "This was essential technology for looking at the spin state of photons in a perfect balance state, and light had to be detected precisely and evenly at any wavelength. During the development process, we received the dedicated cooperation of Hamamatsu Photonics K.K., the manufacturer of the inner workings of the Kamiokande neutrino observatory. I am still very grateful to for this."

Later on, Koizumi was involved in the development of MRI (magnetic resonance imaging) using the Zeeman effect for hydrogen nuclei (protons), and in the development of MRA (magnetic resonance angiography) and fMRI (functional magnetic resonance imaging), and made progress in the development of optical topography using near infrared light and in neuroscientific research.

Says Koizumi, "Here too, the foundation was the measurement principle of balance. I expect the Polarized Zeeman Atomic Absorption Spectrophotometer that was my starting point as a researcher to be usable in future for research into the function of the brain in terms of its elucidation and the understanding of humanity itself."



6. A powerhouse for technical innovations, with numerous breakthroughs

One example of a technical innovation in the Hitachi Polarized Zeeman Atomic Absorption Spectrophotometer is the use of the polarized Zeeman correction method to the "frame method" to generate atomic vapor using a chemical flame, which launched a new generation of devices in 1980. Among them, the 180-80 model was equipped with two atomization methods, the frame method and electric heating, and each device was capable of analysis in the order of mg/L (ppm) to μg/L (ppb).

Plus, in 1987, the Z-9000 Electric Heating Atomic Absorption Spectrophotometer was developed as an industry first allowing the simultaneous analysis of four elements, and was widely praised as the ideal device for analysis of tap water and sewage.

Tobe reflects "In principle, this was not different from the device developed by Koizumi, but various improvements had been added to make the generation of atomic vapor more efficient and make measurement more convenient through such features as automated measurement. My particular involvement was in further improving detection capability in response to stricter regulatory values in water quality standards in the 1990s."

To satisfy a measuring condition of 10 μg/L as a standard for tap water means aiming for a device limit of detection of 1 μg/L. At the time, however, the hollow-cathode lamps used by Hitachi as light sources were unable to achieve this, and high brightness lamps called EDLs (electrodeless discharge lamps) that can emit stronger light were purchased from the United States for use in the product.

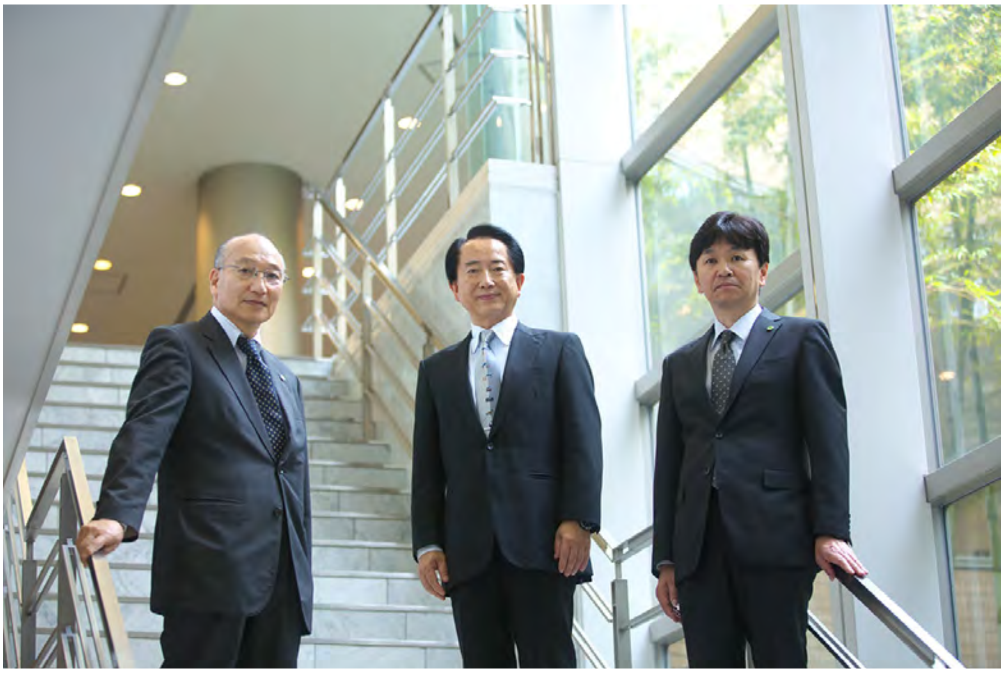
"However, adding an EDL increased the cost of the device, and had a very negative effect on user-friendliness. So we investigated whether it was possible to develop a product that did not use EDLs and came up with the Z-5000 Series, which was released in 1996," Tobe recalls.

One problem was that hollow-cathode lamps did not maintain the brightness required according to the wavelength. In addition, measurement made use of electrical heating using a graphite tube to enable detection in the order of μg/L (ppb). This method involved the generation of atomic vapor from liquid samples of a few tens of μL by heating to around 3,000°C, but the light emitted from the graphite tube would enter the spectrometer and interfere with the measurements. Tobe managed to solve this problem in just 2 months, keeping product development on schedule.

