Vol.5 No.4 March 2013

ISSN 1883-0978 (Print)
ISSN 1883-2318 (Online)

Synthesiology

English edition

Dose standards for safe and secure breast cancer screening

Reconstruction of the 869 Jogan tsunami and lessons from the 2011 Tohoku earthquake

Evaluating uncertainty for the standardization of single cell/stack power generation performance tests for SOFC

Development of switchable mirror glass

Standardization of environmental analysis methods of hazardous chemicals

Synthesiology editorial board

2012

④

MESSAGES FROM THE EDITORIAL BOARD

There has been a wide gap between science and society. The last three hundred years of the history of modern science indicates to us that many research results disappeared or took a long time to become useful to society. Due to the difficulties of bridging this gap, this stage has been recently called the valley of death or the nightmare stage (Note 1). Rather than passively waiting, therefore, researchers and engineers who understand the potential of the research should actively try to bridge the gap.

To bridge the gap, technology integration (i.e. *Type 2 Basic Research* – Note 2) of scientific findings for utilizing them in society, in addition to analytical research, has been one of the wheels of progress (i.e. *Full Research* – Note 3). Traditional journals, have been collecting much analytical type knowledge that is factual knowledge and establishing many scientific disciplines (i.e. *Type 1 Basic Research* – Note 4). Technology integration research activities, on the other hand, have been kept as personal know-how. They have not been formalized as universal knowledge of what ought to be done.

As there must be common theories, principles, and practices in the methodologies of technology integration, we regard it as basic research. This is the reason why we have decided to publish "*Synthesiology*", a new academic journal. *Synthesiology* is a coined word combining "synthesis" and "ology". Synthesis which has its origin in Greek means integration. Ology is a suffix attached to scientific disciplines.

Each paper in this journal will present scenarios selected for their societal value, identify elemental knowledge and/or technologies to be integrated, and describe the procedures and processes to achieve this goal. Through the publishing of papers in this journal, researchers and engineers can enhance the transformation of scientific outputs into the societal prosperity and make technical contributions to sustainable development. Efforts such as this will serve to increase the significance of research activities to society.

We look forward to your active contributions of papers on technology integration to the journal.

Addendum to Synthesiology-English edition,

"Synthesiology-English edition" is a translated version of "Synthesiology", which is published quarterly, ISSN 1882-6229, by AIST.

Papers or articles published in "Synthesiology-English edition" appear approximately four months after the publication of the original "Synthesiology". Those published in Japanese are translated into English, so the views expressed in translated versions are exclusively those of the Japanese authors and editors. The Japanese authors are generally consulted regarding the translation of their papers, but are not responsible for the published English version.

Papers or articles in the "Synthesiology" originally submitted in English are also reproduced just as they were published in "Synthesiology". Some papers or articles in "Synthesiology" are not translated due to the authors' or editors' judgement.

Synthesiology Editorial Board
(written in January, 2008)

Note 1 : The period was named "nightmare stage" by Hiroyuki Yoshikawa, the then President of AIST, and historical scientist Joseph Hatvany. The "valley of death" was used by Vernon Ehlers in 1998 when he was Vice Chairman of US Congress, Science and Technology Committee. Lewis Branscomb, Professor emeritus of Harvard University, called this gap as "Darwinian sea" where natural selection takes place.

Note 2 : *Type 2 Basic Research*
This is a research type where various known and new knowledge is combined and integrated in order to achieve the specific goal that has social value. It also includes research activities that develop common theories or principles in technology integration.

Note 3 : *Full Research*
This is a research type where the theme is placed within the scenario toward the future society, and where framework is developed in which researchers from wide range of research fields can participate in studying actual issues. This research is done continuously and concurrently from *Type 1 Basic Research* (Note 4) to *Product Realization Research* (Note 5), centered by *Type 2 Basic Research* (Note 2).

Note 4 : *Type 1 Basic Research*
This is an analytical research type where unknown phenomena are analyzed, by observation, experimentation, and theoretical calculation, to establish universal principles and theories.

Note 5 : *Product Realization Research*
This is a research where the results and knowledge from *Type 1 Basic Research* and *Type 2 Basic Research* are applied to embody use of a new technology in the society.

Synthesiology – English edition Vol.5 No.4 (Mar. 2013)

Contents

Messages from the editorial board

Research papers

Dose standards for safe and secure breast cancer screening

— Establishment of X-ray dose standards for mammography and construction of a calibration service system —

Takahiro Tanaka *, **Tadahiro Kurosawa and Norio Saito**

[Translation from *Synthesiology*, Vol.5, No.4, p.222-233 (2012)]

Breast X-ray screening (mammography) was introduced in 2000 to detect breast cancer at an early stage. Since then, the number of examinees has increased steadily. The X-ray dose must be optimized to obtain high-quality images that ensure diagnosis reliability without compromising safety. Mammography utilizes low-energy X-rays with a special energy spectrum for breast cancer screening. This X-ray energy spectrum is significantly different from the reference X-ray spectrum used to calibrate dosimeters. Members of industry and academia were concerned about the reliability of dose evaluation for mammography quality control. Thus, the National Metrology Institute of Japan/National Institute of Advanced Industrial Science and Technology (NMIJ/AIST) has established an X-ray dose standard based on the X-ray energy spectrum for mammography and has disseminated this standard to industry. NMIJ has succeeded in rapidly establishing this standard by making the utmost use of existing research equipment and technology, and by utilizing the standard in the existing mammography quality control system. Moreover, it created a research and development (R&D) scenario beforehand considering both domestic and international situations regarding mammography dosimetry that has enabled rapid and extensive dissemination of the standard with international consistency.

Keywords : Mammography, dosimetry standard, calibration, dosimeter, reliability

1 Introduction

Owing to the recent increase in mortality due to breast cancer, mammography was introduced in Japan from 2000 to ensure early detection of breast cancer. After its introduction, the number of mammography examinees has increased, and this number surpassed 2.5 million people in fiscal year (FY) 2009. To effectively diagnose breast cancer, high quality diagnostic images and excellent interpretation techniques (e.g., the ability to discern lesions on diagnostic images) are required. However, to ensure patient safety, mammography must be performed with a minimum yet appropriate X-ray dose. The maintenance and improvement of mammography quality control are mainly conducted by academic societies and industries. Further improvement in the reliability of mammography X-ray dose assessment was demanded by the societies and industries involved because of the large discrepancy between the radiation quality (energy spectrum) for mammography and the calibration reference field, and this difference might affect the sensitivity of the dosimeters. Therefore, to manage this issue, the National Institute of Advanced Industrial Science and Technology (AIST) set out to develop and disseminate the national standard for X-ray dose based on mammography X-rays.

Measurement standards become meaningful only when they are used widely in society, and it is therefore important to meet the social demand for such standards in a timely manner. The typical period required for the development of a radiation dose standard is approximately 3–5 years. Here, by fully utilizing existing research facilities and technologies, the period from the commencement of development to dissemination was reduced to approximately 1.5 years. Moreover, a widely available calibration service system was established rapidly by utilizing the standard in the current quality control system for mammography. In this paper, we describe the scenario established by AIST for developing the mammography X-ray standard and improving the reliability of X-ray dose evaluation in mammography quality control.

2 Background of the research and development

2.1 Expansion of mammography in society

The age-adjusted incidence rate[Term 1] and the age-adjusted mortality rate[Term 2] for breast cancer has been increasing steadily in recent years.[1] Because the prognosis of breast cancer is good when treated early, early detection leads to a decrease in mortality. The rapid increase in the number of breast cancer patients was seen much earlier in Europe and in the US than in Japan. Since mammography was introduced as a screening methodology for the early detection of breast cancer, the mortality rate of breast cancer has decreased.[2]

In Japan, in addition to visual inspection and palpation, mammography was introduced for breast cancer screening beginning in 2000. The Ministry of Health and

---

National Metrology Institute of Japan, AIST Tsukuba Central 2, 1-1-1 Umezono, Tsukuba 305-8568, Japan
* E-mail : takahiro-tanaka@aist.go.jp

Original manuscript received January 31, 2012, Revisions received August 7, 2012, Accepted August 15, 2012

Welfare (currently the Ministry of Health, Labour and Welfare)[3] recommended that patients aged 50 and older undergo screening (4th Elderly Health Care Project). The recommendation was revised in 2004,[4] and the age range was expanded to 40 years and older (5th Elderly Health Care Project). Enforcement of the Cancer Control Act began in 2007, and since March 2008, cancer screening was included in the health promotion project (based on the Health Promotion Act). With the expansion of the age range recommended for screening, the number of examinees has increased since the introduction of mammography in 2000, and this number surpassed 2.5 million in FY 2009.[5]

2.2 Characteristics of mammography X-rays

In all diagnostic procedures involving X-rays, including mammography, an X-ray tube is used as the X-ray source. This tube is a device that generates X-rays by accelerating thermal electrons released from the filament to a metal plate (target) using high voltage (several kV to several hundred kV). The high voltage applied between the filament and target is called the tube voltage. These X-rays may include both characteristic and Bremsstrahlung X-rays depending on the combination of the target material and the tube voltage. The energy spectrum (radiation quality) is altered by passing the X-rays generated from the X-ray tube through a pure metal filter. The tube voltage and the material of the added filter and its thickness are adjusted to obtain X-rays with optimal quality for a given subject. Since the energy spectrum (radiation quality) is strongly depends on the target material and the filter, the expression of “target material / filter material” is commonly used. For example, if the target material is tungsten (W) and the filter is aluminum (Al), the energy spectrum (radiation quality) is expressed as W/Al.

Compared to general radiography such as that used for the chest, the X-rays used in mammography have 2 features: (1) they have lower energy and (2) their energy spectra include characteristic X-rays.

Regarding X-ray energy, while a tube voltage of approximately 80 kV is used in general X-ray radiography, 30 kV is used for mammography. Because the difference in the linear attenuation coefficient[Term 3] between glandular tissues and tumor tissue becomes larger as the X-ray energy decreases, low-energy X-rays are necessary to obtain high contrast images. However, X-ray absorption by the skin increases as the X-ray energy decreases. Therefore, in mammography, an X-ray tube voltage of approximately 30 kV is used to maintain both dose and image quality. At a tube voltage of approximately 30–80 kV, the absorption per unit length of matter, including air as well as the material of the dosimeter, increases as the X-ray energy decreases, which is a factor that prevents highly precise dosimetry.

Another characteristic of mammography X-rays is their energy spectrum. Tungsten (W) is used as the target material of the X-ray tube in general X-ray radiography, whereas molybdenum (Mo) is mainly used in mammography. In mammography, the tube voltage settings between 25 and 35 kV are typically used, depending on breast tissue thickness and composition. This is because the tube voltage is above the ionizing energy of the Mo K-shell and characteristic X-rays are emitted in abundance. For mammography, a Mo target X-ray tube and a Mo additional filter are typically used. As a result, the energy spectrum contains an abundance of characteristic X-rays as shown in Figure 1. Using the Mo additional filter, all except the characteristic X-rays are filtered out, and the energy spectrum becomes monochromatic. This combination is used because X-rays with lower energy than the Mo characteristic X-rays lead to relatively strong radiation exposure of the skin, whereas high-energy X-rays decrease the image contrast.

As described above, mammography is characterized by the use of low-energy X-rays that contain an abundance of characteristic X-rays.

2.3 Dosimetry in mammography

As an aid to the optimization of the radiation protection of the patient, dosimetric quantities need to be measured for radiography systems. In general X-ray radiography such as chest radiography, for example, the absorbed dose to the skin is used in dose evaluation.. However, in mammography, dose evaluation is done using a special dose called the average glandular dose (AGD) for the following reasons:

- only the breasts are exposed to X-rays,
- the glandular tissues are assumed to be most vulnerable to radiation in the breast, and
- the dose changes rapidly within the breast because the absorption per unit length is large, which is because of the low energy of the X-rays used.

The AGD is calculated as the X-ray dose absorbed by all glandular tissues within the breast divided by the total mass

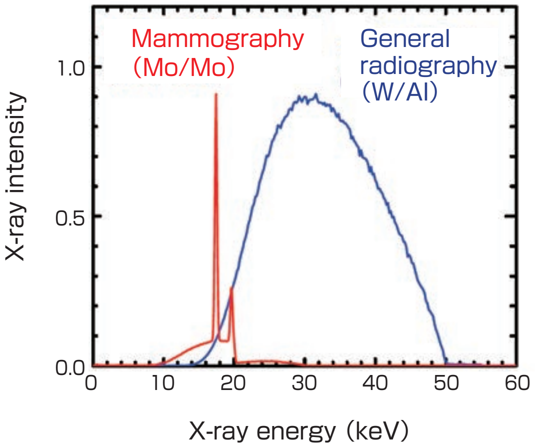


Fig. 1 Examples of the X-ray spectra for mammography (Mo/Mo) and general radiography (W/Al)

of the glandular tissues (the absorbed dose per unit mass of glandular tissue). The International System (SI) of units for AGD is J/kg, and this unit is designated as grey (Gy). The AGD is used as a representative of the absorbed dose to glandular tissues, which decreases as X-rays penetrate deeper into the breast (direction from the X-ray source to the receiving device, see Fig. 2). However, the AGD may change according to the amount (percentage) and distribution of the glandular tissues within the breast or the compressed breast thickness. Therefore, in mammography quality control, the standard breast is a breast with a thickness of 45 mm (42 mm in some cases) with uniform distribution of adipose and glandular tissues by weight. The AGD is evaluated using this standard definition of a breast.[6][7] To optimize (minimize) the AGD, reference levels (or minimum dose targets) have been set by related academic societies.

The AGD for an individual human body is extremely difficult to evaluate, and it is evaluated using a phantom, which is a material that simulates the standard breast as recommended by academic societies. Figure 2 shows an evaluation of AGD using a mammography machine.

The dosimeter is placed so that its reference plane matches the surface of the phantom, and the dose of X-rays irradiated onto the phantom surface (X-ray source side) is measured. Because the dose measured by the dosimeter in this case is expressed by the unit "air kerma"Term 4, it is necessary to convert from air kerma to AGD. This conversion factor can be determined using the Monte Carlo calculation, and the tables for corresponding X-ray qualities are given in quality control manuals and other references.[6][7] Therefore, to evaluate the AGD, an evaluation of the radiation quality of X-rays from the mammography machine is necessary. However, the measurement of an energy spectrum in actual medical practice is not realistic considering the time and cost. Therefore, the mammography radiation quality is expressed as the thickness of the material (aluminum is used in mammography) required to reduce the amount of air kerma by half. This thickness is called the half-value layer. As described above, it is necessary for evaluation of the AGD to measure the dose (air kerma) and quality (half-value layer) using a dosimeter.

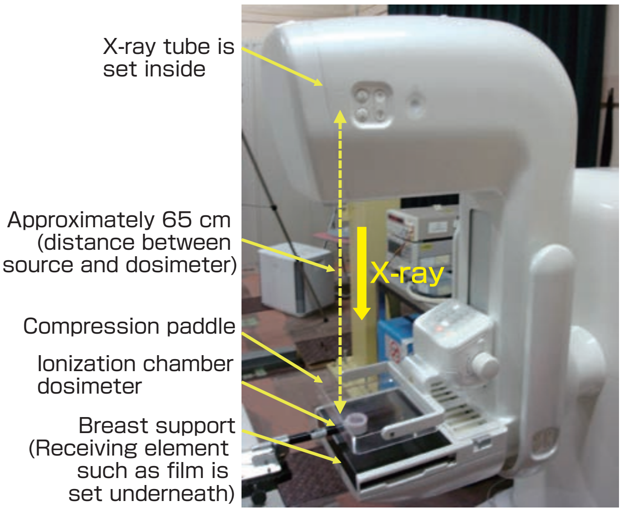


Fig. 2 Example of the installation of a dosimeter for the dose evaluation of a mammography machine
The reference plane of the dosimeter is lifted from the breast support because of the thickness of the phantom. In the photograph, only the ionization chamber dosimeter is mounted.

2.4 Dosimeters for mammography X-rays

There are many types of dosimeters with different measurement principles. In the medical practice of mammography, 2 types of dosimeters are widely used: the ionization chamber type and the semiconductor type.

The ionization chamber dosimeter measures the amount of ionization (ion-electron pair) generated by the interaction between X-rays and air. In mammography, X-rays with low energy (or those strongly attenuated by matter) are used. Therefore, the entrance window in an ionization chamber used for mammography X-rays is composed of a thin film (mainly metal vapor-deposited resin) that allows for high transmittance of X-rays. Because an ionization chamber can measure the X-ray dose close to the definition of air kerma, it is used as a reference dosimeter. However, because the volume of air changes according to environmental conditions such as temperature and pressure, correction for environmental conditions is necessary. Because the X-ray entrance window is composed of a thin film, care must be taken in handling the device. Additionally, because the thin film absorbs X-rays, the sensitivity of the ionization chamber is likely to change depending on the X-ray energy, which may create problems for the measurement of low-energy X-rays.

Silicon is mainly used in semiconductor dosimeters, and the depletion layer formed by the P-N junction (application of reverse bias voltage) is used as the radiation sensitive layer. In the PIN–type semiconductor dosimeters, the intrinsic semiconductor layer (i layer) acts as the radiation sensitive layer. While the carrier of the current is the electron-ion pair in the ionization chamber dosimeter, the current is carried by the electron-hole pair in the semiconductor dosimeter. Therefore, the semiconductor dosimeter is referred to as a solid ionization chamber. Compared to the ionization chamber dosimeter, the semiconductor dosimeter is sturdy and convenient to use with no correction required for temperature and pressure, and it is therefore used frequently for dose evaluation in actual medical practice. However, because the surface SiO_2 layer and the non-sensitive layer absorb a large amount of X-rays, the sensitivity is greatly dependent on X-ray energy in the low-energy region such as mammography X-rays.

Both the ionization chamber and semiconductor dosimeters have been developed as dosimeters for mammography X-rays (or low-energy X-rays); however, the energy dependence of the sensitivity (hereinafter energy dependence) cannot be avoided because of the physical structure of the dosimeters. Therefore, for the measurement of the X-ray energy region used in medical practice, academic societies recommend calibration of the dosimeters using a reference X-ray field with accurately determined characteristics.

2.5 International trend

Because the rapid increase in the number of patients with breast cancer was seen earlier in Europe and the US than in Japan, the construction of quality control systems started much earlier in Europe and the US. In the US, the American College of Radiology (ACR) established a quality standard for mammography in 1986 and began work on quality control. In 1992, the Mammography Quality Standard Act was established as a federal law, and mammography screening became legislated.[8] Under the mammography screening law, all facilities conducting mammography screenings must receive certification from inspection institutes (ACR or state governments) accredited by the Food and Drug Administration (FDA) and are required to undergo medical inspection and receive clearance from the FDA. This law states that the dosimeter must be calibrated once every 2 years, and traceability to the national standard must be guaranteed. The National Institute of Standards and Technology (NIST), which is responsible for the American national standard, disseminates the mammography air kerma standard based on Mo/Mo radiation qualities. The Quality Control Manual[9] published by ACR was adopted into a quality control manual for Japan.

The European Reference Organization for Quality Assured Breast Screening and Diagnostic Services (EUREF) played a central role in creating the guideline for mammography quality control in Europe.[10] This guideline states that the dose must be evaluated once every 6 months. European countries conduct quality control using individual methods that are based on this guideline. The air kerma standard based on Mo/Mo qualities was disseminated mainly in Germany and the UK. However, several European institutes calibrate mammography dosimeters using the W/A1 qualities, and there were concerns that differences in radiation quality may affect the calibration results. Therefore, institutes belonging to the European Collaboration in Measurement Standards (EUROMET, currently known as the European Association of National Metrology Institutes; EURAMET) performed an international comparison for the calibration of mammography dosimeters.

In this international comparison, several ionization chamber and semiconductor dosimeters were circulated and calibrated with the radiation qualities (either Mo/Mo or W/A1) used by the institutes, and the calibration results were compared. The results indicated that for the dosimeters with a small energy dependence, such as the ionization chambers for mammography (soft X-rays), the effect of radiation quality on the calibration result was not a major issue in practice. However, dosimeters with a large energy dependence, such as the semiconductor dosimeters, should be calibrated under radiation quality conditions similar to that of mammography X-rays (such as Mo/Mo).[11]

With this background, the Consultative Committee for Ionizing Radiation in the International Bureau of Weights and Measures (Bureau International des Poids et Mesures; BIPM) made a resolution that the BIPM establish the air kerma standard for mammography based on the Mo/Mo radiation qualities. This means that the dosimeters should be calibrated using the air kerma standard for mammography radiation qualities. BIPM prepared the reference field for mammography X-rays based on Mo/Mo radiation qualities, and an international comparison with BIPM began in 2009.[12]

2.6 Societal need for the mammography X-ray air kerma standard

With low-energy X-rays such as those used in mammography, the energy dependence of the dosimeter (both ionization chamber and semiconductor types) is large, and academic societies recommended that the calibration be performed at an energy close to that of the X-rays used in medical practice. Conventionally, the dose standard of X-rays in the mammography energy region was disseminated with W/A1 radiation qualities. Figure 3 illustrates an example of the energy dependence of the ionization chambers (range of

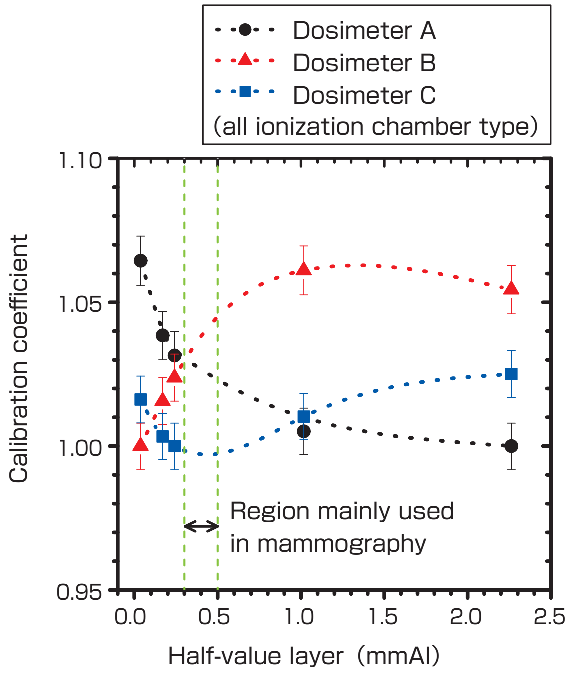


Fig. 3 Example of the energy dependence of the ionization chamber

the half-value layer for AIST's soft X-ray standard of W/A1 radiation qualities).

In the X-ray energy range used in mammography, the sensitivity (calibration coefficient) of ionization chambers with a relatively small energy dependence changes with X-ray energies more than their uncertainties (95 % confidence interval) as shown by the vertical bar for each data point in Figure 3. The change in sensitivity differs according to the type of dosimeter, i.e, the calibration coefficients of the dosimeter A decrease with the HVL whereas those of dosimeter B increase. This change is due to differences in the material and thickness of the X-ray entrance window of the dosimeter as well as the internal structure of the dosimeter. The semiconductor dosimeters, which have a larger energy dependence than the ionizing chambers, are used more often in medical practice; thus, Japanese industries and academic societies were concerned about the effect of the radiation quality and energy dependence of the dosimeters on the calibration coefficient. To manage this problem, AIST developed and disseminated a dose standard based on the radiation qualities of mammography X-rays.

3 Scenario for improving the reliability of mammography X-ray dose evaluation

To improve the reliability of mammography dose evaluation in medical practice, it is necessary to (1) establish a dose standard based on the radiation qualities of mammography X-rays used in practice and (2) create a calibration service system to disseminate the dose standard to society. Figure 4 shows a scenario for improving the reliability of mammography dose evaluation.

To quickly respond to social demands, time required for standard development was shortened by utilizing the existing primary standard without developing a new primary standard optimized for mammography X-rays. To reduce the uncertainty of dose evaluation in medical practice, to which the standard was mainly disseminated, an X-ray field close to that of an actual mammography machine was developed. Additionally, to confirm the international equivalence of the standard, an X-ray reference field was developed at the same time in compliance with the International Electrotechnical Commission (IEC) standard. In addition to participating in the international key comparison, the calibration capability of the developed dose standard was verified by comparing the dose measurements of X-rays from an actual mammography machine with several dosimeters calibrated using the standard, and the results were evaluated.

Because mammography quality control (including dose evaluation) was already being performed in many medical practices, rapid and widespread dissemination of the standard was achieved by evaluating the glass dosimeter that was already being used in this quality control. Therefore, AIST developed a method for calibrating the glass dosimeters.

In the conventional traceability scheme of the dose standards, the standards were disseminated through networks of secondary calibration laboratories by means of calibrations. In this case, it would not be useful if the conventional W/A1 radiation quality owned by the calibration laboratories was used as the reference (X-ray) field. However, it costs several tens of millions of yen to develop a reference field for the radiation qualities of mammography X-rays. Therefore, AIST developed a system in which the AIST's irradiation facility could be used for the calibration/testing service to ensure

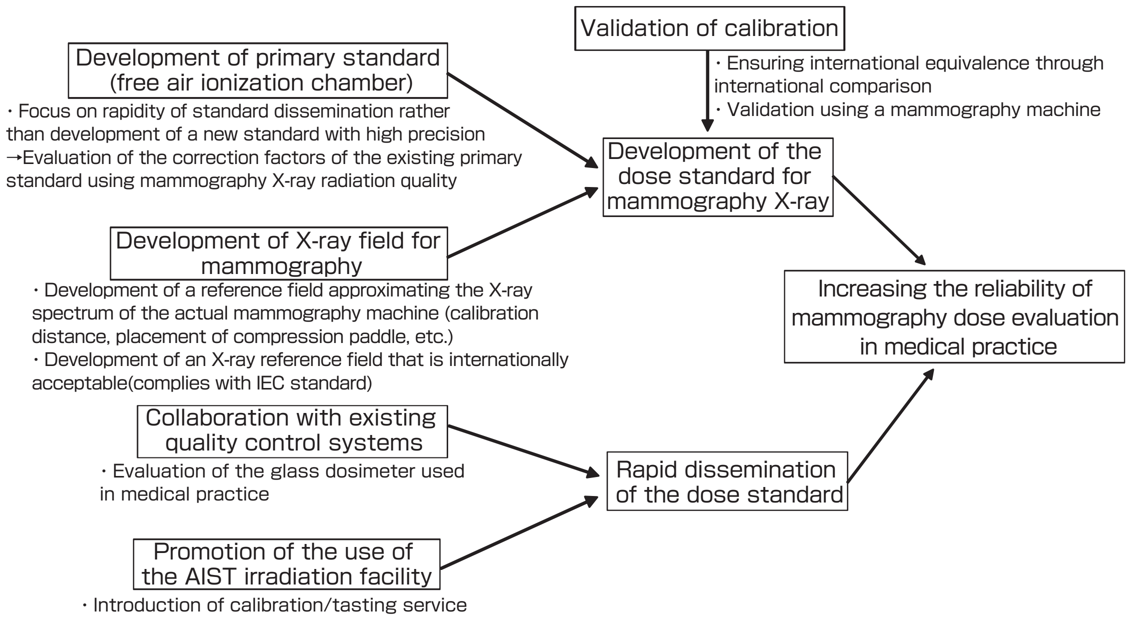


Fig. 4 Scenario for improving the reliability of mammography X-ray dose evaluation

smooth dissemination of the standard.

This scenario was created to ensure rapid and widespread dissemination of the internationally equivalent dose standard to medical practitioners and to improve the reliability of dose evaluation.

4 Development of the national primary standard

To develop a primary standard for mammography X-ray dose, a primary standard instrument for absolute dose measurement (measurement according to the definition of a unit) and a reference X-ray field with the same radiation quality as mammography X-rays must be developed. The development of a primary standard instrument and a mammography X-ray reference field will be described in these sections.

4.1 Development of the primary standard instrument

In the case of soft X-rays (here, a tube voltage of 50 kV or less), including those used in mammography, the dose standard (in Gy [or C/kg]) has already been disseminated for the air kerma[Term 4] (or exposure[Term 5]) that has been physically defined.

The free air ionization chamber, which is capable of absolute measurement of the radiation dose, is used worldwide as the primary standard instrument. Currently, this instrument is used as the primary standard instrument for the measurement of soft X-ray doses at AIST (Fig. 5).

In the free air ionization chamber, the ion charge generated within the ionization volume is measured, and the radiation dose (or air kerma) is evaluated. When the mass of air within the ionization volume is set as m, the exposure rate $\dot{X}$ (C·kg^{-1}s^{-1}) is obtained using equation (1).

$$\dot{X} = \frac{I}{m}\prod_{i=1}^{10} k_i \quad \cdots \text{(1)}$$

In this equation, I is the ionization current measured by the free air ionization chamber and Πk_i is the product of the correction factors. The correction factors are used to correct for the deviation between the actual experimental condition and the ideal condition defined for the dose, and there are a total of 10 different correction factors. For mammography X-rays, the largest correction factor (approximately 1.5–2 %) is the correction for the attenuation of X-ray along the air path between the reference plane and center of the collective electrode. There is a minor correction (approximately 0.5 %) for scattering radiation, and the rest of the correction factors are fairly small (less than 0.1 %). The correction factors that are difficult to experimentally evaluate, such as the correction for scattering radiation, are evaluated using the Monte Carlo simulation.

Figure 6 shows a photograph of the present mammography dose standard equipment. To develop the national standard for mammography, the correction factors of the free air ionization chamber (the primary standard instrument for soft X-ray dose) were evaluated for the radiation quality of mammography X-rays without developing a new primary standard instrument (free air ionization chamber) specific for mammography X-rays. This significantly shortened the time required for the development of a standard and allowed for a quick response to the social demand for dissemination of the standard. As shown in Figure 6, the free air ionization chamber is installed on the XY stage and can be shared with the dose standard for soft X-rays (W/A1 radiation quality).

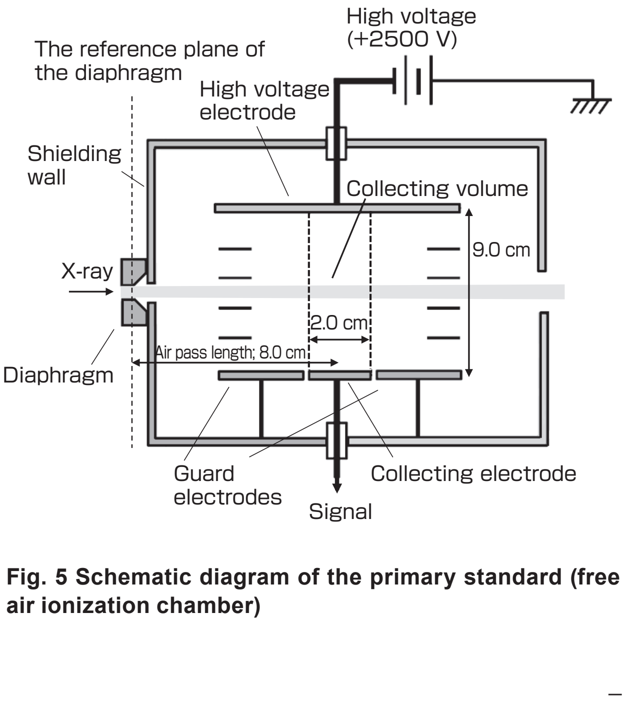


Fig. 5 Schematic diagram of the primary standard (free air ionization chamber)

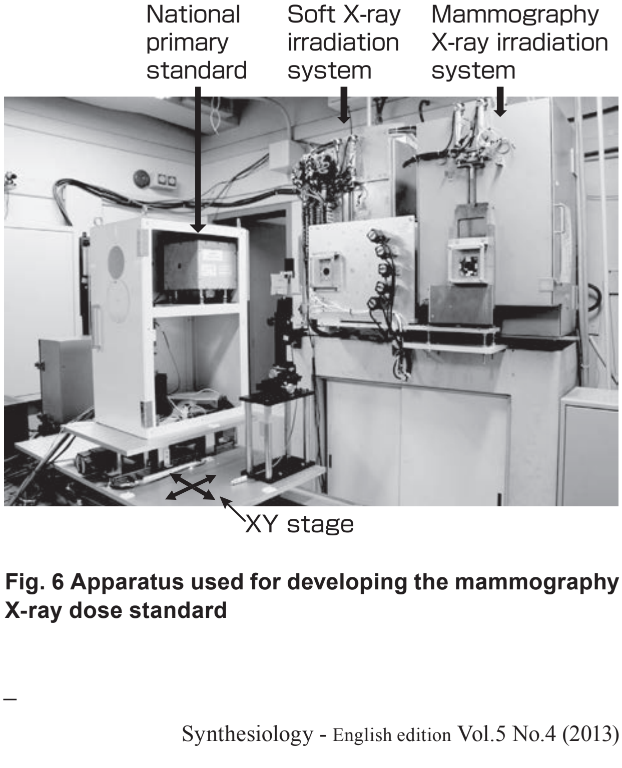


Fig. 6 Apparatus used for developing the mammography X-ray dose standard

4.2 Development of the mammography X-ray reference field

A reference field for the radiation quality of mammography X-rays was developed starting mainly from the dominant radiation qualities used in practice. As mentioned earlier, the radiation quality is determined by the target material of the X-ray tube, the tube voltage, and the material and thickness of the additional filter. We ensured that we were using a radiation quality that could be used overseas as well as in Japan, as exemplified by the International Organization for Standardization (ISO) and IEC standards (for mammography, IEC 61267).[13] Such a radiation quality is necessary for international key comparisons that are conducted to confirm the equivalence of the dose standard around the world. However, a radiation standard other than that of the IEC is used in the Japanese quality control manuals, and compliance with the Japanese standard would lead to a smooth dissemination of the standard. Consideration of both overseas and domestic situations when establishing a standard is the first step toward disseminating a dose standard that is internationally equivalent.

Because the linear absorption coefficient for air that is used in mammography is larger than that used in other diagnostic X-ray modalities, the radiation quality changes significantly because of the calibration distance (distance from the focus point of the X-ray tube to the reference plane of the free air ionization chamber); therefore, it is important to set the calibration distance. In countries such as Germany and the US that have begun disseminating standards before Japan, the calibration distance is 1 m. However, AIST set the calibration distance at 60 cm considering the irradiation distance of the mammography machine. Later, BIPM set the calibration distance at 60 cm.

A dose standard based on the radiation quality through the compression paddle was originally developed in Japan. In actual mammography screening, the breasts are irradiated with X-rays through the compression paddle. The low-energy X-rays used in mammography tend to be absorbed by the compression paddle, and the radiation quality changes greatly. Thus, an original radiation quality was developed considering the quality of radiation exposure to the breasts. This radiation quality was required for the calibration of the dosimeter used in mammography quality control.

5 Construction of the calibration service system for mammography

The construction of a calibration service is essential for improving the reliability of dose evaluation in medical practice. Therefore, multiple calibration services were established with the cooperation of industries and academic societies.

5.1 Performance test of the glass dosimeter used for mammography quality control

Before mammography was utilized for breast cancer screening in Japan, mammography quality control was performed mainly by related academic societies. A mammography glass dosimeter was developed to easily evaluate the dose and the radiation quality necessary for mammography quality control.

The glass dosimeter is an integrated-type radiophotoluminescence[Term 6] dosimeter, and silver-activated phosphate glass is used as the fluorescent glass element. Figure 7 shows a photograph of the mammography glass dosimeter.

The mammography glass dosimeter consists of a fluorescent glass element and aluminum filters with 4 different thicknesses covering the surface of the element. The thicknesses of the aluminum filters are 0.3, 0.4, 0.6, and 1.0 mm, and an attenuation curve can be obtained from one irradiation. The half-value layer and tube voltage can be calculated from this attenuation curve, and the air kerma can be calculated from the amount of fluorescence at the open window (without the Al filter) glass element. Thus, the AGD required for mammography quality control can be evaluated with only one irradiation. The performance of this glass dosimeter was evaluated using the reference field.

Our results confirmed that the half-value layer, tube voltage, and air kerma values are in good agreement with the values measured using the free air ionization chamber (within 2 % uncertainty at the 95 % confidence level).[14]

5.2 Use of the irradiation facility at AIST

A mammography X-ray source is necessary for calibration laboratories to perform calibration using the radiation quality of mammography X-rays. However, such an X-ray source costs a minimum of tens of millions of yen; therefore, the calibration service would not be viable as a business. To solve the issue, AIST initiated a calibration/testing service in which the calibration laboratory is allowed to bring the reference dosimeter (assumed to be traceable to the primary standard) and the dosimeter to be calibrated to the mammography

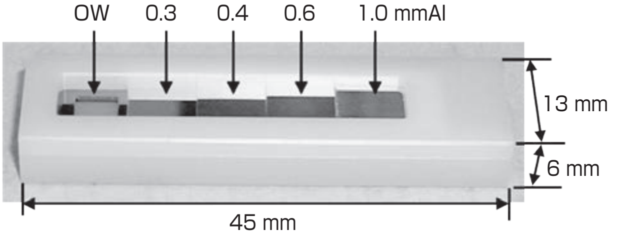


Fig. 7 Glass dosimeter developed for quality control of mammography (with cooperation from Chiyoda Technol Corporation)

reference field at AIST to perform calibration. The fees for the calibration/testing service are calculated according to the number of days the irradiation facility is used. Therefore, the expenditure that must be borne by the calibration labs was reduced, and a smooth dissemination of the standard was expected.

6 Validation of the calibration

6.1 Confirmation of the international equivalence of the national standard

To confirm international equivalence, all standards must be compared with the standards of other countries. As mentioned earlier, BIPM developed the dose standard for mammography X-rays and has performed key comparisons[Term 7] since 2009. AIST participated in the international key comparison in 2009.[15]

There are 2 methods for international comparison of a radiation dose standard. The first method is a direct comparison between the primary standards of the countries involved. For example, the primary standard instrument (free air ionization chamber) at AIST is taken to the reference field at BIPM, and the absolute values of the dose are compared. This method is limited to cases in which the primary standard instrument is transferrable. Another method is an indirect comparison, in which the transfer instruments are calibrated using the primary standard at the institutes involved and the calibration results (calibration coefficient) are compared. This method is useful in cases where the primary standard instrument cannot be transported easily because of its size.

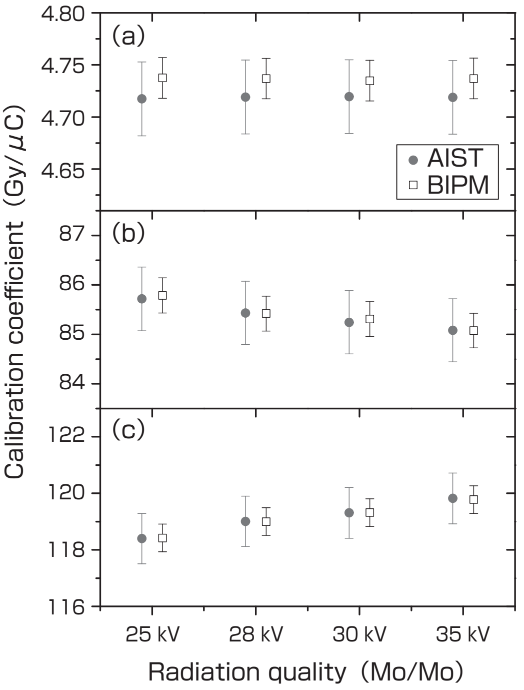


Fig. 8 Comparison between AIST and BIPM calibration coefficients of 3 types of dosimeters (a, b, and c)

The energy characteristic of the dosimeter is (a) flat, (b) declining, and (c) increasing.

The free air ionization chamber, which is the standard instrument used for measuring mammography X-rays at AIST, is also used to determine the conventional soft X-rays (W/Al) dose. This standard instrument was compared directly with the BIPM standard in 2004, and its equivalence was confirmed.[16] Therefore, in this key comparison, the latter method of the indirect comparison was selected. Three ionization chamber dosimeters with different energy characteristics were selected for a detailed comparison. Figure 8 shows a comparison of the calibration results obtained for the 3 types of dosimeters measured at the 2 institutes.

As shown in Figure 8, the calibration coefficients of the dosimeters showed good agreement between institutes. The calibration uncertainty of BIPM (error bar in Fig. 8) was smaller than that of AIST for all 3 types of dosimeters because BIPM has a newly developed free air ionization chamber that has been optimized (i.e., the correction coefficient for equation (1) is small) for the radiation quality of mammography X-rays.

Figure 9 shows the results of the international key comparison for mammography dose standards. Germany (the PhysikalischTechnische Bundesanstalt, PTB), the US (NIST),

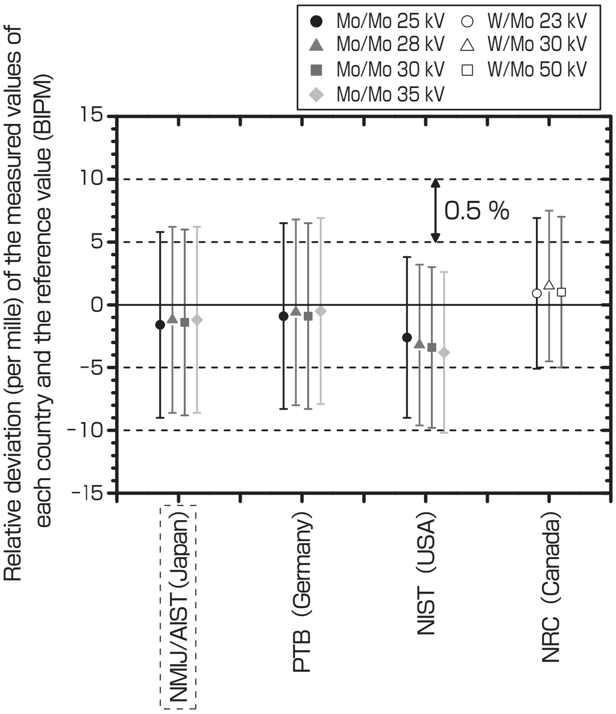


Fig. 9 International key comparison for the mammography dose standard[17]

The vertical axis shows the deviation (per mille) from the BIPM reference value. For each data point, the vertical bar shows the uncertainty at the 95 % confidence level.

and Canada (the National Research Council, NRC, radiation quality is slightly different) participated in this international key comparison, and equivalence was confirmed among the mammography dose standards at all institutes.[17] It was also found that the uncertainty in the AIST dose standard was comparable to that in the dose standards of other countries.

6.2 Validation using a mammography machine

The X-rays produced by mammography machines used in medical practice are generated as a short pulse. However, the dose rate at the reference field is constant over time because stability is required. Additionally, in an actual mammography machine, the structure of the irradiation device is compact and it is difficult to put in the national primary standard, whereas there is spatial allowance in the standard field. The investigation of such differences between an actual mammography machine and the standard field will help improve the reliability of dosimetry in medical practice. Therefore, AIST conducted a comparison of the dose evaluation results between ionization chamber dosimeters (calibrated at AIST) and a glass dosimeter using a mammography machine employed in medical practice.

As a result, it was confirmed that the AGDs measured by the ionization chambers and glass dosimeter agreed within the uncertainties (Fig. 10). The dosimeters calibrated at the AIST's standard field were found to be reliable for dose evaluation of an actual mammography machine.

7 Conclusions

AIST has developed a dose standard for mammography radiation qualities and has established a calibration service to improve the reliability of mammography dose evaluation in medical practice. The time required to develop a mammography dose standard was greatly reduced by utilizing the existing primary standard instrument (free air ionization chamber) for soft X-rays. Additionally, AIST participated in an international key comparison to confirm international equivalence. Rapid and widespread dissemination of the standard was possible by fully utilizing the existing calibration service system. The calibration service system will be further developed in the future through collaborations with academic societies and calibration services.

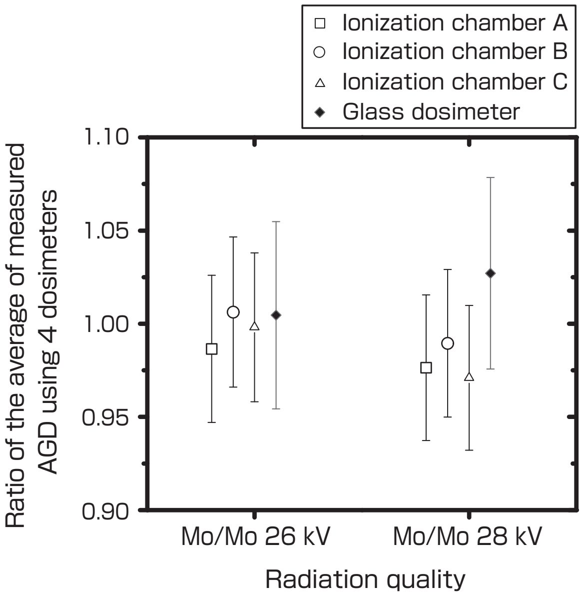


Fig. 10 Comparison of dose measurements for the actual mammography machine

For each data point, the vertical bar shows the uncertainty at the 95 % confidence level.

Currently, digital mammography, which uses digital images and computers, is becoming common instead of conventional screen-film mammography. Compared to evaluation using a conventional film image, dose evaluation from digital image is thought to be more difficult; therefore, the importance of dosimetry in mammography quality control is expected to increase. Additionally, various radiation qualities (W/Rh or W/Ag) will be used in digital mammography. The sensitivity of the semiconductor dosimeter used in medical practice changes significantly depending on the radiation quality, and the development of a reference field is urgently required. Currently, a reference field for digital mammography is being developed in the US, and focused research is being performed to evaluate the semiconductor dosimeter. AIST will continue developing its reference field to manage the increase of radiation qualities efficiently and to contribute to the quality control and safety of advanced mammography.

Acknowledgements

The excellent quality control system in Japan played a major role in the rapid and widespread dissemination of this standard. We are deeply grateful to the staff members who constructed such an excellent quality control system. We are also grateful to the people of Chiyoda Technol Corporation who assisted in the development and evaluation of the mammography glass dosimeter.

Terminologiy

Term 1. Age-adjusted incidence rate: The incidence rate corrected for the age composition of the standard population (1985 population model). This enables comparisons among groups with significantly different age compositions.

Term 2. Age-adjusted mortality rate: The mortality rate corrected for the age composition of the standard population (1985 population model). This enables comparisons among groups with significantly different age compositions.

Term 3. Linear attenuation coefficient: When a single-energy photon of strength I_0 enters and permeates a uniform substance, the strength I of the permeating photon decreases exponentially as the thickness of the material d (cm) increases, as follows:

$I = I_0 \times e^{-\mu d}$

The coefficient μ (cm^{-1}) is termed the linear attenuation coefficient.

Term 4. Air kerma: The mean sum of the initial kinetic energies of all the secondary charged particles liberated in the air per unit mass via interaction with uncharged particles. It is expressed in J/kg as per the International System of Units; however, the special name, grey (Gy), is also used.

Term 5. Exposure: The absolute value of the mean total charge of the ions of one sign produced when all the electrons and positrons liberated or created by photons incident in the dry air per unit mass are completely stopped in dry air. It is expressed as C/kg in the International System of Units.

Term 6. Radiophotoluminescence: The phenomenon in which luminescence occurs in proportion to the dose of radiation that glass is exposed to when ultraviolet rays are irradiated to the luminescence center produced in the glass by irradiation. This phenomenon is exploited in personal dosimeters.

Term 7. Key comparison: Consultative committees from each metrology field established under the International Committee for Weights and Measures (Comité International des Poids et Mesures; CIPM) conduct important international comparisons in their respective fields termed CIPM key comparisons. There are 8 quantities subject to key comparisons in the radiation dose field:

K1: Air kerma for ^{60}Co γ-rays
K2: Air kerma for low-energy X-rays
K3: Air kerma for medium-energy X-rays
K4: Absorbed dose to water for ^{60}Co γ-rays
K5: Air kerma for ^{137}Cs γ-rays
K6: Absorbed dose to water for high energy photons
K7: Air kerma for mammography beams
K8: Air kerma rate for high-dose-rate ^{192}Ir brachytherapy sources

Other than these 8 quantities, the amount of personal dose, β-ray absorbed dose, and some others are the subjects of supplementary comparison.

References

[1] Center for Cancer Control and Information Services, National Cancer Center, Japan. http://ganjoho.jp/public/statistics/pub/statistics02.html#prg3_1 (in Japanese).

[2] WHO Mortality Database [database online]. http://www.who.int/healthinfo/morttables/en/

[3] Director, Division of the Health for the Elderly, Health and Welfare Bureau for the Elderly, Ministry of Health, Labour and Welfare: "Gan Yobo Juten Kenko Kyoiku Oyobi Gan-Kenshin No Tameno Shishin" No Ichibu Kaisei Ni Tsuite (On the Partial Amendment to the "Guideline for Focused Health Education for Cancer Prevention and Cancer Screening"), Notification #65 of the Health and Medical Service Law for the Elderly, March 2000 (in Japanese).