Says Tobe, "I solved the problem by regulating the amount of emission that entered the spectrometer from the emission distribution trends of graphite according to the wavelength and actively harvesting light at the wavelength of the measurement element that is actually being detected. In addition, while performing repeated experiments, I stumbled across the cause of the emissions entering the spectrometer. It was the window of the atomizing furnace opposite the spectrophotometer. By changing the structure of the electric heating furnace, we were able to cut emissions in half.

It was a difficult problem, but I think the time pressure actually gave me added motivation," says Tobe.

Subsequently, the Z-2000 Series developed in 2004 was unique in the world in having a dual detection method fitted



with a detector for each polarized component and employing the polarized Zeeman correction for hydride generation atomic absorption spectrophotometry. This improved sensitivity even more and enabled more stable analysis. In 2012, the ZA3000 Series, the first in the world to be equipped with twin injection (which injects the measurement sample separately through graphite tubes at two locations) and an energy saving mode, was released. Analysis lines are at long wavelengths, and the device uses the advantages of the polarized Zeeman correction method to enable measurement of cesium, for which in principle only limited background correction techniques are available. This makes a big contribution to its detection accuracy.

Meanwhile, technological innovations have not been restricted to hardware. Hitachi has made an effort to improve software development and the user interface by including a voice guidance function to help beginners at analysis and developing various applications.

Yonetani was involved for many years in the development of applications for the Polarized Zeeman Atomic Absorption Spectrophotometer.

"These days," says Yonetani, "it is easy to search for recipes using your smartphone. In a similar way, we have set up a members' site called S.I. Navi to enable our clients to easily search for methods of preprocessing or data acquisition for the samples they want to analyze. We currently have more than 1500 applications in our database. This initiative is one of the things our customers like."

Yonetani says that this comes from Hitachi's constant attention to customer feedback on product development.

"Researchers tend to be devoted and project-oriented, but our application staff and salespeople actively worked to ensure that our customers' opinions reached Koizumi, Tobe, and their teams," says Yonetani. "I think this is why customers say our devices are easy to use. If this has helped us to reach the 10,000 unit mark, then I am very happy."

7. The role of measuring devices and Hitachi in supporting people's lives

As people become more and more aware of food safety and health and environmental problems, the role of measuring devices is becoming increasingly important. Also, we are now living in a time when people with some knowledge are able to make objective evaluations based on analytical values that were once the preserve of experts. In light of this, what should Hitachi do to follow up on its work on measuring devices exemplified by the Polarized Zeeman Atomic Absorption Spectrophotometer?

Tobe expresses his hopes for the future. "As globalization continues in future, it is likely that events will arise that cannot be dealt with in local or national units. I think our task is to contribute to resolving such social issues. To achieve this, device automation and increased sensitivity are vital. By pouring our efforts into technological development for this purpose, we can help people to enjoy better lives."

Koizumi, on the other hand, explains that measurements are a means of identifying objective facts, and that it is important to return to first principles and thoroughly investigate the principle of the balance and the zero point method as basic concepts that are indispensable to scientific and technological progress.

"A genius of measurement who I respect is Pierre Curie, who discovered the "piezoelectric effect" and "radium," and even looked into the "theory of conservation of symmetry." Both Curies became famous for the discovery of Radium, but actually Pierre had already revealed the presence of a new radioactive element based on his measurements. Radium was also discovered using the zero point method to accurately measure the intensity of radiation using literal balance weights. This is how he was able to engage in difficult prospective work with no way of isolating trace amounts of radium.

The recent direct observation of gravitational waves was also achieved using the principle of the balance, and measurement is indispensable in the search for truth. I think this also means that Hitachi should follow up its previous involvement in measurement to fulfill an ever more important role and mission in the future."

When asked what is needed to fulfill this responsibility, Koizumi answered that the most important thing is enthusiasm. Koizumi summed up his comments, saying "Remaining enthusiastic to the end promotes teamwork and enables you to overcome difficulties. We need to work hard in future to train people in a way that builds their enthusiasm."

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https://members.hht-net.com/sinavi/

Editor's note

The Hitachi Polarized Zeeman Atomic Absorption Spectrophotometer has been used in a wide variety of settings, but it is sometimes useful for unexpected purposes. I was surprised to hear that it had been used to measure evidence in criminal investigations and hair taken from mummies. "Japanese people have a higher concentration of mercury in their hair than Europeans and North Americans," says Koizumi. This is because they are fond of eating seafood such as tuna in which metals are concentrated. In particular, the mercury content of marbled tuna is relatively high. There is an anecdote about using the device to measure the hair of our former Vice-President. They were surprised to find high levels of mercury. After hearing that he was very fond of marbled tuna, it made perfect sense.

Koizumi is now active as an authority on neuroscience, but it was wonderful to hear about his enthusiasm for the development of the Polarized Zeeman Atomic Absorption Spectrophotometer in his younger days. Before we knew it, we had talked for far longer than our scheduled time. I would like to thank all three interviewees for their valuable contributions.

(Location of photos: Hitachi High-Tech Science Naka Office, Center for Exploratory Research, Hitachi, Ltd.)
(Interview and text: Madoka Tainaka)