[4] Director, Division of the Health for the Elderly, Health and Welfare Bureau for the Elderly, Ministry of Health, Labour and Welfare: "Gan Yobo Juten Kenko Kyoiku Oyobi Gan-Kenshin No Tameno Shishin" No Ichibu Kaitei Ni Tsuite (On the Partial Amendment to the "Guideline for Focused Health Education for Cancer Prevention and Cancer Screening"), Notification No. 0427001 of the Division of the Health for the Elderly, Health and Welfare Bureau for the Elderly, April 2004 (in Japanese).

[5] Chiiki Hoken Kenko Zoshin Jigyo Hokoku (Report on Regional Public Health Services and Health Promotion Services) (Health Statistics Office, Vital, Health and Social Statistics Division, Ministry of Health Labour and Welfare) http://www.e-stat.go.jp/SG1/estat/eStatTopPortal.do (in Japanese)

[6] Mammography Guideline Diffusion Team, Radiography Section, Japanese Society of Radiological Technology: *Radiological Technology Library (14-3) Nyubo Satsuei Seido Kanri Manuaru Kaiteiban* (Mammography Quality Control Manual, Revised Edition), Japanese Society of Radiological Technology (2004) (in Japanese).

[7] The Central Committee on Quality Control of Mammographic Screening NPO (ed): *Dejitaru Mamogurafi Seido Kanri Manuaru* (Manual of Digital Mammography Quality Control Management), Igaku Shoin (2009) (in Japanese).

[8] Mammography Quality Standard Act.

[9] Committee on Quality Assurance in Mammography, American College of Radiology: *Mammography Quality Control Manual 1999*, American College of Radiology, USA (1999).

[10] European Commission: *European Guidelines for Quality Assurance in Breast Cancer Screening and Diagnosis, Fourth Edition*, European Communities, Luxembourg (2006).

[11] J. Witzani, H. Bjerke, F. Bochud, I. Csete, M. Denoziere, W. de Vries, K. Ennow, J. E. Grindborg, C. Hourdakis, A. Kosunen, H. M. Kramer, F. Pernicka and T. Sander: Calibration of dosemeters used in mammography with different x ray qualities: EUROMET Project No. 526, *Radiation Protection Dosimetry*, 108, 33-45 (2004).

[12] C. Kessler, P. Roger and D. T. Burns: Establishment of reference radiation qualities for mammography, *Rapport* BIPM 2010/01 (2010).

[13] *IEC61267 Ed. 2.0, Medical Diagnostic X-ray Equipment - Radiation Conditions for Use in the Determination of Characteristics*, IEC (2005).

[14] T. Tanaka, T. Kurosawa, N. Nouda, T. Matsumoto, N. Saito, S. Matsumoto and K. Fukuda: Reference X ray field for mammography dosimetry in Japan, *Proceedings of the International Symposium, Standards, Applications and Quality Assurance in Medical Radiation Dosimetry*, 2, 43-51 (2011).

[15] C. Kessler, D. T. Burns, T. Tanaka, T. Kurosawa and N. Saito: Key comparison BIPM.RI(I)-K7 of the air-kerma standards of the NMIJ, Japan and the BIPM in mammography X-rays, *Metrologia*, 47, 06024 (2010).

[16] D. T. Burns, A. Nohtomi, N. Saito, T. Kurosawa and N. Takata: Key comparison BIPM.RI(I)-K2 of the air-kerma

standards of the NMIJ and the BIPM in low-energy x-rays, *Metrologia*, 45, 06015 (2008).
[17] BIPM Key Comparison Database [database online]. http://kcdb.bipm.org/

Authors

Takahiro TANAKA

Completed the course in Physics at the Graduate School of Science and Technology, Sophia University in 2008. Doctor (Science). Joined AIST in 2008. Researcher at the Ionizing Radiation Section, Quantum Radiation Division, National Metrology Institute of Japan, AIST. Engages in research for the dose standard of soft X-ray and mammography X-ray. In this paper, was mainly in charge of the R&D and calibration service for the overall mammography dose standard, international key comparison, and drafting of the paper.

Tadahiro KUROSAWA

Completed the course at the Department of Quantum Science and Energy Engineering, Graduate School of Engineering, Tohoku University in 2000. Doctor (Engineering). Joined the Electrotechnical Laboratory, Agency of Industrial Science and Technology (currently AIST) in 2000. Worked on the β-ray standard as a visiting researcher at the Physikalisch-Technische Bundesanstalt (PTB), Germany for three months in 2003. Senior researcher at the Ionizing Radiation Section, Quantum Radiation Division, National Metrology Institute of Japan, AIST. Engages in the development of γ-ray and X-ray standards. In this paper, was in charge of the Monte Carlo calculation and the international comparison of the mammography dose standard.

Norio SAITO

Completed the course in Electric Engineering at the Graduate School of Science and Engineering, Waseda University in 1984. Joined the Electrotechnical Laboratory, Agency of Industrial Science and Technology (currently AIST) in 1984. Doctor (Science). Senior researcher in 1991; senior research at the Ionizing Radiation Section, Quantum Radiation Division, National Metrology Institute of Japan, AIST in 2001; section chief in 2005; and division head in 2011. Researcher at the Fritz-Haber-Institut, Germany in 1993~1994. Engages in research of dosimetry standards and radiometry. In this paper, was in charge of planning and organizing the overall concept of mammography dose standard.

Discussions with Reviewers

1 Overall evaluation

Comment (Naoto Kobayashi, Center for Research Strategy, Waseda University)

I think this paper is highly significant from the perspective of "establishing the dose standard and traceability for mammography X-rays." Particularly, the major result is that you have achieved this in a short time of about one and half years, from the start of development to the start of dissemination.

Comment (Akira Ono, AIST)

This paper describes an excellent research result where you set up a solid scenario covering the whole from the establishment of the primary standard for X-ray dose to the development of the standard dissemination system. You realized both the reliability and safety of mammography, and achieved it in a short time. I think there are many points that will be useful to the readers. Also, the firm frame and development of logic as seen in the individual chapters enhance the reliability of the contents and allow easy understanding by the readers.

2 Utilization of existing resources

Comment (Akira Ono)

In Chapter 1 Introduction you state that the development and dissemination of standards were achieved in a short period of about one and half years "by fully utilizing the existing research facilities and technologies." Also you state that you worked "to construct quick and wide dissemination by incorporating the standards into the current mammography quality control system that existed in private sectors." I think your efforts in utilizing the existing resources and current systems were the keys in conducting the R&D at a faster pace than usual.

If there are any points that the authors paid attention in utilizing the existing resources and incorporating the standards into current quality control system, please mention them, as they will be useful to other researchers. They may be lessons learned by the authors from this experience.

Answer (Takahiro Tanaka)

The points to keep in mind when utilizing the existing resources were to note their potential as well as their limitations. For example, the ability to conclude whether the free air ionization chamber, which was the resource used in this research, was capable of sufficient performance as a national standard for mammography radiation quality or not, was required of the researchers. I think the ability to see this affects the success or failure of *Full Research*.

Additionally, when developing a standard dissemination service, I think it is important to comprehensively understand the process of dose evaluation in the industry and in the academic societies. I think that AIST, the industry, and academic societies had a strong desire to incorporate traceability, the final objective, into the current control system.

3 Technological issues that were overcome

Question (Naoto Kobayashi)

I ask about the technological issues in achieving the objective of this research. The mammography X-rays are characterized by the low energy of about 30 keV. I think the technical point is to use the method of determining the correction factors for the current free air ionization chamber to establish the dose standard. What were the difficult issues that you had to overcome?

Also, there are large differences in the calibration coefficients of the ionization chambers A, B, and C (see Fig. 3). What are the reasons for these differences?

Answer (Takahiro Tanaka)

Although there were several technological issues in the development of this standard, there were no major problems. We determined that the issues could be solved by applying the dosimetry technology for low-energy X-rays that had been previously developed at AIST. Specifically, for the primary standard, the dosimetry technology for existing soft X-rays (W/Al radiation quality) was used, and correction factors for the primary standard were newly evaluated using the radiation quality of mammography X-rays. Using the Monte Carlo calculation, we confirmed that there would be no major negative effects on the measurement results or uncertainties in the early stages of development. Therefore, we employed this method for standard development.

Other than the above method, there are other ways of developing a new primary standard specifically for mammography X-rays. For example, a free air ionization chamber that is optimized (with small corrections) for mammography radiation quality can be developed. This is a method wherein the correction factors are calculated using the Monte Carlo method (or other methods) and are fed back to the design of the free air ionization chamber for optimal results. BIPM developed the dose standard for mammography using this method. Of course, the uncertainty will be smaller if an optimized primary instrument is developed (at the 95 % confidence level, the uncertainty is 0.6 % for AIST and 0.4 % for BIPM). However, the development period will be longer. While this is an extreme case, BIPM started development in 2001 and embarked on an international key comparison in 2009. In cases where it is necessary to quickly meet the social demand, as in our case, the greatest merit is the shortest possible development period.

Another technological issue was the improvement in the reliability of mammography machine dose evaluation in medical practice. Because the irradiation geometries are different between the reference field of AIST, overseas metrology institutes, and the actual mammography machine, the uncertainty of dose evaluation in medical practice becomes higher. Because mammography X-rays are of low energy, differences in irradiation geometries (e.g., the irradiation distance and presence of compression plates) greatly affect the uncertainty of dose evaluation in addition to the difference in radiation quality. Therefore, we developed a dose standard in which the irradiation geometry was similar to that of a mammography machine, and we tried to reduce the uncertainty in dose evaluation in medical practice. The irradiation distance and compression plate are taken into account by AIST, although they are not considered in overseas standards. However, we were careful to maintain the international compatibility of the standard, and at the same time, we ensured that the radiation quality complied with the IEC standard.

The differences between the calibration coefficients of dosimeters A, B, and C (Fig. 3) may be mainly attributable to differences in the X-ray entrance window material in the ionization chambers as well as the internal structures of the chambers. With low-energy X-rays, a large difference is noted in the energy dependency of the calibration coefficient—even in the ionization chamber dosimeter, which is known to be highly precise. I have added an explanation in the paper.

4 New efforts to establish a standard dissemination system

Question (Naoto Kobayashi)

On the calibration service system, you write that the standard was disseminated smoothly by having the calibration laboratories bring the client's dosimeter to AIST to do the calibration (subcontracted irradiation test), without fabricating a new calibration facility. You give the example of the glass dosimeter. Were there any new efforts and attempts unseen before connected to this? It seems that it was routine and there was hardly any problem, but how was it actually?

Answer (Takahiro Tanaka)

The most notable feature of this study was that reliability improvement was performed via evaluation of the glass dosimeter, which is conventionally used in medical practice, in addition to the conventional calibration service system through the calibration of dosimeters.

In the initial plan for standard development, we were thinking about the conventional traceability mediated by dosimeter calibration. I was thinking of the following flow: 1) the dosimeter owned by the calibration laboratory is calibrated at AIST and 2) the calibrated dosimeter is used as a secondary standard to calibrate the user's dosimeter at the X-ray reference field of the calibration laboratory. However, because the radiation quality of mammography X-rays is different from that of the X-rays used in calibration, step 1 with an X-ray field of mammography radiation quality is insufficient, and an X-ray field of mammography radiation quality is needed for step 2. However, even if there are demands for the standard, the calibration laboratories were of the opinion that the facility investment required to introduce an X-ray irradiation machine would be too expensive. Therefore, we devised a way to disseminate the standard smoothly by having the calibration laboratories use the irradiation facility at AIST.

Although it is estimated that there are approximately 1000 mammography dosimeters distributed throughout Japan, there are only a few calibration laboratories, and I thought that further planning would be needed for widespread standard dissemination. Therefore, in the development phase of this standard, we began looking at the mammography glass dosimeter that was being widely used for dose evaluation in medical practice. By evaluating glass dosimeters according to AIST's dose standard, the reliability of the dose evaluation for many mammography machines will improve. However, there is one problem with evaluating glass dosimeters using this standard: a special reader is needed to read the accumulated dose information from the glass dosimeters. Thus, the dose cannot be determined immediately upon irradiation. Because the irradiation of glass dosimeters at the reference field of AIST and the reading and analysis of the irradiation data were separated, time was required to overcome issues such as the evaluation of uncertainty. Our mammography glass dosimeter is a unique Japanese dosimeter, and I think it has excellent potential.

5 A comparison of situations in other countries

Comment (Naoto Kobayashi)

In this international key comparison, good results have been obtained as shown in Fig. 9. AIST was the first to participate and obtained good results which show that the international equivalency of the national standard was verified, and this is extremely significant. I think the high quality of AIST will become clearer if you discuss the situation of other countries that participated in the comparison (such as the type and performance of the detectors).

Answer (Takahiro Tanaka)

In this international key comparison, the transfer ionization chamber was employed by all institutes including AIST. AIST was original in its choice of the transfer standard. Institutes other than AIST selected only 1 transfer standard with a flat energy characteristic in the mammography X-ray energy range. AIST selected 3 types of transfer ionization chambers with different energy dependences to conduct a thorough comparison. As a result, sufficient compatibility was obtained with the BIPM values for all 3 dosimeters.

6 Outcome of this research

Question (Naoto Kobayashi)

I will ask about the outcome of this research. Now that the standard for low-energy X-ray dose has been newly established and is being disseminated, what practical outcome do you expect? For example, do you expect that the increased reliability of mammography will make more people go to cancer screening? If that will not happen, what other efforts are needed for the further diffusion of mammography in society?

Answer (Takahiro Tanaka)

The reliability of mammography dose evaluation has increased owing to the development of this standard. The manufacturers of mammography machines are making efforts to develop machines with lower dosages and higher quality images. While this standard may not contribute to the improvement of image quality, I think it will contribute to a lower dose, because a dose standard is essential for quantitative dose evaluation.

We have received several offers for joint research from the industry, universities, and academic societies, and we are currently working to increase the precision of mammography dose evaluation. In the future, I hope we can help to reduce the mammography dose using data obtained from joint research projects.

7 Research goals

Comment (Naoto Kobayashi)

Initially, the diagram for the scenario in Fig. 4 showed only the establishment of the standard for general X-ray dosimetry and precision improvement. I don't think it shows the scenario for the establishment and distribution of the mammography X-ray dose evaluation method that you described in this paper.

I think there are the following characteristics in the mammography X-ray dose evaluation. Please add how they were positioned in the scenario, and present the diagram of the scenario for achieving your goal.

(1) The existing soft X-ray standard (W/Al radiation quality) was used as the national standard, and the correction factors of the national standard were newly evaluated for the mammography X-ray radiation quality.

(2) Although there is no technological novelty in (1), it was preliminarily confirmed using the Monte Carlo calculation that there would be no fatal effect on the measurement results and uncertainty.

(3) Rather than developing a primary standard optimized for mammography radiation quality and aiming at high precision, importance was placed on the speed of standard establishment using the existing standard, even if precision was somewhat sacrificed. (This is an extremely important R&D strategy.)

(4) The objective was set as the improvement of the reliability of the dose evaluation of mammography machines in medical practice. Therefore, development effort was made to create a dose standard with irradiation geometry close to the mammography machine, aiming for the reduction of the uncertainty of dose evaluation in medical practice.

(5) Moreover, in standard dissemination, focus was placed on the glass dosimeter used in medical practice. Attempt was made to improve the reliability of dose evaluation of mammography machines by evaluating the glass dosimeters using AIST's dose standard.

Answer (Takahiro Tanaka)

I revised the scenario diagram as you have indicated to clarify the characteristics of this research. Additionally, I have revised the arrangement of the chapters following chapter 4 to match the scenario diagram.

8 Technological characteristics of the standard in this research

Question (Naoto Kobayashi)

I ask the following questions for confirmation. Are the following reasons valid in terms of the difference from the conventional X-ray dose standard?

(1) It is necessary to use low energy of about 30 keV instead of 80 keV to reduce the effect of radiation to the human body. Also, since the absorption per unit length (stopping power) of the X-rays within that energy range is greater than that of the medium energy X-rays, sufficient contrast can be obtained between the mammary tissues and the lesions. On the other hand, special measures must be taken because the precision of X-ray dose evaluation decreases for low energy X-rays.

(2) Since an X-ray tube with a molybdenum target anode and a molybdenum filter are used for the mammography X-ray beam at around 30 keV, the energy spectrum approaches monochromatic, and the energy spectrum after absorption by substances is greatly different from the X-rays that use W/Al at around 80 keV.

Answer (Takahiro Tanaka)

I think your understanding is correct. To obtain sufficient contrast between the mammary tissues and lesions, an energy lower than that used in general radiography is needed for mammography. In the dosimetry of low-energy X-rays where the sensitivity of the dosimeter changes with the X-ray energy, the difference between the radiation qualities of general radiography X-rays and mammography X-rays affects the precision of the dose evaluation. The paper was revised to address the radiation quality of mammography X-rays.

Reconstruction of the 869 Jogan tsunami and lessons from the 2011 Tohoku earthquake

— Significance of ancient earthquake studies and problems in announcing study results to society —

Yukinobu Okamura

[Translation from *Synthesiology*, Vol.5, No.4, p.234-242 (2012)]

To estimate the magnitude of the 869 Jogan tsunami (described in the historical record), we surveyed tsunami deposits and constructed a source-fault model by combining geological data with geophysical simulation. Although the 2011 Tohoku earthquake was larger than the earthquake estimated by our Jogan model, the 2011 earthquake proved that tsunami deposits are evidence of past giant tsunamis, and reliable warnings of future giant tsunamis. Our study results on the Jogan tsunami were submitted to the Headquarters of Earthquake Research Promotion, and in March 2011, the evaluation was near completion. However, the earthquake occurred just before issuing a warning against a giant tsunami. We need to announce our study of ancient earthquakes and tsunamis to society as quickly as we can so as not to repeat such a tragedy. Moreover, we have to concurrently carry out reliable studies based on rigorous surveys.

Keywords : Jogan earthquake, Tohoku-oki earthquake, tsunami deposits, announcement, disaster mitigation

1 Introduction

The ultimate goal of earthquake research is to mitigate the disastrous effects of earthquakes. Since the 1995 Kobe Earthquake (in the news media, Great Hanshin-Awaji Earthquake or Great Hanshin Earthquake), the emphasis of the earthquake research was placed on disaster prevention and mitigation. However, several earthquakes occurred in places where active faults were not recognized after the 1995 earthquake. In adition, effective warnings could not be issued in the 2011 Tohoku-oki Earthquake (in the media, Great East Japan Earthquake). But, our research group has been studying the tsunami generated by the Jogan Earthquake that devastated the Sendai Plain in AD 869. We are regretful that the Tohoku-oki Earthquake occurred before our study results could be reflected in the disaster prevention measures in the region. The difficulty of predicting the natural phenomenon has become very apparent. It is also true that this earthquake illuminated the weaknesses of earthquake research based on geophysics, and instead, shifted the focus to paleoseismology or the study of past earthquakes based on geology as conducted at AIST.

In this paper, we describe AIST’s research method of reconstructing the Jogan Earthquake and tsunami that occurred in AD 869 by integrating the studies of history, geology, and geophysics. Also, we present the importance and issues of research for estimating the scale of a tsunami from the tsunami deposits that became clear in the 2011 Tohoku-oki Earthquake, and discuss the problems in announcing the results to society and contributing in disaster mitigation. How the demand and request from society toward earthquake research changed before and after the earthquake is reviewed, and how AIST should respond to the social demands will be considered.

2 Earthquake evaluation method

Since the 1995 Kobe Earthquake, the Headquarters for Earthquake Research Promotion (hereinafter, will be called Earthquake Headquarters) was established in the Agency of Science and Technology (currently Ministry of Education, Science, Sports, Culture, Science and Technology; MEXT). Under its leadership, earthquake research shifted its direction from scientific research to research that contributes to earthquake disaster prevention. One of the most important projects of the Earthquake Headquarters is the “Long-term Evaluation of Earthquakes.”[1]

Based on the assumption that great earthquakes occur repeatedly in approximately the same place at the same scale, the earthquake that might occur in the future was predicted based on the information of the location, scale, and age of the past earthquakes. In this case, the reliability of the earthquake evaluation increased in accordance to the level of reliability of the information on past earthquakes.

The most accurate record of earthquakes is the record detected by the seismometer, but such information is available only for about a hundred years (Fig. 1). The older

---

Active Fault and Earthquake Research Center, AIST 1-1-1 Higashi, Tsukuba 305-8567, Japan E-mail: okamura-y@aist.go.jp

Original manuscript received March 1, 2012, Revisions received June 4, 2012, Accepted June 8, 2012

records exist as written historical records. The oldest historical record of an earthquake is the description of the earthquake that occurred in AD 599.[2] However, the records from the distant past are sparse and the information volume is low, and in many cases, the information is insufficient to estimate the magnitude of past earthquakes. The historical earthquake records with sufficiently high quality and volume are those during the Edo Period (AD 1603~1868) or later. The greatest advantage of historical records is that the date of occurrence and the place affected by the earthquake damage can be known fairly accurately, and it has been used widely as past earthquake records. The geological records such as tsunami deposits and active faults offer information about earthquakes before historical records, and the crustal movements and tsunamis caused by earthquakes are left in the topographies and geological strata. The records of the giant earthquakes and tsunamis left in nature include some errors in terms of date, but the greatest advantage is that they offer information on past earthquakes and tsunamis for the period of several thousand years.

In general, inland earthquakes occur by slip of active faults and the recurrence intervals of the slip events are long, such as thousand years or more. Although the latest slip events may be known from historical records, many events remain unrecorded in history, and thus we must rely on the slip records left in nature. On the other hand, subduction zone earthquakes often have occurrence intervals of decades to two hundred years, and therefore, information of multiple occurrences and scales can be obtained from the historical records.[3] For Tokai and Nankai Earthquakes, nine occurrences have been recorded in history since over a thousand years ago.[2] For the Japan Trench, many earthquake have been recorded during the Edo Period and later, and their magnitudes were 7 to 8. The subduction zone earthquakes have been evaluated based on such historical records.[4]

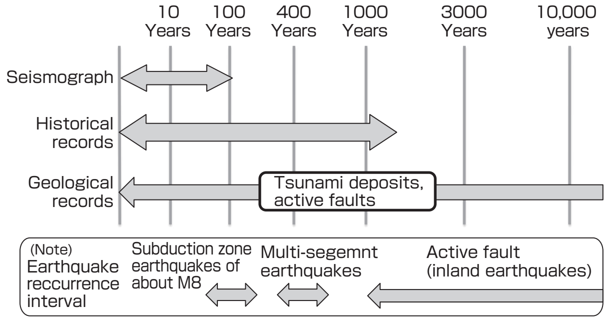


Fig. 1 Periods during which the information about past earthquakes exists and the intervals of earthquake occurrences

Only the geological record can solidly cover the period that is longer than the intervals of giant earthquake occurrences. Note: Earthquake recurrence intervals show the approximate interval of occurrence of the different types of earthquakes, and do not show the age of occurrence of the earthquake.

The evidences for giant tsunamis unrecorded in history were found in the Pacific coastal area of east Hokkaido. The tsunami deposits were distributed wider and further inland than the inundation zone of the tsunami known in history, in the Pacific coastal area of Tokachi, Kushiro, and Nemuro regions.[5][6] In these areas, earthquakes of around magnitude 8, such as the Tokachi-oki Earthquake and Nemuro-oki Earthquake, have occurred at intervals of several decades to hundred years, but it was inferred that giant tsunamis were probably caused by multi-segment earthquakes in which multiple earthquakes occur simultaneously.[7]-[9] The last multi-segment earthquake is estimated to have occurred in the 17th century, but there is no historical record in Hokkaido because the region has a short historical record. Through the survey and analysis of the tsunami deposits, the earthquake that caused the giant tsunami was estimated to have a magnitude of about 8.5 and a recurrence interval of about 500 years. In these studies, it was shown that the scale of the past giant earthquakes and tsunamis could be reconstructed from the geological data, and that much larger earthquakes and tsunamis may occur even in areas where the subduction zone earthquakes of about magnitude 8 occur repeatedly. This hypothesis was proven correct in the 2004 Indian Ocean Earthquake.

3 Limit of the conventional earthquake scenario for the Tohoku region

The subduction zone earthquakes that occurred in the Pacific coast of the Tohoku region were evaluated and predicted based mainly on the historical records during the Edo Period and later. Except for the Sanriku offshore area, these earthquakes had the scale of magnitude 7~8, and no earthquake of magnitude 9 had been recorded. In the Sanriku coastal area, the 1611 Keicho Sanriku Tsunami, the 1986 Meiji Sanriku Tsunami, and the 1933 Showa Sanriku Tsunami were known as destructive tsunamis. People's awareness for tsunamis was high in this region and some measures were taken accordingly. In contrast, the awareness against a giant tsunami in the coastal area of the Sendai Plain and further south was extremely insufficient, although it was known that the coastal area of Sendai Plain was damaged severely in the 1611 Keicho Sanriku Tsunami,[10] and there was a historical record of a giant tsunami in AD 869.[11] The latter one was known as the Jogan Earthquake. The *Nihon Sandai Jitsuroku* that was written at the court of Kyoto during the Heian Period (AD 794~1185) describes the fact that there was a great earthquake in Mutsu-no-Kuni (current Tohoku region). The ground shakes were so severe that people could not remain standing, many buildings collapsed, and the tsunami flooded vast inland areas. It is believed that this is a description of the disaster which occurred in Tagajo area which was the capital of Mutsu-no-Kuni at that time, however, the scale of the tsunami and the distribution of damage remained unclear.

4 Reconstruction of the Jogan Tsunami

The research to reconstruct the 869 Jogan earthquake and tsunami (hereinafter, Jogan tsunami) involves the survey of tsunami deposits in the field, analysis of the geological samples, and construction of the tsunami source model. The greatest characteristic of our paleo-tsunami research is to combine geological survey of tsunami deposits and the geophysical method of tsunami simulation.[12] (Fig. 2)

The distribution of tsunami deposit was revealed by detailed field survey. Because whether the tsunami deposit is preserved well or not depends on various natural conditions and the human activities, it is important to conduct coring as much as possible at the site (Fig. 3). The distribution area of tsunami deposits can be determined accurately by accumulating the data from many places. Also, since there may be several tsunami deposits of different ages with similar appearances, it is important to correlate each of the tsunami deposits by a detailed and careful survey. At the same time, surveys in a wide region as much as possible are necessary to increase the reliability of the tsunami source model.

Yoshida [11] reviewed the description of the Jogan earthquake and tsunami in the historical record and pointed out the risk of a giant tsunami around Sendai. The tsunami deposits formed by the Jogan tsunami were reported in the Sendai Plain after 1990.[13][14] Using these survey results as reference, the survey area was widened from Ishinomaki to the northern part of Fukushima Prefecture to clarify the distribution of tsunami deposits, and the position of the coastline at the time was reconstructed (Fig. 4).

In Ishinomaki, the deposits from the Jogan tsunami were

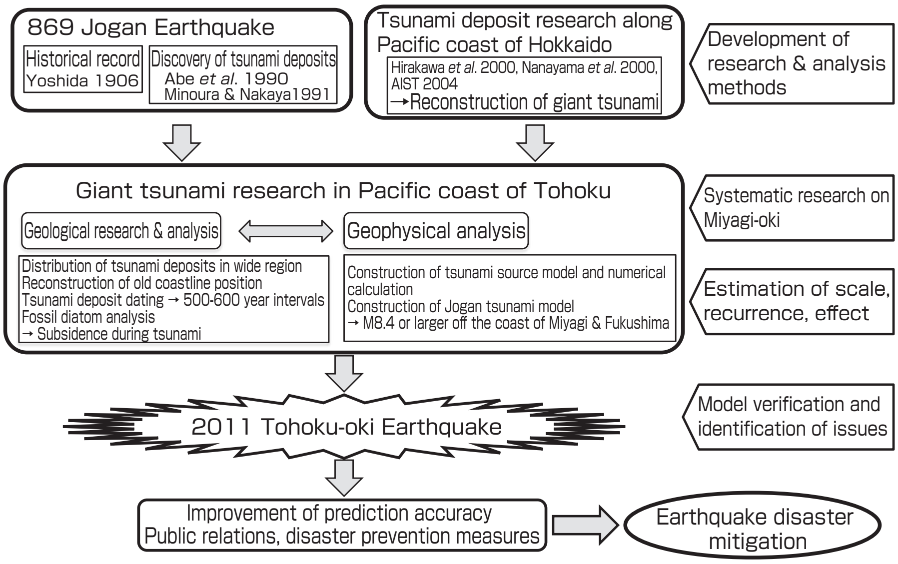


Fig. 2 Progress of research on past giant earthquakes

Fig. 3 Tsunami deposit research in Sendai Plain
The underground strata are collected using the geoslicer in the rice field after harvest.

found 5 km inland from the current coastline.[15] At least two layers of tsunami deposits below and above the 869 tsunami deposits were confirmed. The Ishinomaki Plain expanded gradually over the past several thousand years, and the coastline was about 1.5 km inland from the current coastline during the Jogan earthquake.

In the Sendai Plain, the tsunami deposits were distributed 4 km or more inland from the current coastline and the coastline during the Jogan earthquake was located about 1~1.5 km inland. It was estimated that there were three or more inundations before the Jogan tsunami, and at least one after the Jogan tsunami.[16]

The date of tsunami occurrence and the crustal movement due to an earthquake can be estimated by analyzing the deposits obtained in the fieldwork. To estimate the date, fragments of fossil plants were removed from the peat layers just above and below the tsunami deposit, and radioactive carbon ^{14}C was measured in the fragments. In this dating method, large errors may occur depending on the measured samples, thus it is important to choose an appropriate material without contamination of younger and older materials. Based on the carbon dating, we inferred that the tsunami deposits were formed at intervals of approximately 500 years. By analyzing the fossil diatoms in the peat, we presumed that subsidence occurred during the Jogan and the precedent tsunamis in northern Fukushima.

The epicenter and the magnitude of the earthquake that caused the tsunami that inundated the deposit distribution zone were estimated by numerical simulation. Since it was difficult to determine the position of the source region only from the distribution zone of tsunami deposits, different types and scales of earthquakes were assumed based on the earthquakes that occurred in the past along the Japan Trench(Fig. 5), and then the inundation zones were calculated, and compared with the distribution zone of tsunami deposits

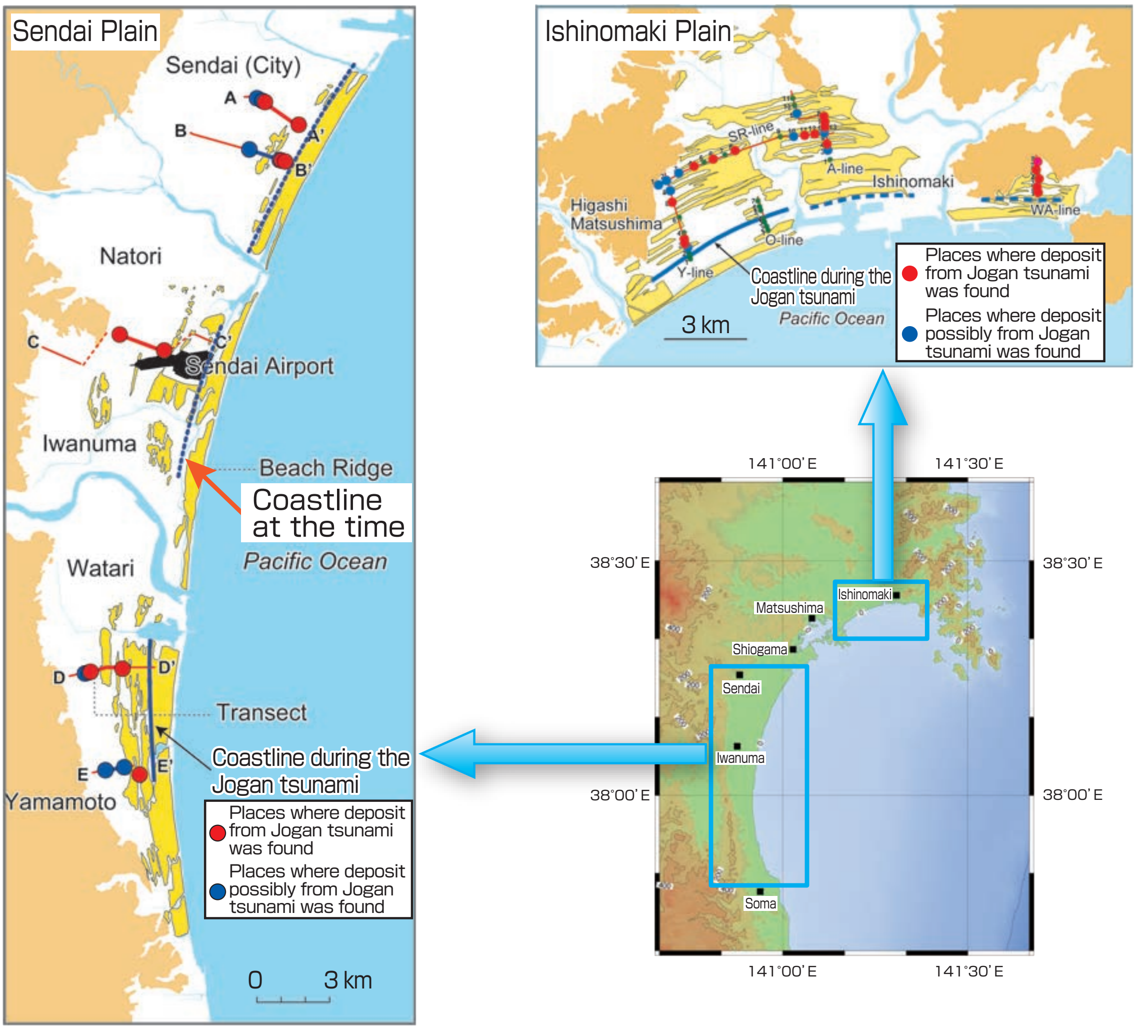


Fig. 4 Distribution area of Jogan tsunami deposits in the Ishinomaki and Sendai Plains and the coastline at the time[12]

Detailed researches of the deposits were conducted along several survey lines to clarify the distribution area. At the same time, the position of coastline during the earthquake was confirmed.

(Fig. 6). As a result, we presumed that a tsunami inundates all the way to the distribution zone of the tsunami deposits by an earthquake of magnitude 8.4 caused by a 7 m slip (fault displacement) of an area with length of 200 km and width of 100 km along the plate boundary at a depth of 15-46 km off the Miyagi to Fukushima Prefectures.[17][18] However, this earthquake source fault model did not consider the possibility that the tsunami inundation zone was wider than the distribution zone of tsunami deposits. Also since the northern and southern limits of the inundation zone were unclear, there was a possibility that the scale of the earthquake might be greater[12] (Fig. 7).

5 Jogan Earthquake model evaluated by the actual earthquake

One of the major reasons that the earthquake prediction research does not advance is because actual experiments cannot be conducted. The currently used science and technology were built upon repeated experiments, and there must have been numerous failures. On the other hand, the scale of a natural phenomenon is incomparably large. While rock deformation experiments can be done in the laboratory, a natural earthquake cannot be predicted by such experimental results only. The dynamic characteristics of deep underground rock is becoming clarified by the rock deformation experiments under high temperature and pressure conditions, but there are many unknowns about the actual deep underground conditions such as the diversity of rock types and the presence of fluid. It is impossible to recreate such natural conditions perfectly in the laboratory. Therefore, seismology has been advanced by the analysis of earthquakes that actually occurred.

Even if the images of past earthquakes are recreated based on the tsunami deposits, they cannot be verified unless an earthquake actually occurs. The 2011 Tohoku-oki Earthquake was the first earthquake and giant tsunami that occurred in the area where the past earthquakes have been estimated by researches using the tsunami deposits, and it has provided an opportunity to examine the reliability of our paleoseismological research.

The Jogan Earthquake model estimated to be of magnitude 8.4 or greater was smaller than the magnitude of the 2011 Tohoku-oki Earthquake. However, in the Sendai Plain, there was no major difference between the inundation areas of tsunamis by the 869 and 2011 earthquakes [19] (Fig. 8). According to the study of tsunami deposits formed by the 2011 earthquake, it was shown that the tsunami (seawater) reached about 1~2 km inland further than the area where tsunami deposit (sand layer) was formed.[19] This finding is extremely important for the estimation of the magnitude of the tsunami from the distribution of tsunami deposits. It is necessary to reevaluate the magnitude of the Jogan tsunami taking this difference into account. It is expected that the

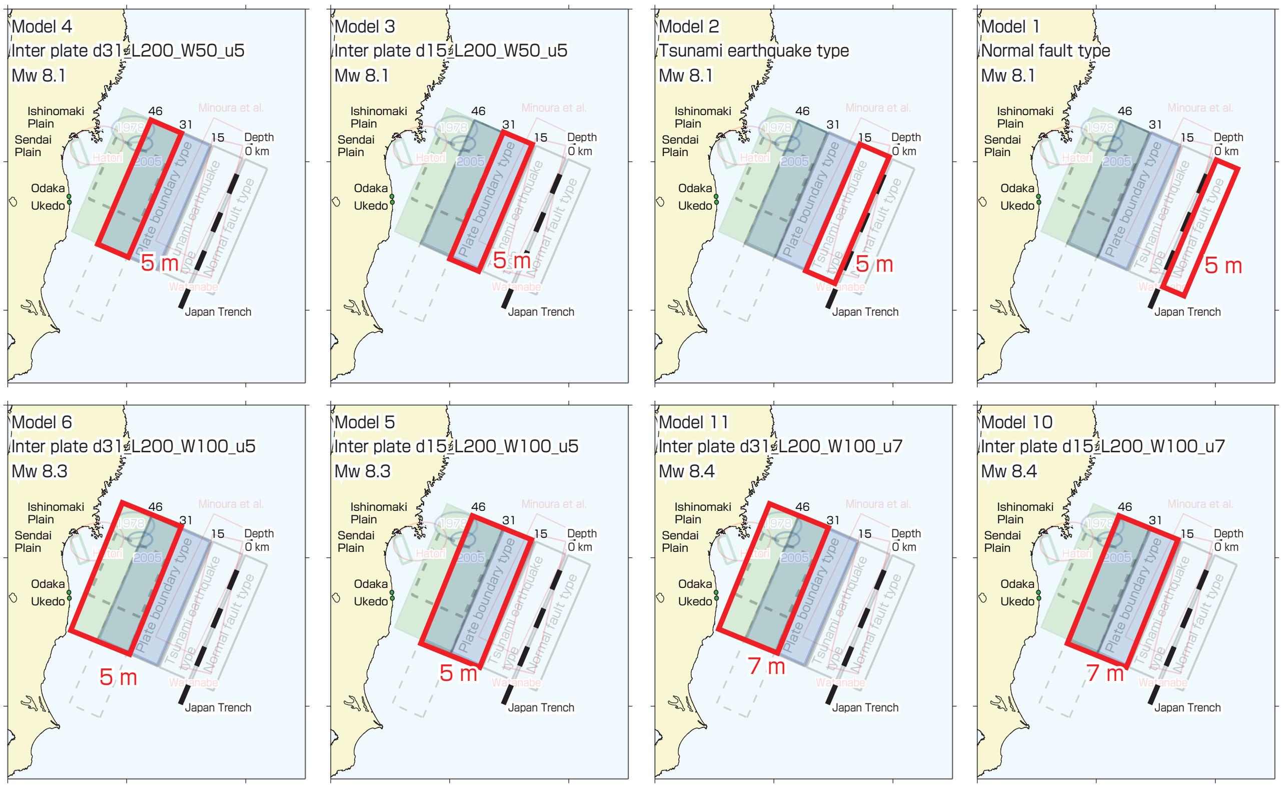


Fig. 5 Example of calculation of the Jogan tsunami source model (edited from References [17] and [18])
The tsunami was calculated by assuming the fault planes with different scale on the subducting Pacific Plate offshore of Tohoku.

accuracy of tsunami magnitude prediction can be improved by applying this result of tsunami deposit research in other ocean areas.

The Tohoku-oki Earthquake proved that the tsunami deposits were highly reliable evidences of the past giant tsunamis, and these deposits must be taken as important warnings from nature. On the other hand, there were some problems for estimation of tsunami magnitude.

6 Announcing the earthquake study to society

There was a common preconception that earthquakes would not strike the Kansai district before the 1995 Kobe Earthquake, but active fault researchers clarified that Mt. Rokko had been uplifting due to fault activity and that there was a possibility of a major earthquake in Kobe. The knowledge of such researchers were not utilized in the regional disaster prevention. To utilize the research results of earthquake research in the earthquake disaster prevention in society, it was determined that the government must evaluate the research results objectively and then provide this information to society as reliable crucial information important for disaster prevention. The Earthquake Headquarters was established to achieve this mission (Fig. 9).

After the 1995 Kobe Earthquake, the danger of active faults became widely known, the research to clarify the activity history was conducted, and the active fault evaluation was published by the Earthquake Headquarters. The subduction zone earthquakes were evaluated based mainly on historical records. Through such evaluation and publication of the dangers of earthquake by the Earthquake Headquarters, the local governments and society became aware of the danger and had to take action for disaster mitigation.

The research results of the Jogan Earthquake discussed earlier were submitted by AIST to the Earthquake Headquarters in the spring of 2010, and the headquarters conducted evaluations for about one year, for earthquakes along the entire Japan Trench. If the Tohoku-oki Earthquake did not occur, the evaluation of the Jogan Earthquake would have been announced in April 2011. Since it would take some time to prepare for the disaster prevention measures, it is unknown how it could have helped the disaster mitigation. At least it would have been an opportunity for many people to know the possibility that a giant tsunami might strike the Ishinomaki, Sendai, and the Fukushima coasts.

We are regrettable that the research results were not announced from the Earthquake Headquarters before the earthquake, and we are still thinking that the information might have mitigated the damage to some degree. At the same time, we had been trying to inform others of our research

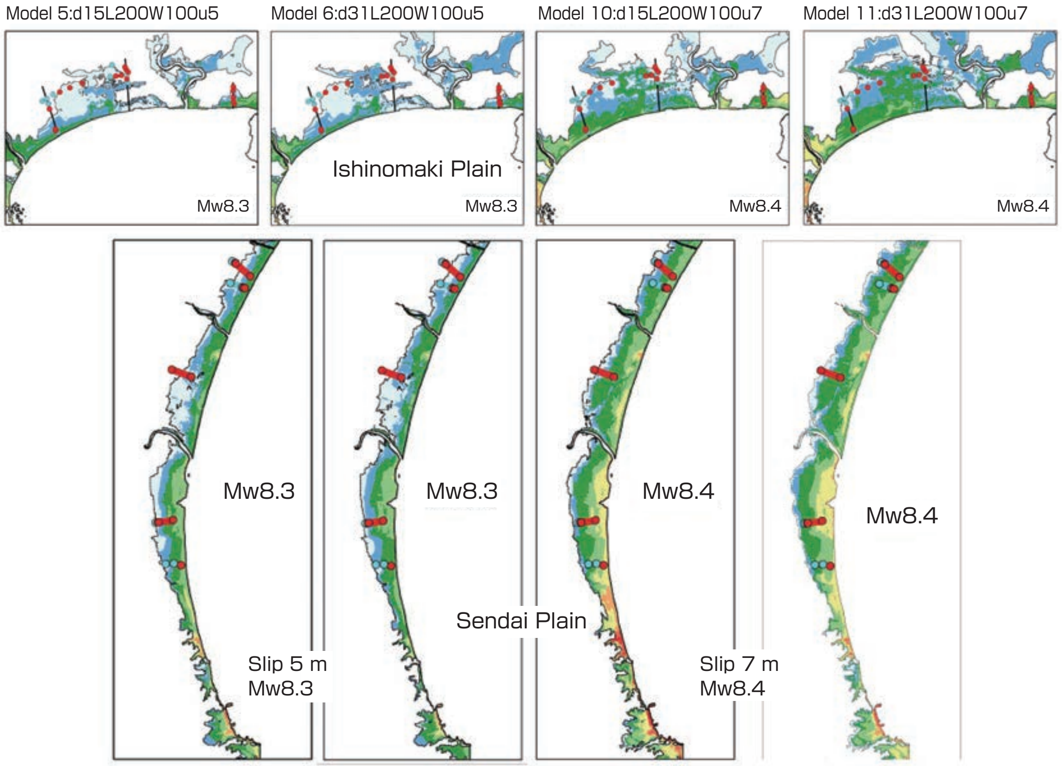


Fig. 6 Example of calculation of the inundation area based on the Jogan tsunami source model (edited from References [17] and [18])

The inundation zones of Ishinomaki Plain (top) and Sendai Plain (bottom) based on models 5, 6, 10, and 11 of Fig. 5. Ultimately model 10 (second from right) was selected as the Jogan model.

before the earthquake. We presented our study at academic meetings, and the contents drew media attention and were covered by the newspaper and TVs. However, it did not lead to consciousness raising or disaster prevention measures of the region. In addition, we conducted lectures to the public in Miyagi Prefecture a few times. Although the number of audiences was small, we might have been able to change the awareness for earthquakes if we continued the lectures. However, warning to society about the risk of a giant tsunami is difficult work beyond the ability of the researchers at AIST, and we believe that using the communication resources centered at the Earthquake Headquarters is the most effective and efficient way. Because the Earthquake Headquarters officially evaluate earthquakes, it was probably difficult for the local governments to actively promote disaster prevention measures before the final evaluation was issued from the headquarters.

The system where the Earthquake Headquarter, representing the government, informs the earthquake risk to society is very important and mandatory. Because this is the official information, it takes time to complete reliable evaluations based on careful examination. If some research results showed the possibility of serious damage by an unknown earthquake or tsunami, we believe that we need to inform the risk to the public through some brief objective evaluation.

After the earthquake, since the concern and interest of society for earthquakes increased, the opinions of many researchers on tsunami deposit research and earthquakes were easily reported by the media before sufficient investigations were done. I think there are both advantages and disadvantages in releasing the brief research results to society. The advantage is that the information is released quickly to society. It is possible to minimize the possibility of being too late, as it was in 2011. On the other hand, it should not be forgotten that the reliability of prompt report has not been confirmed, and the mass media likes to report the information of larger tsunamis. If survey results were shown to be not true, earthquake researches will lose confidence. To avoid such confusion, we hope for the official organization for quick objective evaluation.

7 Changes in society before and after the earthquake

Since several inland earthquakes had been occurring during the several years before the 2011 Tohoku-oki Earthquake, the awareness in the Japanese society for earthquakes was high, but the awareness for tsunamis was low. We have to persuade society that there is a risk of giant tsunamis and to take action for the disaster prevention measures, therefore we need to show convincing evidences of giant tsunamis. This is why

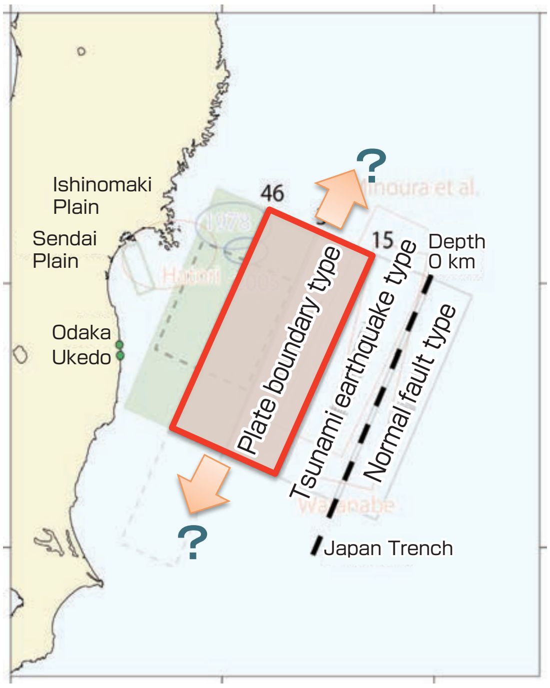


Fig. 7 Source fault model for Jogan tsunami proposed before the earthquake (model 10)[17][18]
Since this model was created based on the data from Ishinomaki Plain to northern part of Fukushima Prefecture, it could have spread further north and south.

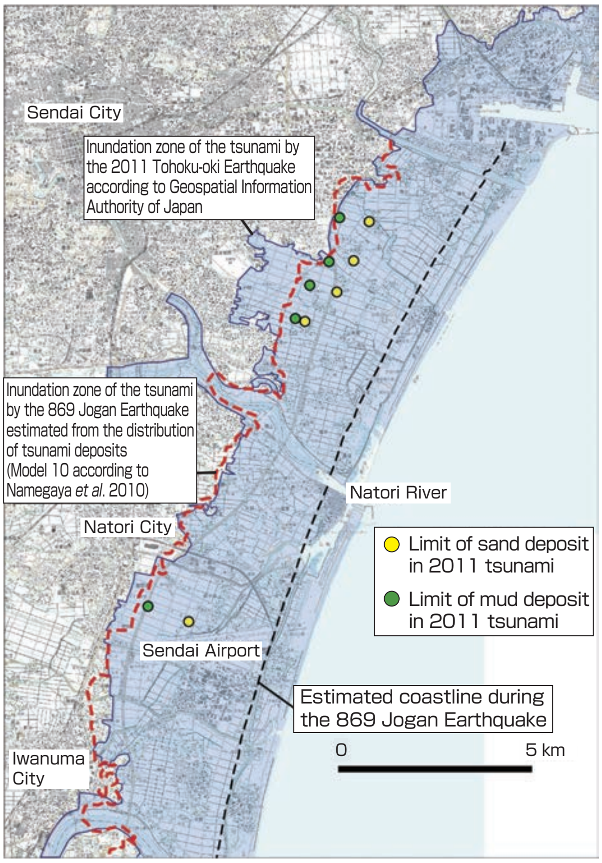


Fig. 8 Inundation zone calculated by the Jogan tsunami model and the inundation zone of the 2011 Tohoku-oki Earthquake[19]
The tsunami inundation zone based on the distribution of the Jogan tsunami deposits and the inundation zone of 2011 match approximately.

we took considerable time in conducting tsunami deposit research carefully. We estimated the minimum magnitude of the tsunami by the Jogan earthquake based on the detailed tsunami deposit research. Our study will lose reliability if we estimated too large an earthquake and tsunami without convincing evidences. After the 2011 earthquake, there was a period where we wondered whether this policy was correct. However, if we had announced a large tsunami prediction without presenting clear evidence to society before the earthquake, we think that our model would have been neglected. We believe our research policy was not wrong.

The concern for earthquakes immediately rose after the tsunami devastated the coastal area of Tohoku on March 11, 2011. While the government and the local governments used to be reluctant to assume large earthquakes without sufficient evidence before the 2011 earthquake, they changed the policy to assume the worst possible earthquake and tsunami.[20] Under this policy, assumption of the worst possible earthquake and tsunami that may happen have been adopted, rather than an earthquake which had been confirmed in the past. The earthquake researches are demanded to determine the magnitude of the largest earthquake. It is not too much to say that the demand for earthquake research changed around 180 degrees. Unfortunately, current earth science cannot determine the largest earthquake reasonably. As a result, there are possibilities that unnecessarily large earthquakes and tsunamis may be assumed. The research to determine the appropriate maximum earthquakes is necessary.

8 Future issues

The Japanese society will be unable to recover from the shock of Tohoku-oki Earthquake for a while. Whatever size of earthquake and tsunami will be assumed in the future, we will not be freed from the fear of earthquakes and tsunamis. The disaster prevention measures to mitigate the damages from earthquakes and tsunamis must be steadily conducted to decrease the fear, but it is not easy to determine the appropriate measures against the large tsunamis. The sense of crisis over natural disaster must be sustained even after the disaster prevention measures are taken. Considering the role of the geology fields at AIST (Geological Survey of Japan), the most important missions are to conduct careful research of the past earthquakes, to clarify what earthquake occurred in which area, and to continue providing this information to society. In addition, it is necessary to show what is known and unknown about ancient earthquakes based on the current level of natural sciences. It is then necessary to consider how the measures should be taken as a society as a whole.

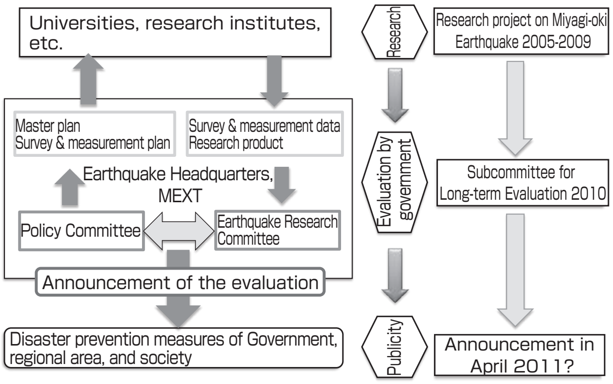


Fig. 9 Role of the Earthquake Headquarters
The Earthquake Headquarters or the Headquarters for Earthquake Research Promotion, MEXT, gathers information from the survey and research institutes for earthquakes, reevaluates the information, and announces the scale and probability of the earthquakes that may occur in the future.

For the research results of AIST to be utilized widely in society, I mentioned that we need a system in which the results are reevaluated and announced by the Earthquake Headquarters as an official organization. However, this alone does not ensure sufficient dissemination of information to the regional communities, and the process usually takes time. It is considered that AIST must directly provide detailed information to the local governments and communities about the information on which the evaluation of the Earthquake Headquarters is based and what are the issues, and at the same time actively exchange information. Moreover, we may consider information provision to local governments before the announcement of the Earthquake Headquarters. To conduct such information exchange, it is necessary to establish mutual trust by holding meetings with the prefectural and other local governments regularly.

At the same time, it is necessary to design land use plans in Japan based upon an understanding of nature and the evaluation of various disasters. For better land use, comprehensive knowledge about the geological characteristics of the Japanese Archipelago needs to be provided. The Japanese have experienced various damages from natural disasters and have overcome them and built the prosperity today. For example, the technology of earthquake resistant structures of Japan is the most advanced in the world. However, it must be said that society as a whole is becoming vulnerable to natural disasters. One of the reasons may be that the people are becoming less knowledgeable about nature. By understanding the crustal movement in the Japanese Archipelago that occurred in the past tens of thousands of years based on geology, I hope people will become prepared against natural disasters. The mission of the geology field of AIST is to provide such information to society.

Acknowledgement

The research of the Jogan Earthquake was conducted through the collaboration of the following researchers: Masanori Shishikura, Yuki Sawai, and Yuichi Namegaya, researchers of the Active Fault and Earthquake Research Center, AIST; and Professor Kenji Satake, Earthquake Research Institute, The University of Tokyo. This research was made possible by the cooperation of the landowners and related organizations at the site. I am grateful to all the people who were involved.

References

[1] The Headquarters for Earthquake Research Promotion: Fundamental Earthquake Survey and Observation Plans http://www.jishin.go.jp/main/seisaku/hokoku97/s8kei.htm#1-1 (1997) (in Japanese).

[2] T. Usami: *Saishinban Nihon Higai Jishin Soran 416-2001* (Materials for Comprehensive List of Destructive Earthquakes in Japan, Latest Edition), University of Tokyo Press (2003) (in Japanese).

[3] K. Ishibashi and K. Satake: Problems on forecasting great earthquakes in the subduction zones around Japan by means of paleoseismology, *Zisin (J. Seism. Soc. Japan)*, 50, Appendix, 1 -21 (1998) (in Japanese).

[4] The Headquarters for Earthquake Research Promotion: Sanriku Oki kara Boso Oki ni kakete no jishin katsudo no choki hyoka no ichibu kaitei nitsuite (Regarding the partial revision of the long-term evaluation of earthquake activity of off-shore of Sanriku to Boso area) http://www.jishin.go.jp/main/chousa/09mar_sanriku/index.htm (2009) (in Japanese).

[5] K. Hirakawa, Y. Nakamura and T. Haraguchi: Hokkaido Tokachi engan chiiki ni okeru kyodai tsunami to sairai kankaku (Giant tsunami in the Tokachi coastal region, Hokkaido and the recurrence interval), *Chikyu Monthly Symposium*, 28, 154-161 (2000) (in Japanese).

[6] F. Nanayama, K. Satake, K. Shimokawa, K. Shigeno, R. Furukawa, I. Hirota, A. Makino, J. Nojima, S. Koitabashi and M. Ishii: Chishima Kaiko engan iki, Kiritappu Shitsugen ni oite kakunin sareta kyodai jishin tsunami ibento (Mega earthquake tsunami event observed in the Kiritappu marsh in the coastal area of Kuril Trench), *Chikyu Monthly Symposium*, 28, 139-146 (2000) (in Japanese).

[7] F. Nanayama, K. Satake, R. Furukawa, K. Shimokawa, B. F. Atwater, K. Shigeno and S. Yamaki: Unusually large earthquakes inferred from tsunami deposits along the Kuril trench, *Nature*, 424, 660-663, doi:10.1038/nature01864 (2003).

[8] K. Satake and F. Nanayama: Tsunami inundation maps for the Pacific coast of Hokkaido, Numerical Geological Map EQ-1, Geological Survey of Japan, AIST, (2004) (in Japanese).

[9] K. Satake, F. Nanayama and S. Yamaki: Fault models of unusual tsunami in the 17th century along the Kuril trench, *Earth Planets Space*, 60, 925-935 (2008).

[10] Y. Tsuji and K. Ueda: Kencho 16 nen (1611), Enpo 5 nen (1677), Horeki 12 (1763), Kansei 5 nen (1793), oyobi Ansei 3 nen (1856) no kaku Sanriku Jishin tsunami no kensho [Investigation of Sanriku Earthquake tsunami in Kencho 16 (1611), Enpo 5 (1677), Horeki 12 (1763), Kansei 5 (1793) and Ansei 3 (1856)], *Rekishi Jishin* (J. Soc. Historical Earthquake), 11, 75-106 (1995) (in Japanese).

[11] T. Yoshida: Jogan 11 nen Mutsu-fu-jo no shindo koitsu (Earthquake and flooding of Mutsu State Castle in Jogan 11), *Rekishi Chiri* (Historical Geography), 8 (12), 1033-1040 (1906) (in Japanese).

[12] M. Shishikura, Y. Sawai, Y. Namegaya and Y. Okamura: Heian no hitobito ga mita kyodai tsunami wo saigensuru – seireki 869 Jogan Tsunami (Reconstructing the giant tsunami seen by the people of Heian Period – Jogan Tsunami of AD 869), *AFERC News*, 16 (2010) (in Japanese).

[13] H. Abe, Y. Sugeno and A. Chigama: Estimation of the height of the Sanriku Jogan 11 earthquake-tsunami (A.D.869) in the Sendai plain, *Zisin (J. Seism. Soc. Japan)*, 43, 513-525 (1990) (in Japanese).

[14] K. Minoura and S. Nakaya: Traces of tsunami preserved in inter-tidal lacustrine and marsh deposits: some examples from northeast Japan, *Journal of Geology*, 99, 265-287 (1991).

[15] M. Shishikura, Y. Sawai, Y. Okamura, J. Komatsubara, T. T. Aung, T. Ishiyama, O. Fujiwara and S. Fujino: Age and distribution of tsunami deposit in the Ishinomaki Plain, Northeastern Japan, *Annual Report on Active Fault and Paleoearthquake Researches*, 7, 31-46 (2007) (in Japanese).

[16] Y. Sawai, Y. Okamura, M. Shishikura, T. Matsuura, T. T. Aung, J. Komatsubara and Y. Fujii: Historical tsunamis recorded in deposits beneath Sendai Plain - Inundation areas of the A.D. 1611 Keicho and the A.D. 869 Jogan tsunamis, *Chishitsu News*, 624, 36-41 (2006) (in Japanese).

[17] K. Satake, Y. Namegaya and S. Yamaki: Numerical simulation of the AD 869 Jogan tsunami in Ishinomaki and Sendai plains, *Annual Report on Active Fault and Paleoearthquake Researches*, 8, 71-89 (2008) (in Japanese).

[18] Y. Namegaya, K. Satake and S. Yamaki: Numerical simulation of the AD 869 Jogan tsunami in Ishinomaki and Sendai plains and Ukedo river-mouth lowland, *Annual Report on Active Fault and Paleoearthquake Researches*, 10, 1-21 (2010) (in Japanese).

[19] M. Shishikura: Tsunami taisekibutsu kara mita 869 Jogan Jishin to 2011 nen Tohoku Chiho Taiheiyo Oki Jishin nitsuite (Comparison of the 869 Jogan Earthquake and the 2011 Earthquake off the Pacific coast of Tohoku from tsunami deposits), *Seism. Soc. Japan News Letter*, 23 (3), (2011) (in Japanese).

[20] Central Disaster Management Council: Report of the Committee for Technical Investigation on Countermeasures for Earthquakes and Tsunami Based on the Lessons Learned from the “2011 Off the Pacific Coast of Tohoku Earthquake” http://www.bousai.go.jp/jishin/chubou/higashinihon/index_higashi.html (2011) (in Japanese).

Author

Yukinobu OKAMURA

Completed the master’s course at the Graduate School of Science, Nagoya University in 1980. Joined the Geological Survey of Japan, Agency of Industrial Science and Technology, Ministry of International Trade and Industry in 1980. Engaged in the marine geological surveys around Japan for about 24 years, created the marine geological maps, and studied the formation of the geologic structures. Participates in the research of tsunami deposits at the Active Fault and Earthquake Research Center, AIST from 2004. Director of AFERC since 2009.

Discussions with Reviewers

1 Overall comment 1

Comment (Shigeko Togashi, AIST)

This paper discusses the way in which science may contribute to society through the research of long-term earthquake prediction that may help disaster prevention, by thoroughly clarifying the geological evidences of tsunami deposit and then estimating the image of past earthquakes using the geophysical methods.

Specifically, 1) the paper presents a scientific methodology in which the reconstruction model of past earthquake is created by integrating the data with differing time scale such as geological record of tsunami deposit, historical record, observation record, and others, then simulating a geophysical model, and improving the prediction accuracy by verifying the model against the earthquake that actually occurred. 2) It also discusses the method for realistically contributing to disaster prevention by quickly and accurately announcing the latest research results to society, even if it is in mid-research stage, including the areas that may be still uncertain.

This paper raises important issues from the perspective of methodology for how science may contribute to society, and I think it is appropriate as a paper to be published in *Synthesiology.*

Upon review, the paper was revised to clearly state the significance of the aforementioned methodology.

2 Overall comment 2

Comment (Akira Ono, AIST)

I think the earthquake model construction method, in which the elemental research of geological survey of tsunami deposit and the geophysical method were combined to achieve the research objective of reconstructing paleo-earthquakes, is an excellent *Type 2 Basic Research*. I respect the fact that this research was perfected at a high level before the occurrence of the 2011 Tohoku-oki Earthquake.

In this research, the Jogan Earthquake was reconstructed accurately. It is regretful that the results could not be announced before the tsunami of the Tohoku-oki Earthquake. On the other hand, while it was completely coincidental that the constructed earthquake model was verified immediately by the actual phenomenon, it was greatly significant in considering the measures against future large-scale earthquakes. I think the earthquake model that was constructed will be useful in reliably predicting large-scale earthquakes and accompanying tsunamis that are expected to occur in the future in the Tokai, Tonankai, and Nankai areas.

3 Approaches in geology and geophysics

Comment (Akira Ono)

In this paper, you describe the role, mission, and position of the geology groups within AIST. Considering that *Synthesiology* is read by people of wide-ranging fields, can you expand the description to “seismology” or “earthquake studies” rather than keeping yourself within the geology of “AIST”?

Answer (Yukinobu Okamura)

The mainstream of “seismology” or “earthquake studies” is the research based on geophysics, and the research based on geology conducted at AIST is a minority. This minor research drew attention after the Tohoku-oki Earthquake. The mainstream researchers are working to figure out the reason why they were unable to issue preliminary warnings, and are discussing the direction of future research based on the lessons learned. The objective of this paper is to emphasize the importance of earthquake research based on geology and to discuss the various issues. Widening the discussion to the entire seismology will derail from the main topic, and I feel it is too much of a load for me. In the “Introduction,” I added some simple description of the difference between AIST and the mainstream earthquake researches.

4 Presentation of a flowchart of the paleo-tsunami research as a scientific methodology

Comment (Shigeko Togashi)

I think it will help our understanding if you draw a generalized flowchart of the paleo-tsunami research as a scientific methodology.

Answer (Yukinobu Okamura)

I created my version of the flowchart in Fig. 2, based on the sample.

5 Action for the “organization of a system for quick objective evaluation”

Comment (Shigeko Togashi)

What are the actions for the “organization of a system for quick objective evaluation” mentioned at the end of chapter 6?

Answer (Yukinobu Okamura)

The objective evaluation must be conducted by a national organization such as the Earthquake Research Committee, and I think it will be most efficient if the government’s evaluation process is accelerated, but it is not easy to do so. Another method is the publication as papers of the correct method for tsunami deposit research. If the researchers publish highly reliable results, I think highly reliable tsunami evaluation will spread quickly throughout society.

Evaluating uncertainty for the standardization of single cell/stack power generation performance tests for SOFC

— Standardizing test methods and ensuring reliability of test results for the commercialization of SOFC —

Akihiko Momma*, Kiyonami Takano, Yohei Tanaka and Tohru Kato

[Translation from *Synthesiology*, Vol.5, No.4, p.243-252 (2012)]

SOFC (solid oxide fuel cell) is a very promising technology that achieves high power generation efficiency, while being very nearly usable. It is high time we considered enhancing commercialization and dissemination of SOFC by setting a standard for the evaluation method of SOFC cell/stack performance. In setting the standard, it is neither appropriate to describe the specific content or form of the test object, nor appropriate to unify the test conditions, because each type of SOFC has been developed for a different application owing to the diversity of SOFC. On the other hand, uncertainty evaluation of the test results has been introduced to ensure reliability. In setting a standard for the SOFC performance test, it is necessary that the method for uncertainty evaluation be specifically described in the text, because the performance of SOFC depends on many parameters. This report describes the approaches we have taken in order to set the international standard of the SOFC test method and to evaluate the uncertainty of the test results.

Keywords **:** Solid oxide fuel cell, SOFC, uncertainty, performance evaluation, standardization

1 Introduction

Since the 1970s, Solid Oxide Fuel Cell (SOFC) has been a major focus of research and development in Japan. As a result of government-funded and other projects, the technology is now fast approaching commercialization. A number of manufacturers outside Japan are believed to already have the capability to provide a continuous supply of SOFC systems ranging from 1 kW to a few hundred kW. In Japan, 700 W-class SOFCs were introduced on the market last year as the core technology of the ENE-FARM system.

While SOFC systems are thus already available for practical and commercial purposes from some manufacturers, the technology has not yet attained the level where cell/stack (i.e. single cells in a stack) products backed by sufficiently reliable data are widely traded. These products are still in the development stage, with issues relating to long-term durability and manufacturing cost unresolved in many cases.

In order to address these issues, Europe took initiatives to harmonize and standardize testing conditions through such projects as the Fuel Cell TEsting and STandardisation NETwork (FCTESTNET) and its successor, the Fuel Cell Systems TEsting, Safety and Quality Assurance (FCTESQA),[1] thereby accelerating the research and development efforts. The main aim of the standardization work was to facilitate cross-border comparisons of the results of round robin tests by harmonizing the test procedures and conditions. For this reason the test conditions were very specifically described, and the flat-plate type was the only type of SOFC single cell/stack covered extensively, since it was the focus of development in Europe.

In Japan, while there were ongoing SOFC-related research and development projects conducted by the New Energy and Industrial Technology Development Organization (NEDO) and other organizations, the efforts to standardize testing methods were lagging behind those of Europe.

In addition, research and development on SOFCs in Japan took a wide variety of approaches. The goal was to ensure reliability in all applications by securing mechanical strength and reducing the rate of degradation under many different service conditions conceivable at high temperature, the operating environment associated with SOFC. This has led to the development of many types of SOFCs differing in geometry and cell size. Since different operating conditions are appropriate for different types of SOFC, establishing test conditions by simply integrating these different operating conditions would disregard the fact that each SOFC was designed with a certain type of service condition in mind. Comparisons of SOFCs based on such test conditions are not appropriate and defeat the purpose of making such comparisons in the first place.

Given such circumstances, it was necessary that Japan take a leading role in the development of international standards on

---

Energy Technology Research Institute, AIST Tsukuba Central 2, 1-1-1 Umezono, Tsukuba 305-8568, Japan
* E-mail: mo.momma@aist.go.jp

Original manuscript received April 3, 2012, Revisions received May 2, 2012, Accepted May 11, 2012

the testing methods for SOFCs in commercial transactions. Japan's leadership would allow many types of SOFCs designed for different service conditions to be tested fairly; data obtained from the test results would be used as the basis for commercial transactions of SOFCs, making it possible to select SOFCs appropriate for different applications and thereby accelerating the development and widespread application of SOFCs.

Our group has been leading the research efforts relating to the standardization initiatives aimed at the broad-based acceptance and development of SOFCs. Our projects include the preparation of a Japanese Industrial Standard Technical Specifications (JIS TS)[2] on efficiency measurement methods based on such studies as: the development of the flow rate standards of hydrogen and city gas[3]—both of which are potential fuels for fuel cells—and the development of high-precision efficiency measuring methods for SOFC systems (figure 1).[4] In addition, we have been consolidating the SOFC measurement technology by conducting measurements on various types of single cells as well as cell stacks and systems.[5]

Based on these technologies and experiences and in light of the future prospects of SOFC, our group was commissioned in 2007 by the Ministry of Economy, Trade and Industry (METI) to begin work on the standardization and harmonization of the single cell/stack testing methods for SOFC. Standardized testing methods were considered vital in order to facilitate the commercial transactions of SOFCs and accelerate the widespread use of SOFCs, which were believed to be close to commercialization.

In preparing an international standard for SOFC performance tests, it is necessary to address the accuracy of data to ensure the reliability of measurements. Standards published by the International Electrotechnical Commission (IEC) and other international standards propose the inclusion of uncertainty—a concept traceable to international and national standards—as a benchmark for the quantitative evaluation of the reliability of measurement results. Measurement results with uncertainty data would permit cross-border comparisons of test results, an essential part of any relevant international standard.

Against this background, we have taken active steps to introduce the concept of uncertainty into the evaluation of SOFC performance. As part of the JIS TS work and a 2007 project on efficiency measurements using an actual 10-kW SOFC system, we conducted uncertainty analyses of measured input and output values and included uncertainty data in our evaluation of the measured efficiency.[6]

This paper describes the three-year project commissioned by METI in 2007 to develop an international standard for the cell/stack performance testing of SOFC, and our group's work on uncertainty evaluation as part of this project.

2 Study objectives and a scenario for realizing the objectives

As mentioned above, the objectives of this research were to propose an international standard for SOFC testing methods and to incorporate into the standard the equations and methods for evaluating uncertainty that are practical for the current level of technology.

The first step was to form a committee for discussing and reviewing the draft standard. To do so we first conducted an inquiry, which included a questionnaire survey, with

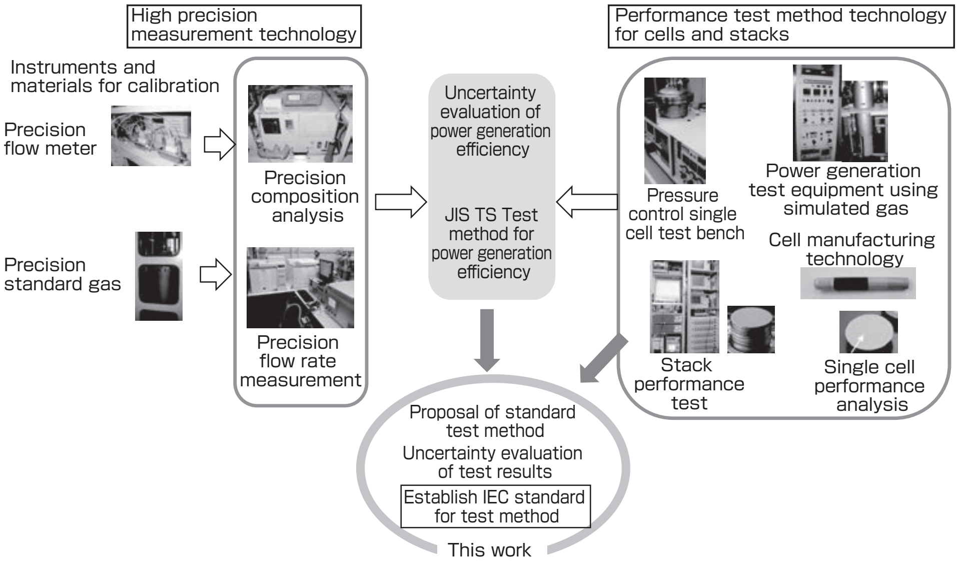


Fig. 1 The integration of and relationship between the technologies used for this study

SOFC manufacturers to ascertain their views concerning the testing methods they used and the standardization of such testing methods. It was important that the composition of the committee membership be equally distributed among the manufacturers, users, and neutral parties, so that discussions would reflect a balanced perspective. Regrettably, however, because SOFC was still in the development phase and the number of its actual users was limited, the committee debates tended to favor the manufacturers' views.

The second step was to establish the scope of measurements in the proposed standard. As described above, SOFCs came in a wide range of shapes and sizes; it was therefore neither easy nor realistic to set standards on all details of the components and their physical states and testing conditions during the tests. This was one of the most troubling issues that we had to address as we prepared the standard. In the end we selected the following approach:

(1) Define the scope of the tests as "cell/stack assembly" to make clear that the standard covers both cells and stacks;
(2) Treat the cell/stack assembly as a "black box" so that it can be applicable to any type of SOFC;
(3) Define the interface between the measurement instrument system and the cell/stack assembly, and describe the necessary interfaces and the measurement methods of input and output values based on such interfaces.

In sum, this approach is based on the view that it is not necessarily advisable to set standards for all details of the composition of test subjects; those components that should not be decided by the standard (i.e. those aspects that should be left to the discretion of manufacturers or test operators) are to be included in the "black box" of the cells/stack assembly, and the standard should only cover the interface between these components and the measurement instrument system. This approach makes it possible for the standard to cover not only the cells but also the stacks.

Finally, after deciding to introduce the concept of uncertainty in order to ensure the reliability of measurement results, we needed to consider how to incorporate it into the standard and how to approach the evaluation equation. While a general equation for uncertainty is included in the Guide to the Expression of Uncertainty in Measurement (GUM),[7] we believed it was not appropriate to adopt this directly as the equation for evaluating the uncertainty of the results of the SOFC performance tests. When a general equation is used for a specific application, many aspects are left to the discretion of users. In addition, there was concern that applying the general equation as is would leave too much work to the reviewer of the results, making the standard not very useful (and hence not usable). Thus we believed it was necessary to make the uncertainty equation for the standard as simple as possible, and clearly define and unify the method of using the equation in detail. The following is the approach we took to incorporate the uncertainty equation into the standard.

3 Uncertainty of SOFC performance testing

3.1 Approaches to uncertainty evaluation

Because the performance evaluation of SOFC is dependent on a wide range of parameters set for the measurement, calculating the uncertainty of the measurement results is not an easy process. Hence we investigated the approaches to uncertainty evaluation adopted in existing international standards related to fuel cells as well as in those standards currently under preparation.

The following are examples of approaches to uncertainty evaluation adopted in the international standards on fuel cells. It is clear from the issued years of the standards that, as of 2007, there were only a very limited number of standards proposing to incorporate uncertainty evaluation into the performance evaluations of fuel cells.

(1) In "Stationary fuel cell power systems - Performance test methods," the Committee Draft for Voting (CDV) circulated in 2010 for IEC 62282-3-200,[8] uncertainty consists of and is evaluated in two categories: systematic uncertainty, which derives from factors such as the accuracy of measurement instruments and calibration errors; and random uncertainty, which derives from data variations. The CDV provides an example of how to combine and evaluate these two in one of the Annexes (including a table of computation results), but specific procedures are to be determined by consulting the GUM. The CDV's approach to uncertainty is roughly identical to that of the Performance Test Code for Fuel Cell Power System Performance published by the American Society of Mechanical Engineers (ASME)(ASME PTC 50-2002[9]), and in both cases the test is to be conducted in a steady state.

Uncertainty is calculated only for the measured efficiency of the system, and the sensitivity coefficients of component gases can be theoretically obtained by calculations. The performance evaluation of the SOFC system as a whole does not require setting the temperatures of the cells or the stack; thus there are fewer input quantities for the uncertainty evaluation of the system than for the uncertainty evaluation of a cell or stack. Only the uncertainties of thermal input and power output, which are dependent on factors such as fuel composition and flow rate, need to be considered.

(2) At the end of 2009, the above-mentioned FCTESQA submitted to IEC a Draft for Comment (DC) on the testing method of the current-voltage (I-V) characteristics of Polymer Electrolyte Fuel Cells (PEFC) (An unofficial IEC document; not included in the reference list for the present document). This testing method defines the allowable range

for “measurement uncertainty.” However, the document fails to draw a clear distinction between the variation of measurements and the uncertainty of measurements; for example, it defines “steady state” as the state in which the variation falls within a given range of measurement uncertainty. The document defines “measurement uncertainty” using a general equation that addresses the correlation between input parameters but does not provide any specific method for calculating uncertainty.

(3) The TS on “Single Cell Testing Methods for PEFC,” which was published in 2010,[10] was still a Committee Draft (CD) when we were preparing the draft standard. The CD defined the maximum allowable variation of input quantities and the maximum uncertainty of testing equipment. The final version of the TS recommends that measurement uncertainty be included in the test report, as it is shown in the template provided in one of the Annexes. But again, the document points to the GUM as a guide for specific procedures.[7]

Based on the circumstances above, we established the following guiding principles on uncertainty evaluation in the proposed international standard for SOFC performance tests:

(a) Use the GUM as the guide for uncertainty evaluation and describe both the evaluation equation and the specific procedures for calculating uncertainty.

Uncertainty is obtained by combining the results of a Type A evaluation using statistical methods and a Type B evaluation using any other methods. We propose this approach because it would be difficult to derive the actual steps for evaluating uncertainty from the general uncertainty equation alone; leaving this task to the reviewer would result in a complete lack of consistency in the actual method used.

(b) Define the maximum variation of input quantities and the allowable uncertainty of measuring instruments, and perform all measurements in a stable state where input quantities stay within the allowable range.

This has the effect of setting approximate allowable values for both Type A and Type B uncertainty evaluations. Moreover, conducting measurements in a stable state eliminates the need to consider any correlation between input quantities when uncertainty is evaluated.

(c) Do not impose an unreasonable amount of work on the reviewer.

The purpose of the standard is to establish performance test methods for commercial purposes, not to obtain an accurate value of uncertainty. We believe that the goal of uncertainty evaluation would be achieved if the evaluation can show the level of accuracy at which a test operator has conducted the test and produced the results for submission; the test operator should not be expected to deviate substantially from the daily test procedures just to achieve this goal.

Based on these principles, we removed those aspects of the general equation of uncertainty evaluation that are believed to have little impact on uncertainty. We also provided a description of the specific procedures involved in uncertainty evaluation, so that the test operator would be able to easily conduct the evaluation.

3.2 Description of uncertainty evaluation in the draft standard

With the above circumstances taken into account, we included the following details concerning uncertainty evaluation in the draft standard:

The performance tests incorporated in the draft standard include the rated power test, I-V characteristic test, the effective fuel utilization dependency test, the long-term durability test, the internal impedance test and so on. Because uncertainty evaluations of some of these tests were likely to be very difficult or troublesome, our proposed draft standard only mandated that the uncertainty evaluation be conducted on the results of the rated power tests. Here, the rated power test was defined as the test in which either the current or the voltage is measured while the other is kept at a certain level: it is a single-point test in which all other control parameters are kept constant. An explanation is given below using an example where the voltage is measured while the current is kept constant—the more commonly used of the two methods.

Based on the guiding principles above, the draft standard established the maximum allowable variations of input quantities such as the current and the gas flow rate that were applicable to all the tests stipulated in the standard (Table 1). In an actual measurement, each test operator is to set a maximum allowable variation within this defined range, so that he/she would be able to obtain the target uncertainty value of a particular measurand (a quantity subject to measurement). This in effect establishes the allowable range of uncertainty arising from random error.

In addition, “stable state” was defined as the state in which the system is stable enough for any input quantity to fall within the tolerance range set by the test operator and the measurement result to meet the target uncertainty level. All measurements were to occur after the test sample was confirmed to have attained the stable state. This would prevent the measurement from being conducted while the system is in a transient response arising from a sudden change in a condition or in various drift states. Consequently, measurement variations would be limited to those due to random noise or the uncontrollable minute variation of

Table 1. Range of allowable variations and instrument uncertainty set by the draft standard and the feasibility of uncertainty evaluation of each input quantity

input parameter	tolerable range of variation	instrument uncertainty	sensitivity coefficient	action to uceratinty evaluation
voltage	±1 % of set value (in case of voltage control)	±0.5 % of OCV	experimentally decided	incorporated
current	±1 % of rated current (in case of current control)	±1 % of rated current	experimentally decided	incorporated
unit temperature	±1 % (℃) of set temperature	±1 % (℃) of rated temperature	experimental (rated temperature±50 ℃)	incorporated
fuel flow rate	±1 % of rated value	±1 % of reading	experimental (rated flow rate±10 ~ 20 %)	incorporated
oxidant flow rate	±1 % of rated value	±1 % of reading	experimental (rated flow rate±10 ~ 20 %)	incorporated
fuel composition	H_2, H_2O, N_2:±1 mole%、 CO, CO_2, CH_4:±0.25 mole%	H_2, H_2O, N_2:±2 mole%、 CO, CO_2, CH_4:±1 mole%	depends on the method of mixture supply (cannot change indivisually)	partially achieved (e.g. presentation of the composition table published by gas manufacturer)
oxidant composition	O_2:±0.3 mole% (N_2:balance)	O_2:±0.3 mole% (N_2:balance)	depends on the method of mixture supply (cannot change indivisually)	partially achieved (e.g. presentation of the composition table published by gas manufacturer)
fuel temperature	not prescribed particularly with the condition that it does not attect the performance	±1 % of reading	n/a	not incorporated (compromized with the prescription that the test should be conducted under the condiiton that it does not affect the performance)
oxidant temperature	not prescribed particularly with the condition that it does not attect the performance	±1 % of reading	n/a	not incorporated (compromized with the prescription that the test should be conducted under the condiiton that it does not affect the performance)
fuel pressure	±3kPa (atmospheric pressure operation)	±1 % of reading	n/a	not incorporated
oxidant pressure	±3kPa (atmospheric pressure operation)	±1 % of reading	n/a	not incorporated
atmospheric pressure	Not to be included in uncertainty evaluation, because it is not possible to change ambient pressure with common test equipment. It was alternatively decided to report atmospheric pressure. It may become problematic if atmospheric pressure differs much from 1 atm. Normally it was confirmed by experiment that this effect on the performance is small.		n/a	not incorporated
temperature distribution	If the object has more than one temperature measurement points as is always the case with large cells or stacks, it was decided that manufacture has to provide the tolerance range of temperature distribution and the measurement has to be conducted within the range. It was also decided that the temperature distribution should not be included in the uncertainty evaluation. It was experimentally confirmed that the temperature distribution could become negligible using 100 cm^2 or such a level cells.		n/a	not incorporated

input quantities, thereby minimizing the need to take into account any possible correlation between input quantities for uncertainty analysis.

The draft standard additionally defined the maximum allowable uncertainties of measurement instruments (i.e. uncertainty due to systematic error) (Table 1). This was specifically intended for the uncertainty of the instruments at the time of calibration. However, the draft standard also allowed a simplified Type B evaluation that assumes a uniform distribution, using catalog values such as the degree of accuracy of the instruments, on the condition that the instruments have been calibrated.

4 Uncertainty of measurement of SOFC properties

4.1 Selection of factors affecting uncertainty through experimental verification

The properties of SOFC depend on various factors such as cell temperature, fuel flow rate, air flow rate, operating pressure, and temperature distribution. It follows that the uncertainty of the control and measurement of these input quantities would inevitably have an effect on the uncertainty of the measurand. We decided to investigate how these input quantities would impact the uncertainty of the measurand, and, based on the results, grouped them into those that should be incorporated into uncertainty evaluation and those that should not.

As an example, figure 2(a) shows the pressure dependence of the voltage of an SOFC single cell that was measured while the atmospheric pressure was varied. The measurement was conducted in three different conditions: open circuit voltage (current: 0 A); the fuel utilization rate at 50 % (current: 24.4 A); and the fuel utilization rate at 70 % (current: 34.1 A). The slopes of the plots represent the impact of the atmospheric pressure on the uncertainty of voltage measurements when the current and gas flow rate are kept constant and the pressure deviates from the set value.

The pressure dependence of the cell voltage obtained from the data shown in the graphs is approximately 0.3 μV/Pa at around 1 atmospheric pressure, demonstrating that if the measurement is made within the normal range of atmosphere, the impact that the atmospheric pressure variation has on measurand V remains small. Incidentally, in our standard, the uncertainty of the measurand is to be kept at approximately 1 % or below as a rough target.

SOFC varies not only by geometry and size, but also by the type of support used. Figure 2(a) above represents the test results of an electrolyte-supported cell. This type of cell is characterized by relatively thin electrode films on both sides of the electrolyte, making it less affected by diffusion of reaction species and reaction products in the porous electrodes.

In contrast, anode-supported and cathode-supported SOFC cells have a thicker porous medium and are therefore more susceptible to the effects of gas diffusion, raising the possibility that the operating-pressure dependence of the voltage of these types of cells would be substantively different from that of the electrolyte-supported cell mentioned above.

Figure 2(b) shows the pressure dependence of the cell voltage measured in an anode-supported SOFC single cell. While the level of dependence observed on the lower pressure region is significantly different from what is observed above, the pressure dependence of the cell voltage at 1 atmospheric pressure is about 0.2 to 0.5 μV/Pa, confirming its low impact on uncertainty for these types of cells as well.

In contrast, the temperature distribution of SOFC is a very troublesome issue as far as uncertainty is concerned. In theory, the performance of SOFC at a certain temperature can be obtained simply by uniformly maintaining that particular temperature all over the object and conducting measurements. But in practice, taking measurements in such a condition is not always possible. Moreover, based on the actual usage of SOFC, it is arguable that a temperature distribution should be the norm.

Therefore, for the purpose of this study we took measurements of the temperature distribution of a SOFC single cell, an example of which is shown in Fig. 3. In general, the temperature distribution varies depending on the setup in the electric furnace used and the method of temperature control

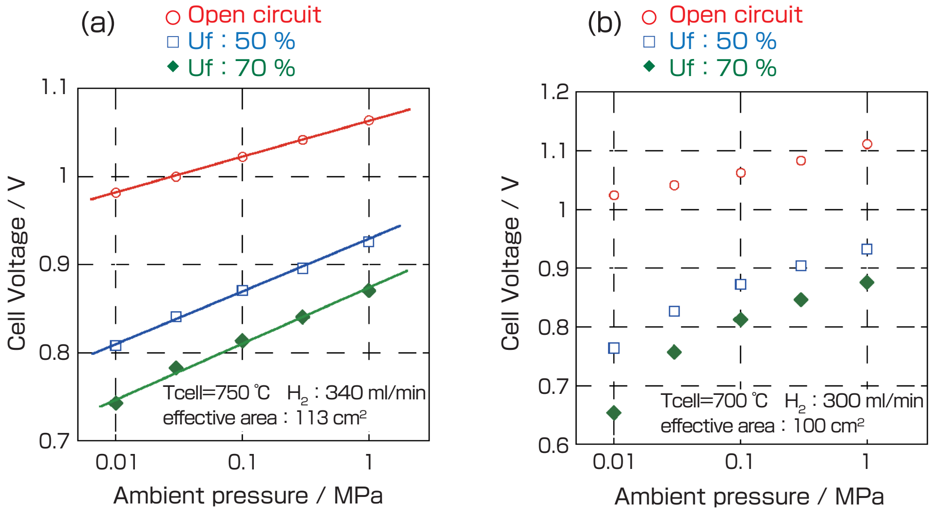


Fig. 2 Pressure dependence of the cell voltage at different fuel utilization rates
(a) Electrolyte-supported cell; (b) Anode-supported cell

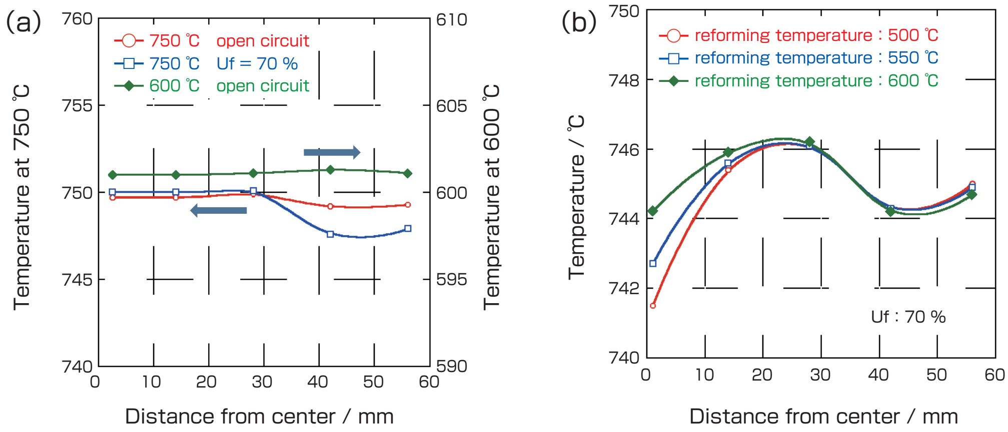


Fig. 3 Examples of temperature distribution measurement of a single cell
Measurement by 0.25 ϕ sheath thermocouple (Okazaki Super Couple 1000H).
(a) Electrolyte-supported cell (Active electrode area: 113 cm². Fuel: pure hydrogen)
(b) Anode-supported cell (Active electrode area: 113 cm². Fuel: partially-reformed methane)

used to keep the temperature high. In our experiment, we set up the SOFC cell in the laboratory system we normally work on and employed the single-point control method for temperature control.

Figure 3(a) shows the temperature distribution of an electrolyte-supported cell—a type of cell of which internal reforming characteristic is not expected to be sufficient enough—when hydrogen was introduced as fuel. The hydrogen gas was supplied from the center of a disc-plate cell and then was circulated to the periphery. The graph demonstrates that, regardless of the load level, the temperature distribution remained within approximately ±2 ºC of the average cell temperature. Judging from the allowable variation of approximately ±1 % of the set value endorsed by the proposed draft standard, we believed this to be a sufficiently acceptable level.

In contrast, figure 3(b) shows the temperature distribution of an anode-supported cell when partially-reformed methane was used as fuel. This type of SOFC, unlike the electrolyte-supported cell, is expected to have sufficient internal reforming characteristic, which is one of the benefits of SOFC. From the graph it is evident that a decrease in the temperature at the inlet area occurred due to the endothermic reaction from the internal reforming of methane. While the temperature distribution varied according to the load level, it nevertheless remained within about ±3 ºC of the average temperature. If we could assume this temperature distribution as a local temperature variation within the cell, we judged that this degree of variation sufficiently falls within the allowable range even when internal reforming occurs. (Actual evaluation of the impact of temperature distribution is very difficult because local impedance changes as a result of temperature distribution, resulting in a change in current distribution.)

As shown above, it was verified through experiments that atmospheric pressure and temperature distribution have little impact on uncertainty, and hence it was decided that they were not to be incorporated into the equation for uncertainty evaluation. In reality their impact on uncertainty is not small enough to be completely ignored, and they should ideally be included in the equation. However, it is not realistic to expect cell manufacturers to make measurements of such parameters as pressure dependence and temperature distribution for all types of cells they produce. In fact, very few studies have been published on the measurements of pressure dependence or temperature distribution such as those conducted for this paper. Moreover, even if temperature distribution is measured, it would be very difficult to estimate its impact on uncertainty. For this reason, it was fortunate, in the end, that the impact of these factors on uncertainty was small and that it was possible to achieve the goal of uncertainty evaluation even when these factors were omitted from the uncertainty evaluation equation.

In addition, the draft standard provides that if there are multiple points of temperature measurement in a test unit, the manufacturer must determine the allowable range of temperature distribution in advance and conduct the measurements within that allowable range. In other words, as long as the temperature is measured within the range, it is not necessary to take into consideration the uncertainty resulting from temperature distribution.

4.2 Uncertainty equation used in the draft standard

Given the circumstances described above, we proposed the following equation in the draft standard for evaluating uncertainty when the voltage of SOFC, V, is measured while input quantity, X_j, is being controlled.

$$u(V)^2 = u_I(V)^2 + u_F(V)^2 + \sum_j \left(\left(\frac{\partial V}{\partial X_j} \right)^2 \left(u_I(X_j)^2 + u_F(X_j)^2 \right) \right)$$

where $u(X)$ is the standard uncertainty of X; subscript I is the uncertainty of measurement instruments; subscript F is the uncertainty due to variations; and

$$\frac{\partial V}{\partial X_j}$$

is the sensitivity coefficient of measurand V to input quantity X_j. The last was to be determined through a laboratory experiment. In addition, it was decided that the sensitivity coefficient should be used to correct the value of the measurand multiplying the difference between the average value and the set value of an input quantity. Table 1 shows the input quantities to be evaluated by the uncertainty evaluation equation based on the circumstances and the experimental results shown above.

In one of the Annexes to the draft standard, we showed the method of calculating the instrument uncertainty of temperature, current, flow rate, and voltage, as well as the method of calculating the uncertainty of the measurand by combining the instrument uncertainty and the uncertainty resulting from measurement variations. We believe that this approach ensures that the evaluation of uncertainty is conducted in a consistent manner without leaving the equation open to interpretation.

4.3 Relationship between measurand and input quantity (measurement of sensitivity coefficients)

We proposed that the sensitivity coefficients used in the uncertainty equation are to be obtained by actual measurements. Because it was decided that the evaluation of uncertainty was to be made only at rated values, as mentioned above, the measurements of sensitivity coefficients were to be made by measuring the voltage while varying the

Table 2. An example of an uncertainty budget table on the current-regulated rated power test using an SOFC single cell

input and measurement parameter	unceratinty factor		accuracy	maximum error bound	standard uncertainty	type of uncertainty	degree of freedom	sensitivity coefficient	standard uncertainty in voltage (V)	standard uncertainty in power (W)
cell temperature					3.20E+00 ℃			1.29E-03 V/℃	4.13E-03	1.24E-01
	variation	–	–	–	4.90E-03	A	29			
	instrument	thermo-couple (K, class 2)	±0.75 % of rdg in degree C	5.253 ℃	3.03E+00	B				
		digital recorder	±(0.15 % of rdg + 0.7 ℃)	1.751 ℃	1.01E+00	B				
current					7.85E-02 A			6.95E-03 V/A	5.45E-04	1.64E-02
	variation	–	–	–	1.83E-03	A	29			
	instrument	shunt resistor	±0.05 % of rdg	0.015 A	8.70E-03	B				
		digital recorder	±(0.05 % of rdg+12digits)	0.135 A	7.80E-02	B				
fuel flow rate					4.14E-01 Nml/min			4.23E-04 Vmin/Nml	1.75E-04	5.26E-03
	variation	–	–	–	8.68E-02	A	29			
	instrument	MFC (calibrated by Dry cal)			4.05E-01	B				
air flow rate					2.89E+01 Nml/min			3.32E-07 Vmin/Nml	9.59E-06	2.88E-04
	variation	–	–	–	5.09E-01	A	29			
	instrument	MFC	±1 % of full range	50 Nml/min	2.89E+01	B				
		digital recorder	±(0.05 % of rdg+12digits)	0.87 Nml/min	5.02E-01	B				
cell voltage					1.07E-03 V			1.00E+00 V/V	1.07E-03	3.22E-02
	variation	–	–	–	6.26E-05	A	29			
	instrument	isolation amplifier	±(0.1 % of rdg + 0.1 mV)	9.25E-04 V	5.34E-04	B				
		digital recorder	±(0.05 % of rdg+12digits)	1.61E-03 V	9.31E-04	B				
combined standard uncertainty									4.30E-03	1.29E-01
expanded uncertainty (k = 2)									8.60E-03	2.58E-01

input quantities around the rated values.

As an example, figure 4 shows the measurement data taken to calculate the sensitivity coefficient of the voltage to the unit temperature. When the rated value is 750 °C and the fuel utilization rate is 70 %, the slope obtained at that particular point in the plot is the sensitivity coefficient. Generally speaking concerning the variation in the experiment for obtaining sensitivity coefficients, SOFC manufacturers make the measurements by varying input quantities, such as temperature and gas flow rate, around the rated values. For unit temperature, a variation of 50 °C is normally used. Thus, we recommended in the draft standard that the range of the unit temperature for calculating the sensitivity coefficient be approximately ±50 °C. The data in figure 4 can be obtained by measuring the I-V characteristics at a rated temperature and at ±50 °C. We took this approach so that this measurement of the sensitivity coefficient would not pose an undue burden on the manufacturers.

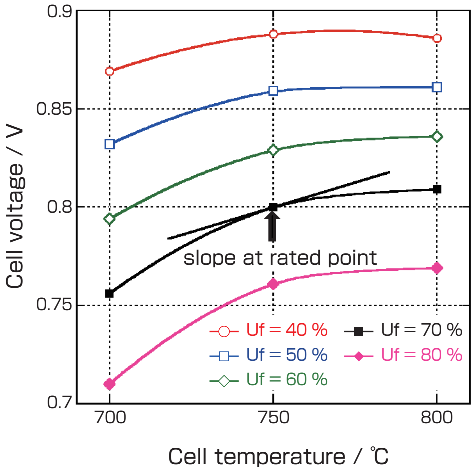


Fig. 4 An experiment to calculate the sensitivity coefficient of the cell voltage to the temperature

The variation range of the input quantity was set at about ±50 °C.

In some cases, it is simply not possible to measure the sensitivity coefficient, and thus it is not possible to evaluate uncertainty. Table 1 shows how to obtain the sensitivity coefficient for each input quantity in the SOFC test and whether it is possible to evaluate uncertainty. However, it may not be possible to evaluate uncertainty originating from fuel and oxidizing gas compositions. When gas is supplied using a mixture gas cylinder, for example, it is virtually impossible to independently change the concentration of one component gas of the gas mixture to measure its sensitivity coefficient, thus making it impossible to evaluate the impact of the uncertainty of a component gas on the voltage.

5 An example of uncertainty analysis for the SOFC performance test

Table 2 shows an example of uncertainty analysis (uncertainty budget table) conducted on the results of the rated power test on a 100 cm^2 planar SOFC single cell. For the test we used the measurement and control instruments that we normally used for performance tests. When there is a large variation in the measurement values, the level of uncertainty may be reduced by making repeated runs of measurements. However, as long as the system is in a stable state, a single run of about 30 measurements (1 measurement/second) would show that the impact of the variation of measurement values on uncertainty is small.

The objective of the rated power test is to produce power output, which is obtained by multiplying the current, the input quantity, and the voltage, the measurand. Thus the column on the right end of Table 2 shows the uncertainty converted to power. A comparison of the uncertainty values demonstrates that the majority of uncertainty derives from the temperature measurement of the cell. It is also clear from the breakdown of this source of uncertainty that the thermocouple used in the test accounts for a significant portion of that uncertainty.

One of the benefits of uncertainty analysis is that by producing a data set like Table 2, one can easily see which measurement needs to be improved in order to reduce the level of uncertainty in the measurand. By changing the thermocouple used for the measurement from a type-k thermocouple (class 2), which was used for this measurement, to a class-1 thermocouple, it is possible to reduce the standard uncertainty of power output measurement from 0.13 W (0.52 %) to 0.08 W (0.33 %).

From the above, we believe that the impact of the uncertainty on the variation of the measured values would remain small, so long as the measurement is made by carefully making sure that the system is in a stable state. It follows, then, that it is possible to derive a rough estimate of the uncertainty of test results solely from the uncertainty of the measuring instruments used in that test.

Thus, when the uncertainty of the above-mentioned cell was calculated with the assumption that the measurement instruments used for the calculation had the maximum allowable range of the instrument uncertainty set by the draft standard, the relative expanded uncertainty was estimated to be 1.4 %. Since the draft standard prescribes that an instrument falling within the allowable range of uncertainty be used, it follows that the test operator would be able to obtain a measurement result with the relative expanded uncertainty of approximately 1.4 % at the maximum. However, it should be noted that this value may change significantly from one test unit to another, such as when the unit has a completely different sensitivity coefficient or when the rated condition is characterized by a high fuel utilization rate.

6 Summary

The maximum variations of input quantities and the uncertainty values of the instruments established in the draft standard were based on a set of working values that were initially prepared by our group and were subsequently discussed and adopted by the committee as the final values acceptable to all manufacturers. In conclusion, our study demonstrated that by conducting a test in accordance with the draft standard, it is possible to obtain a measurement with a relative uncertainty of approximately 1.4 % at the maximum. We believe that the values proposed in the draft standard were reasonable for the commercial transactions of SOFC.

In the end, however, the uncertainty analysis and its equation for the rated power test that we proposed were omitted from the final version of the draft standard by the national committee responsible for preparing the New Work Item Proposal (NP) for submission to IEC. As a result, only the maximum allowable variation of the input quantities (control parameters) and the instrument uncertainty remained in the NP. Nevertheless, it was still fortunate that we were able to verify the maximum uncertainty value as described above.

The main reason that the uncertainty analysis was removed from the draft standard is that many manufacturers are still not familiar with the concept of uncertainty and they focused above all on the troublesome nature of the uncertainty analysis. In proposing the equation for uncertainty evaluation, we did our best to present an equation (method) that would minimize the burden on the test operator, but we failed to provide sufficient evidence on the merit of conducting uncertainty evaluation.

The concept of uncertainty ensures the reliability of data across borders through the traceability system. It is recommended by many international standard organizations and is likely to be incorporated into an increasing number of international standards in the decades to come. At the same time, however, it may take some time to convince the manufacturers in this field that the potential benefit of uncertainty evaluation makes it worthwhile to incorporate it in their testing procedures if they aim to produce quality products.

This draft standard is currently being reviewed by an international Working Group (WG), and it may see an introduction of the uncertainty evaluation any time as a result of a proposal by another country. In addition, as far as our national committee is concerned, it appears that the concept of uncertainty is gradually gaining in prevalence among the committee members as a result of our presentation and the discussions held on the topic. Therefore, given that uncertainty evaluation may be proposed at any time, we believe that our work has helped to lay the groundwork for determining whether or not it should be adopted.

While we, the authors, are not experts on uncertainty, there seems to be a common saying among the specialists in the field that "the biggest uncertainty lies in those factors that have not been considered." In our evaluation of uncertainty for the draft standard, the following may fall under that category:

(1) Change in performance due to temperature distribution (as suggested above);
(2) Operator-to-operator variability;
(3) Sample variability;
(4) Drift due to time-dependent change.

It follows therefore that we have not been able to escape the curse of the above-mentioned proverb, either. Some of these factors were intentionally omitted based on our guiding principles on uncertainty evaluation. The concept of drift due to time-dependent degradation is crucial when discussing the durability of SOFC, and we are currently in the midst of discussions regarding the testing methods for the durability of SOFC.[11]

Thus, we have discussed the approach we have selected for international standardization that is a must for a new technology to become globally commercialized and accepted. We would consider it a work well done if it can in any way serve as a guide for our colleagues involved in the development of technology, and at the same time invite you to submit any feedback or criticisms of uncertainty evaluation.

Acknowledgement

This study was made possible by the Research and Development Project on Standardization and Certification and the Joint Research and Development Project on International Standardization funded by METI. We would like to thank the members of the Committee for the Research and Development of the Standardization of SOFC Unit Cell Assembly Testing Methods as well as all other firms and organizations involved for their cooperation in the preparation of the draft standard.

References

[1] http://fctesqa.jrc.ec.europa.eu/
[2] JIS TS C 0054, Testing method of power generation efficiency for solid oxide fuel cell power systems fueled with gas in which methane is main component(2010) (in Japanese).
[3] T. Kato *et al*.: *View and Development of Solid Oxide Fuel Cells*, ed. by K. Eguchi, CMC Books, 179-190 (2010) (in Japanese).
[4] New Energy and Industrial Technology Development (NEDO): "Research on the Technology for the Evaluation of System Efficiency Measurement," System Performance Evaluation Technology Development, SOFC Fuel Cell System Performance Technology Evaluation Technology, SOFC Fuel Cell System Technology Development, *NEDO Activity Report 2007*, (2008) (in Japanese).
[5] Y. Tanaka, A. Momma, A. Negishi, K. Kato, K. Takano, K. Nozaki and T. Kato: Progress towards realizing distributed power generation with highly efficient SOFC systems, *Synthesiology*, 6(1), 12-23 (2013) (in Japanese).
[6] Y. Tanaka, A. Momma, K. Kato, A. Negishi, K. Takano, K. Nozaki and T. Kato: Development of electrical efficiency measurement techniques for 10 kW-class SOFC system: Part II. Uncertainty estimation, *Energy Conversion and Management*, 50 (3), 467-478 (2009).
[7] ISO/IEC Guide. Guide to the Expression of Uncertainty in Measurement (GUM), International Organization for Standardization, 98 (1995).
[8] IEC 62282-3-200 Ed.1 (CDV). Fuel cell technologies - Part 3-200: Stationary fuel cell power systems - Performance test methods.
[9] ASME PTC 50-2002. Fuel Cell Power Systems Performance - Performance Test Codes.
[10] IEC/TS 62282-7-1. Fuel cell technologies - Part 7-1: Single cell test methods for polymer electrolyte fuel cell (PEFC).
[11] NEDO: "Standardization of SOFC Single Cell/Stack Durability Testing Method," Project for Strategic Promotion of International Standardization/Leading Research on Standardization, *NEDO Activity Report 2010* (2011) (in Japanese).

Authors

Akihiko MOMMA

Completed the doctoral program of the Metallurgical Engineering Department at Tokyo Institute of Technology in 1985. Worked at SRI International as a guest researcher and subsequently joined the Electrotechnical Laboratory Japan (the predecessor of the National Institute of Advanced Industrial Science and Technology (AIST)), where he engaged in the research and development of SOFC. Currently senior research scientist of the Fuel Cell System Group of AIST's Energy Technology Research Institute and specializes in electrochemical measurements and evaluations. In preparing for this paper, he was responsible for managing the committee work, conducting various electrochemical measurements, evaluating the uncertainty equation, and writing and editing.

Kiyonami TAKANO

Graduated from the Department of Electrical and Electronic Engineering of the Faculty of Engineering of the University of Tokushima in 1966. Joined the Electrotechnical Laboratory of the Agency of Industrial Science and Technology of the Ministry of International Trade and Industry (the predecessor of METI). After engaging in the research of the simulation technology of lithium secondary battery from 1991, began working on the research for the power generation evaluation of SOFC in 2001. Currently guest researcher at the Fuel Cell System Group of the Energy Technology Research Institute. In this study, he was in charge of conducting pressure dependence tests for single cells, temperature distribution measurements, and uncertainty evaluation.

Yohei TANAKA

Completed the doctoral program of the Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering of Kyoto University in 2005 and joined AIST in the same year. Currently senior research scientist at the Fuel Cell System Group of the Energy Technology Research Institute. His areas of specialization include catalyst chemistry, fuel cell performance evaluation, and energy engineering. For this paper, he was responsible for preparing the gas supply methods and the uncertainty evaluation methods for the draft standard.

Tohru KATO

Completed the graduate program at Tohoku University and earned a doctorate degree in engineering in 1991. In 1992, joined the Electrotechnical Laboratory Japan of the Agency of Industrial Science and Technology of MITI, where he conducted research on the technology for high temperature electrolysis. Currently serves as Industrial Science and Technology General Director for the Research and Development Division under the Industrial Science and Technology Policy and Environment Bureau of METI. For the preparation of this paper, he was responsible for the establishment and operation of the national committee, preparation and editing of the draft standard, the proposal for the concept of cell stack/assembly unit, and the oversight of the research project as a whole.

Discussions with Reviewers

1 Justification of the parameters chosen for uncertainty evaluation

Question (Hiroshi Tateishi, AIST)

In “3.2 Description of uncertainty evaluation in the draft standard,” it is stated, “Because uncertainty evaluations of some of these tests were likely to be very difficult or troublesome, our proposed draft standard only mandated that the uncertainty evaluation be conducted on the results of the rated power tests.” The reasoning for omitting the “difficult or troublesome” evaluations is not clear. If these omitted steps had a major impact on uncertainty, wouldn’t the entire process lose its credibility?

Answer (Akihiko Momma)

What we meant by this is that we made uncertainty evaluation mandatory only for the results of the rated power test in the draft standard. For other test results, the users themselves were to judge the reliability of data from the information on measurement instruments, which must be included in the test report according to the draft standard. Therefore, it is not that the uncertainty of the rated power test depends on the results of those other tests that the draft standard did not make it mandatory to perform uncertainty evaluation, as you suggested. Uncertainty evaluation was in fact difficult for some tests other than the rated power test. For others, we actually did not know what to do, and decided not to require them. We judged that imposing an excessive burden on test operators for uncertainty evaluation would go against the view of the committee by being not consistent with its overall goal to make the standard as user friendly and accessible as possible.

2 If uncertainty evaluation is not feasible

Question (Hiroshi Tateishi)

At the end of “4.3 Relationship between measurand and input quantity (measurement of sensitivity coefficients),” it says, “When gas is supplied using a mixture gas cylinder, for example, it is virtually impossible to independently change the concentration of one component gas of the gas mixture to measure its sensitivity coefficient, thus making it impossible to evaluate the impact of the uncertainty of a component gas on the voltage.” Wouldn’t the fact that it is “impossible to evaluate” the impact of uncertainty present a problem?

Answer (Akihiko Momma)

In the draft standard, a number of scenarios were considered to establish the methods of supplying fuel gas. When a mixed gas cylinder is used to supply fuel, we judged that it was practically impossible to conduct uncertainty evaluation. In this case, users would determine the reliability of data by referring to the test conditions and gas composition analysis table, which the standard requires to be included in the test report. We had no choice but to resort to this difficult decision even though there is no doubt that it is problematic.

Development of switchable mirror glass

— R&D strategy toward its practical use —

Kazuki YOSHIMURA*, Kazuki TAJIMA and Yasusei YAMADA

[Translation from *Synthesiology*, Vol.5, No.4, p.253-260 (2012)]

“Switchable mirror” is a new thin film material that can be switched between transparent and mirror states. Using this material on window glass saves energy by effectively shading rooms from sunshine, thereby decreasing cooling load in summer. In this paper, we introduce our R&D strategy for further development and practical deployment of this material. In addition to R&D of the material itself we also measured the amount of energy saved when the material was used in the windows of buildings. The results we obtained from such field tests will enable us to develop a window glazing with better energy-saving performance.

Keywords **:** Smart window, energy efficiency, cooling load, chromogenic material, durability

1 Introduction

The Materials Research Institute for Sustainable Development is engaging in research for “energy-saving building components” that are materials useful in reducing the CO_2 emission in the civilian sector. The Energy Control Thin Film Group is in charge of the research of windowpane glass. The percentage of energy consumed in cooling and heating reaches about 30 % of the energy consumption in the civilian sector, and the window is a component that greatly affects cooling and heating efficiency. While the objective of a window is to let in light, ordinary windowpane allows the permeation of heat as well as visible light, and it is a factor that leads to the loss of insulation of the building. Increasing the insulation property of the window has great energy saving effect, and recently, the uses of highly insulating pair glass and low-e glass are becoming common. In Japan where the summers are very hot, the energy-saving effect can be further increased by effectively blocking the sunlight (shading) in addition to increasing insulation. The switchable glass is a windowpane that can automatically control the inflow and outflow of light and heat.

The switchable glass is fabricated by coating the glass with thin film material that can reversibly vary the optical property (chromogenic material). There are several types of switchable glasses. For example, an electrochromic glass accomplishes the switching electrically,[1] a thermochromic glass changes according to temperature,[2] and a gaschromic glass changes by surrounding atmosphere (gas).[3] Among these switchable glasses, there is a long history of research of the electrochromic glass, and some types of glasses are already available on market overseas.

In Japan, the electrochromic switchable glass research was conducted by major glass manufacturers until the 1990s. One of the authors (Yoshimura) was involved in the research of switchable material from the days of the National Industrial Research Institute of Nagoya that was the precursor of AIST Chubu. The switchable material was investigated as one of the passive energy-saving techniques in the national project of ‘Sunshine Project’ and ‘New Sunshine Project’. Although a product with excellent performance was fabricated, the research was terminated at around 2000 because the prospect for practical use could not be conceived due to cost issues. The research entered the so-called “valley of death” or the “period of nightmare.”

At that time, the author (Yoshimura) started to look at the “switchable mirror” that might reignite the research of this switchable glass. The switchable glass was a new switchable material discovered in the Netherlands in 1996.[4] While the conventional switchable material changed from transparent to deep blue color, the new material changed from transparent to a mirror state. In the mirror state, it reflected and cut off the sunlight. Because the mirror state reflected and cut off more sunlight compared to conventional switchable glass, this allowed a window with higher shading performance. In conducting the switchable mirror thin film research, we had in mind the achievement of the practical use of the energy-saving windowpane from the beginning, not just doing research for materials. In this paper, we present how the research was conducted to achieve practical use of the switchable mirror glass.

Materials Research Institute for Sustainable Development, AIST 2266-98 Anagahora, Shimo-Shidami, Moriyama-ku, Nagoya 463-8560, Japan * E-mail: k.yoshimura@aist.go.jp

Original manuscript received April 6, 2012, Revisions received May 16, 2012, Accepted May 18, 2012

2 Issues in achieving the practical use of the switchable mirror

When the research for the switchable mirror was started at AIST in 2001, the following issues were identified as points that must be solved, and researches were started: (1) the improvement of optical property, (2) the improvement of durability, and (3) the development of an electrochromic switchable mirror.

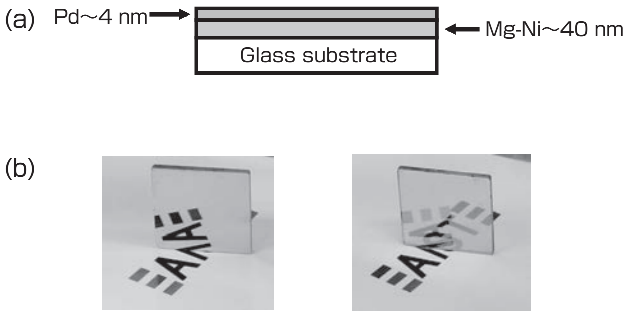
2.1 Improvement of optical property

Figure 1(a) shows the basic structure of the switchable mirror composed of the magnesium alloy thin film as the switching layer, that is coated with a thin catalyst layer. In an as-deposited state after film deposition, the magnesium alloy layer is in a mirror state since it is metallic, and when it is exposed to an atmosphere containing diluted hydrogen, the switching layer becomes hydrogenated by the action of palladium catalysts, and the layer turns into an insulator and turns transparent. Next, when this is exposed to an atmosphere containing oxygen, the hydrogen in the hydride reacts with oxygen by the action of palladium catalysts and gets pulled out as H_2O, and the film returns to a metallic state and becomes a mirror. The switching mirror state where the mirror and transparent states switch back and forth was first found in the thin films of rare earth metals such as yttrium and lanthanum, and several new materials were found later (Table 1). The alloy of magnesium and transition metal was found in the United States in 2001, and this was considered to be a better material to be applied to large glass, because it was less expensive and was thought to have higher durability compared to the rare earth metals. AIST focused on this material and started research for the first time in Japan. However, when this material was first discovered, the transmittance of visible light was about 20 % in its transparent state, and the color was dark brown that was not suitable for practical use. AIST started research on increasing the visible light transmittance in the transparent state of the switching mirror, and found that the visible light transmittance in the transparent state can be increased to about 50 % by using the Mg rich Mg-Ni alloy thin film, as shown in Fig. 1(b).[13] This was a big step forward to practical use.

Table 1. Types of switchable mirror thin film materials

First generation	Rare earth metal Y[4],La[4],etc. Vrije Universiteit, Amsterdam 1996
Second generation	Rare earth/magnesium alloy Gd-Mg[5],Sm-Mg[6],Y-Mg[7],etc. Phillips 1997
Third generation	Magnesium/transition metal alloy Mg-Ni[8],Mg-Ti[9],Mg-Co[10],etc. Lawrence Berkeley Laboratory 2001
Fourth generation	Magnesium/alkaline earth metal alloy Mg-Ca[11],Mg-Ba[12],Mg-Sr[12] AIST 2009

However, when the Mg-Ni alloy thin film is used as the switching mirror layer, the sample is slightly brown in the transparent state although it has excellent switching property. This color is not considered preferable for use in the windows of buildings and vehicles. Therefore, we conducted research for improving the color neutrality in the transparent state, and found that almost coloreless transparency can be obtained in cases of hydrogenation by using the Mg-Ti alloy[14] or Mg-Nb alloy[15] as the switching layer. However, although the Mg-Ti alloy thin film or Mg-Nb alloy thin film is colorless in the transparent state, the visible light transmittance is inferior compared to the Mg-Ni alloy thin film. Our research group recently found that we could obtain colorlessness during hydrogenation and increase the visible light transmittance by using the thin films of Mg-Ca,[11] Mg-Ba, and Mg-Sr[12] alloys. Figure 2 shows the optical transmittance spectra in the transparent state of each material. The materials of magnesium and alkaline-earth metal can be called the fourth generation materials made originally by AIST, unlike the



Mirror state

Transparent state

Fig. 1 (a) Basic structure of the switchable mirror, and (b) the magnesium-nickel (Pd/Mg_6Ni) switchable mirror thin film with excellent optical property developed at AIST

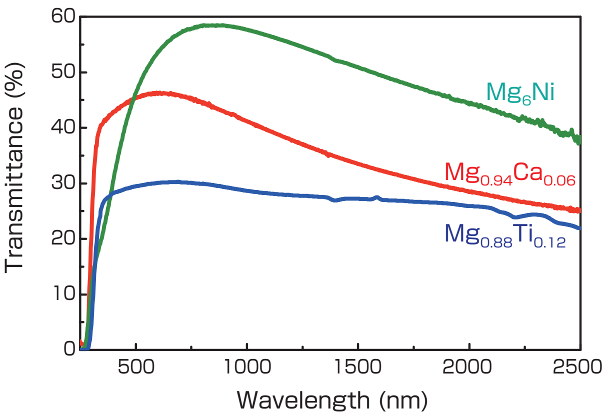


Fig. 2 Comparison of the transmission spectra in the transparent state of the magnesium-nickel (Mg_6Ni) switchable mirror, magnesium-titanium ($Mg_{0.88}Ti_{0.12}$) switchable mirror, and magnesium-calcium ($Mg_{0.94}Ca_{0.06}$) switchable mirror

conventional switchable mirror thin film category. Their practical use is expected.

At what level the variation range of the transmittance and reflectivity is set depends on the use. For example, for use in the windshield of a car, visible light transmittance of 70 % or above in the transparent state is necessary, and this condition has not been cleared at present. To raise the transmittance to this level, it is necessary to optically design the whole multilayer thin film including the palladium and protective film layers, not just the switchable layer composed of magnesium alloy thin film. We are currently engaging in this development.

2.2 Improvement of durability

For the switchable mirror thin film material, a product with fairly practical performance has been achieved in terms of its optical property. However, the greatest problem of this material is the rapid deterioration due to repeated switching. For example, Fig. 3(a) shows the variation in the optical transmittance at wavelength of 670 nm when switching is repeated using hydrogen gas diluted to 4 % using argon, for the Pd/Mg_4Ni thin film. It can be seen that the optical variation range gradually decreases with repeated switching, and the deterioration progresses rapidly particularly after 140 times.[16] In the practical use of the switchable mirror, the improvement of durability is the most important issue, and we have made various attempts to improve this.

Deterioration occurs due to a combination of several factors, and one factor is that the Mg in the Mg-Ni thin film migrates to the surface through the Pd layer, due to the repetition of hydrogenation and dehydrogenation. We found that the migration of Mg can be controlled by inserting a metal thin film of Ti or others as a buffer layer between the Pd and Mg-Ni layers.[17] As seen in Fig. 3(b), the deterioration does not occur up to about 400 times when this buffer layer is inserted. However, rapid deterioration occurs in this sample also. This is due to the change in volume due to the hydrogenation and dehydrogenation, and this damages the Pd layer. To prevent this, a certain type of protective film is useful. For example, when the Teflon (PTFE) protective film was vapor-deposited on the surface of the sample to which the Ti buffer layer is inserted, the switching could be repeated up to about 1,500 times (Fig. 3(c)).[18] Yet for practical use, durability of about 10,000 times is necessary, and we are continuing the research for further improvement of durability.

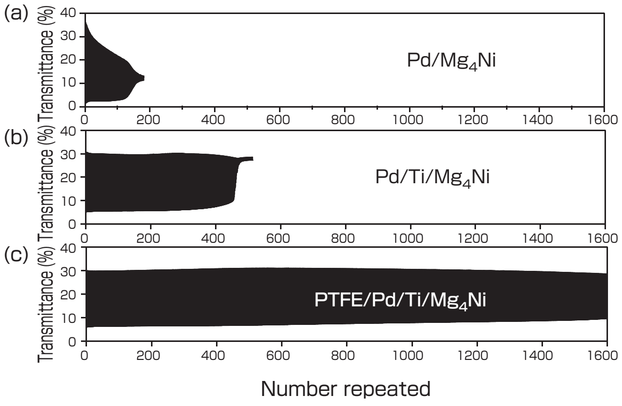


Fig. 3 Comparison of switching durability

(a) Switchable mirror thin film with magnesium alloy layer and palladium layer only, (b) switchable mirror thin film with inserted buffer layer, and (c) switchable mirror thin film with buffer layer and protective film coating (Teflon layer).

2.3 Realization of the electrochromic switchable mirror

To switch the switchable mirror by a gaschromic method, it is necessary to use the double layer (pair) glass. Since this may be difficult depending on the use, electric switching may become necessary in some cases. For switching by an electrochromic method, we initially studied a device using an alkaline water solution. However in a device that uses a solution, the magnesium dissolves when the positive charge is applied to the switchable thin film side and short-circuiting was the only way to return from the transparent to the mirror state, and this was not practical. Therefore we developed an all-solid-state electrochromic switchable mirror that did not use the solution state.[19]

Figure 4 shows the structure of the all-solid-state switchable mirror device that is being fabricated presently.[20] It is a multilayer structure in which the transparent conductive film (ITO), tungsten oxide thin film, tantalum oxide thin film, Al thin film, Pd thin film, and Mg-Ni alloy thin film are stacked. The films are fabricated by the magnetron sputtering method. The tungsten oxide thin film is a layer for storing the hydrogen ion, tantalum oxide thin film is the electrolyte layer, Pd thin film is the layer for promoting the passing of hydrogen, and the Mg-Ni alloy thin film is the switchable layer that switches from the mirror to the transparent state. The Al thin film is the buffering layer that prevents the Pd from dispersing into the tantalum oxide layer through repeated switching. The state of

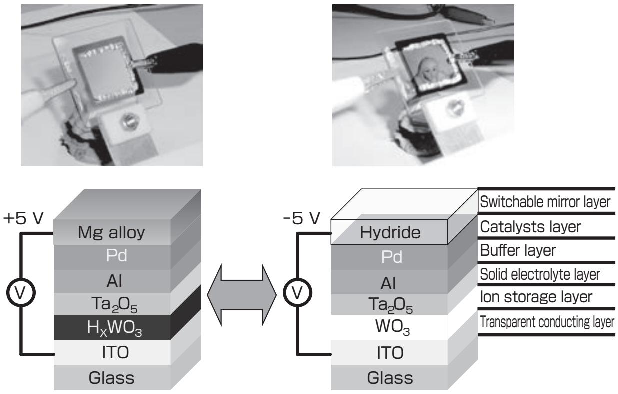


Fig. 4 Photograph and structure of the all-solid-state electrochromic switchable mirror device

switching in the fabricated device (about 3 cm on each side) is shown in Fig. 4. When -5 V voltage is applied to the switchable mirror thin film side, the Mg-Ni layer becomes hydrogenated as the hydrogen ion inside the tungsten oxide thin film transfers, and the mirror state changes to the transparent state in about 20 seconds. When +5 V is applied, the hydrogen ion drops out of the Mg-Ni layer and transfers into the tungsten oxide thin film, and the transparent state changes to the mirror state in about 15 seconds.

The switchable mirror device is characterized by the fact that any substrate can be used for film forming. Therefore, if a transparent plastic substrate is used instead of a glass substrate, a bendable switchable mirror film can be fabricated. The plastic device where switching can be done at the same level as the glass substrate has been successfully developed.[21] If the switchable mirror film can be realized, the switchable mirror property can be achieved by simply covering the existing glass with it, and the range of application will expand significantly.

For the gaschromic switchable mirror, a sample with a large surface area can be fabricated easily by a large sputtering machine, and switching can be accomplished in about 20 seconds even if it is of a meter size. However, for the electrochromic switchable mirror, the switching speed declines rapidly as the size increases, and initially, a piece of glass of about 15 cm square took about one hour to switch. We worked to increase the switching speed using various methods, and currently, switching can be accomplished in about 30 seconds for the 15 cm square sample. Further breakthrough is necessary to realize an electrochromic switchable mirror of larger sizes, and this is being studied as the most important topic for the electrochromic switchable mirror.

3 Research scenario for achieving practical use of the switchable mirror glass

To achieve practical use of the switchable mirror glass, joint research with glass manufacturers is mandatory. However, as mentioned in the “Introduction,” the Japanese glass manufacturers terminated the research for switchable glass at around 2000, and it was necessary to raise the awareness of the glass manufacturers that this can be done practically and it is worth restarting the R&D for switchable glass. Therefore, we thought it was important to speed up solving the unsolved problems at that moment, and to show how much energy-saving performance would increase when this glass was used.

The Materials Research Institute for Sustainable Development not only studies the materials, but also has a dedicated building to measure the energy-saving performance when such materials are used. Figure 5 is the photograph of the Testing Facility of Energy Performance that is built on the compounds of the AIST Chubu in Nagoya. The third floor of this building is divided into small rooms each with a size of about 2.5 m on one side. There is a single window on the south side of each room, and two windowpanes can be installed. Each room is equipped with the same air conditioning device, and the power consumption of the air conditioning can be monitored individually. By installing various types of windowpanes in each room, the load on the air conditioning for each room when it is set at a certain temperature can be compared. As described in the following chapter, the switchable mirror glass that can be installed in a building was fabricated, the energy-saving capacity was evaluated and compared with the conventional energy-saving glass, and the major reduction on the cooling load was demonstrated. By conducting measurements in this environment, important findings were obtained that could not be obtained if the research was limited to studying materials only. For example, it was found that the orientation of the window was very important with the energy-saving glass and that it is necessary to carefully consider the entry of sunlight. By feeding back such findings to the materials research, the development of glass with higher energy-saving performance becomes possible.

On the other hand, the switchable mirror thin film has various uses other than for building glass. Figure 6 shows the major applications. In achieving practical use of these materials,

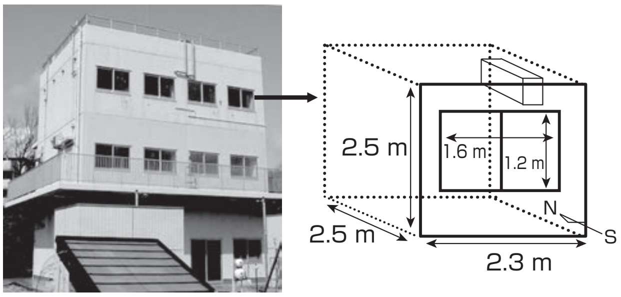


Fig. 5 Environment Friendly Experiment Building

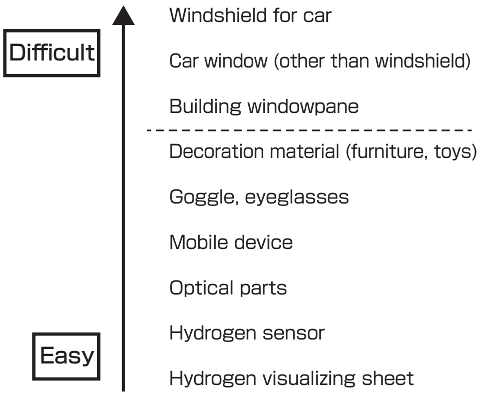


Fig. 6 Application of the switchable mirror thin film

there are cases that can be relatively easily commercialized and those that are quite difficult. While we are ultimately aiming to achieve practical use of the switchable mirror for windows of buildings and vehicles, our strategy is to create commercial products starting from those that are possible, in the process of reaching our final goal.

For example, the switchable mirror thin film undergoes optical change when it comes into contact with an atmosphere containing hydrogen, and therefore, hydrogen can be detected by observing this optical change.[22] The conventional hydrogen sensors must be heated, and the sensor may become an ignition source in cases where the hydrogen leaks. The hydrogen sensor that uses the switchable mirror thin film reacts with hydrogen at room temperature so there is no need of heating. Also, the switchable mirror thin film deposited on the tip of the optical fiber can be used as the sensor, and the reflectivity variation can be used for monitoring using the fiber end. This allows the hydrogen sensor to be of no danger of becoming an ignition source, as there will be no electrical circuit on the detector part. Also, as a unique usage of this material, it can be used as a “hydrogen visualizing sheet” where the presence of hydrogen can be checked visually as with the litmus paper. Since this could be relatively easily put to practice, it was commercialized by our joint researcher Atsumitec Co., Ltd., and the product has become available on the market from 2010. From the last fiscal year, joint research has been started for use in relatively small-scale applications in specific products.

4 Demonstration of energy-saving performance

Among the applications of the switchable mirror thin film, the use for which there is greatest expectation is for the energy-saving windowpane. However, the degree to which energy-saving performance could be obtained when the switchable mirror glass is used was unknown. Therefore, we fabricated a large switchable mirror glass that can actually be installed in a building, and conducted the measurements of energy-saving performance.[23]

For the windowpane that can be installed in a building, we fabricated the switchable mirror glass with the structure shown in Fig. 7(a). Pair glass consisting of two panes of transparent glass of 5 mm thickness with 8 mm gap in between was prepared, and the switchable mirror thin film was deposited using Mg_4Ni thin film as the switchable layer on the inner side of the glass on the outside of the room or building. The size when mounted on the aluminum sash was 1.2 m in height and 0.8 m in width. Figures 7(b) and (c) are photographs of the mirror and transparent states of the fabricated switchable mirror windowpane. This is the view of the switchable mirror window from outside the building. It was almost a perfect mirror in the mirror state, and the interior of the room could not be seen. When it was switched to the transparent state, the window on the opposite side could be seen through the room, and it was like a transparent glass. Another characteristic of the switchable mirror glass is that, in the mirror state, the view outside can be seen when the person inside the room gazes outside from the window.

The fabricated full-size switchable mirror windowpane was installed in the Testing Facility of Energy Performance seen in Fig. 5, and the measurements of the cooling load were taken. Figure 8 shows the measurements taken at the end of August. Before the measurement, the same transparent double glasses were installed in two rooms, and the temperature was set to 28 °C to check that the cooling loads were the same. Next, the window of one room was changed to the switchable mirror glass, switched to the mirror state, and the cooling load power was measured. On that day, the cooling load of the room with the transparent glass window was 1,065 Wh, while the cooling load of the room with the switchable mirror window in the mirror state was 720 Wh, and about 34 % energy savings was accomplished. It was demonstrated that when the switchable mirror windowpane in the mirror state was used, there was a significant reduction of the cooling load particularly on days with high solar radiation.

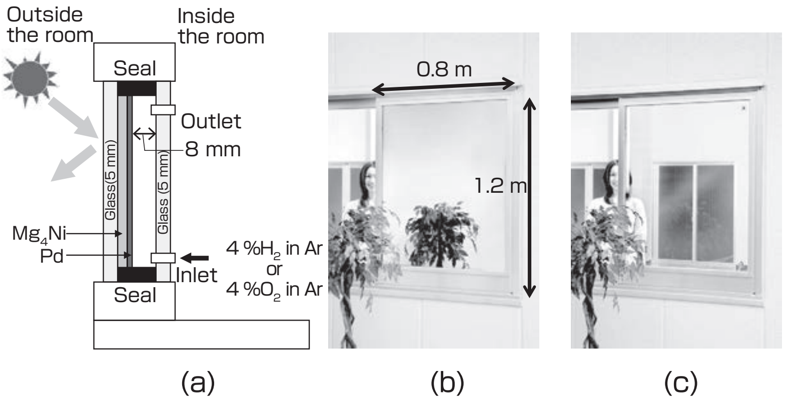


Fig. 7 Switchable mirror windowpane of actual size
(a) Structure, (b) mirror state, and (c) transparent state

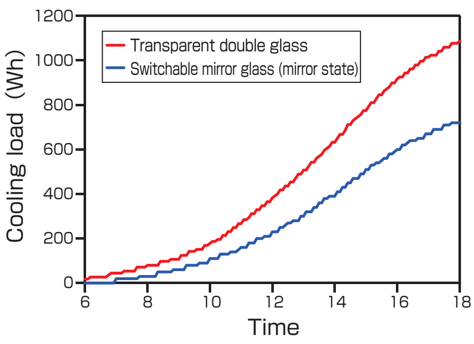


Fig. 8 Comparison of the cooling load using windows fit with transparent double glass and switchable mirror glass

5 Conclusion

We have been conducting research to achieve practical use of the switchable mirror for about ten years. Some applications that were relatively easy to put into practice have been commercialized. In the research for using the switchable mirror thin film in the energy-saving windowpane, we not only conduct the R&D for materials, but also conduct the measurements of energy-saving effect when it was actually used in a building. By reflecting the result in the material development, we are conducting research to realize a windowpane with higher energy-saving performance.

According to the experiment results obtained so far, the cooling load reduction using the switchable mirror windowpane is greater than any other energy-saving windowpane reported so far, and we hope to contribute to the CO_2 reduction in the civilian sector, by achieving practical use of this product as soon as possible.

Acknowledgement

Part of this research was conducted using the grant from the New Energy and Industrial Technology Development Organization (NEDO). We are thankful to Bao Shanhu who was our joint researcher and a special researcher at AIST (currently at the Shanghai Institute of Ceramics, China).

References

[1] C. G. Granqvist: *Handbook of Inorganic Electrochromic Materials*, Elsevier, Amsterdam, (1995).

[2] P. Jin, G. Xu, M. Tazawa and K. Yoshimura: Design, formation and characterization of a novel multifunctional window with VO_2 and TiO_2 coatings, *Applied Physics A - Materials Science & Processing*, 77, 455-459 (2003).

[3] V. Wittwer, M. Datz, J. Ell, A. Georg, W. Graf and G. Walze: Gaschromic windows, *Solar Energy Materials and Solar Cells*, 84, 305-314 (2004).

[4] J. N. Huiberts, R. Griessen, J. H. Rector, R. J. Wijngaarden, J. P. Dekker, D. G. de Groot and N. J. Koeman: Yttrium and lanthanum hydride films with switchable optical properties, *Nature*, 380, 231-234 (1996).

[5] P. van der Sluis, M. Ouwerkerk and P. A. Duine: Optical switches based on magnesium lanthanide alloy hydrides, *Applied Physics Letters*, 70, 3356-3358 (1997).

[6] M. Ouwerkerk: Electrochemically induced optical switching of $Sm_{0.3}Mg_{0.7}H_x$ thin layers, *Solid State Ionics*, 113-115, 431-437 (1998).

[7] D. G. Nagengast, A. T. M. van Gogh, E. S. Kooij, B. Dam and R. Griessen: Contrast enhancement of rare-earth switchable mirrors through microscopic shutter effect, *Applied Physics Letters*, 75, 2050-2052 (1999).

[8] T. J. Richardson, J. L. Slack, R. D. Armitage, R. Kostecki, B. Farangis and M. D. Rubin: Switchable mirrors based on nickel-magnesium films, *Applied Physics Letters*, 78, 3047-3049 (2001).

[9] B. Farangis, P. Nachimuthu, T. J. Richardson, J. L. Slack, B. K. Meyer, R. C. C. Perera and M. D. Rubin: Structural and electronic properties of magnesium-3D transition metal switchable mirrors, *Solid State Ionics*, 165, 309-314 (2003).

[10] T. J. Richardson, J. L. Slack, B. Farangis and M. D. Rubin: Mixed metal films with switchable optical properties, *Applied Physics Letters*, 80, 1349-1351 (2002).

[11] Y. Yamada, S. Bao, K. Tajima, M. Okada and K. Yoshimura: Optical properties of switchable mirrors based on magnesium-calcium alloy thin films, *Applied Physics Letters*, 94, 191910 (2009).

[12] Y. Yamada, H. Sasaki, K. Tajima, M. Okada and K. Yoshimura: Optical switching properties of switchable mirrors based on Mg alloyed with alkaline-earth metals, *Solar Energy Materials and Solar Cells*, 99, 73-75 (2012).

[13] K. Yoshimura, Y. Yamada and M. Okada: Optical switching of Mg-rich Mg-Ni alloy thin films, *Applied Physics Letters*, 81, 4709-4711 (2002).

[14] S. Bao, K. Tajima, Y. Yamada, M. Okada and K. Yoshimura: Color-neutral switchable mirrors based on magnesium-titanium thin films, *Applied Physics A-Materials Science & Processing*, 87, 621-624 (2007).

[15] S. Bao, K. Tajima, Y. Yamada, P. Jin, M. Okada and K. Yoshimura: Optical properties and degradation mechanism of magnesium-niobium thin film switchable mirrors, *Journal of the Ceramic Society of Japan*, 116, 771-775 (2008).

[16] K. Yoshimura, Y. Yamada, S. Bao, K. Tajima and M. Okada: Degradation of switchable mirror based on Mg-Ni alloy thin film, *Japanese Journal of Applied Physics*, 46, 4260-4264 (2007).

[17] S. Bao, Y. Yamada, M. Okada and K. Yoshimura: Titanium-buffer-layer-inserted switchable mirror based on Mg-Ni alloy thin film, *Japanese Journal of Applied Physics*, 45, L588-590 (2006).

[18] S. Bao, K. Tajima, Y. Yamada, M. Okada and K. Yoshimura: Metal buffer layer inserted switchable mirrors, *Solar Energy Materials and Solar Cells*, 92, 216-223 (2008).

[19] K. Tajima, Y. Yamada, S. Bao, M. Okada and K. Yoshimura: Durability of all-solid-state switchable mirror based on magnesium-nickel thin film, *Electrochemical and Solid State Letters*, 10, J52-J54 (2007).

[20] K. Tajima, Y. Yamada, S. Bao, M. Okada and K. Yoshimura: Aluminum buffer layer for high durability of all-solid-state switchable mirror based on magnesium-nickel thin film, *Applied Physics Letters*, 91, 051908 (2007).

[21] K. Tajima, Y. Yamada, S. Bao, M. Okada and K. Yoshimura: Flexible all-solid-state switchable mirror on plastic sheet, *Applied Physics Letters*, 92, 041912 (2008).

[22] K. Yoshimura, S. Bao, N. Uchiyama, H. Matsumoto, T. Kanai, S. Nakabayashi and H. Kanayama: New hydrogen sensor based on sputtered Mg-Ni alloy thin film, *Vacuum*, 83, 699-702 (2008).

[23] K. Yoshimura, Y. Yamada, S. Bao, K. Tajima and M. Okada: Preparation and characterization of gaschromic switchable-mirror window with practical size, *Solar Energy Materials and Solar Cells*, 93, 2138-2142 (2009).

Authors

Kazuki YOSHIMURA

Completed the doctor's course in Materials Science and Engineering at the Graduate School of Pure and Applied Sciences, University of Tsukuba in 1986. Doctor of Engineering. Joined the National Industrial Research Institute of Nagoya (currently, AIST Chubu) in 1986. Engaged in the research for switchable glass under the Sunshine Project and New Sunshine Project. Visiting researcher at the Fritz Haber Institute (Germany) in 1993. Currently, leader of the Energy Control Thin Film Group, Materials Research Institute for Sustainable Development. Received the Tanahashi Award of the Electrochemical Society of Japan in 2010, for the research of switchable mirror. Double duty as the visiting professor of Gifu University since 2004. In this research, was in charge of the supervision of research and the evaluation of the energy-saving performance.

Kazuki TAJIMA

Completed the third year of doctor's program at the Graduate School of Engineering, Tohoku University in 2003. Special researcher at AIST in 2003. Joined AIST in 2006. Doctor (Engineering). Engaged in the R&D of electrochromic switchable mirror. Currently, senior research of the Energy Control Thin Film Group, Materials Research Institute for Sustainable Development. Specialties are metal materials (thin film, bulk), functional ceramic materials, and property analysis of devices made of such materials. Recently, engages in the development of new materials by using the organic polymer materials. Received the Tanahashi Award of the Electrochemical Society of Japan in 2010. In this research, was in charge of the electrochromic switchable mirror.

Yasusei YAMADA

Completed the doctor's course at the Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya University in 1998. Doctor (Engineering). Joined the National Industrial Research Institute of Nagoya (currently, AIST Chubu) in 1998. Visiting researcher at the Ångström Laboratory, Uppsala University (Sweden) for one year from 2005. Worked as the planning officer of the Planning Headquarters, AIST for one year after returning to Japan. Double duty as the part-time lecturer of the Toyota National College of Technology for five years from 2007. Currently, senior researcher of the Energy Control Thin Film Group, Materials Research Institute for Sustainable Development. Received the Tanahashi Award of the Electrochemical Society of Japan in 2010. In this research, was in charge of the gaschromic switchable mirror and the evaluation of thin film.

Discussions with Reviewers

1 Process of discovering the Mg-Ca, Mg-Ba, and Mg-Sr switchable mirror materials

Question (Norimitsu Murayama, Advanced Manufacturing Research Institute, AIST)

Your discovery that Mg-Ca, Mg-Ba, and Mg-Sr have excellent properties as switchable mirror materials is wonderful. Please describe the process by which you made this discovery. Did you evaluate the properties by making certain projections? Or did you come across them through serendipity?

Answer (Yasusei Yamada)

Another research group at the Materials Research Institute for Sustainable Development was conducting research to make magnesium non-flammable, as this metal was difficult to use due to its highly ignitable property. This research had a totally different objective from our research, and it was discovered that magnesium becomes less flammable by adding calcium. In the switchable mirror, it is necessary to control the oxidation of magnesium to increase durability. Knowing the result of that group, we thought if magnesium becomes less flammable by adding calcium, perhaps it would also become less prone to oxidation. That was the start in studying this material. We fabricated the material, took measurements, and found that it had excellent optical property, and this led to the discovery of the new material. In general, calcium is thought to be a highly active, unstable metal, and if we were not at the Materials Research Institute for Sustainable Development, we wouldn't have had the opportunity to learn about fire-resistant magnesium, because that is research in a different field, and we would never have thought of adding calcium to magnesium that is also highly active.

2 Intellectual property strategy for the Mg-Ca, Mg-Ba, and Mg-Sr switchable mirror materials

Question (Norimitsu Murayama)

For obtaining the intellectual property rights for the Mg-Ca, Mg-Ba, and Mg-Sr switchable mirror materials, can you tell us what were your strategies and what problems you faced, as much as you can disclose?

Answer (Yasusei Yamada)

In Japan, our research group owns the patents for the basic materials of the switchable mirror. However, in Europe and the US, the patent for the thin films of alloys of magnesium and almost all transition metals have been taken. To escape this limitation, we applied for the patent for the switchable mirror material using the thin films of alloys of magnesium and alkaline-earth metals. In this case, we carefully studied why the addition of the alkaline-earth metal was more effective compared to the conventional transition metals, and rather than giving the phenomenological description of the effect, we claimed the superiority of the material from a logical perspective. By doing so, we stated that the magnesium alloy thin film with added alkaline-earth metal was a totally new category of material for the switchable mirror. Whenever a patent for a basic material is taken, the patent may not be accepted if it is merely improvement done on the structure of the device that uses that material. Therefore, significance of being able to file the patent as our original basic material is great.

3 Novelty of all-solid-state switchable mirror device

Question (Norimitsu Murayama)

Is the all-solid-state switchable mirror device the authors' idea?

Answer (Kazuki Yoshimura)

Although the all-solid-state device had been developed for the conventional electrochromic material that uses tungsten oxide thin film as the switchable layer, the switchable mirror using the magnesium alloy thin film had not been realized. Initially, the device was fabricated by layering the switchable, electrolyte, and counter electrode layers according to the structure of conventional all-solid-state switchable electrochromic element, but the device did not work. As a result of reviewing why it did not function, we thought that the layers should be reversed for the switchable mirror. We created a device with the reverse structure, and were able to develop a device with a good switching function. This reversed multi-layer thin film structure is our original idea.

4 Organization of the issues for achieving practical use of the switchable mirror glass

Question (Kazuo Igarashi, Institute of National Colleges of Technology, Japan)

As the three issues in achieving the practical use of the switchable mirror glass, you mention the improvement of optical property, the improvement of durability, and the development of an electrochromic method. While the former two are essential issues that must be cleared, the third does not seem to be a requirement since it depends on the use. What are your thoughts on this?

Answer (Kazuki Yoshimura)

Since the usage of a gaschromic method is very limited, switching by an electrochromic method is important in achieving practical use. In 2002, we had no idea whether switching could be done by an electrochromic method for the magnesium alloy thin film, and it was an important point in the practical use research of the switchable mirror.

5 Positioning of the upsizing technology in achieving practical use of the switchable mirror glass

Question (Kazuo Igarashi)

In upsizing from the laboratory level to actual use level, it can be expected that new issues will arise such as optical property or durability. Therefore, I think upsizing was a major issue in practical use, but it is not mentioned in this paper. How should I consider the positioning of upsizing in the practical use strategy?

Answer (Kazuki Tajima)

Upsizing can be done relatively easily for the gaschromic method, while it is a problem for the electrochromic method. I added some description on this point.

6 Durability of the switchable mirror

Question (Norimitsu Murayama)

You mention that the durability for repeated switching in achieving practical use of the switchable mirror is currently about 1,500 times. What is the prospect of extending the durability to about 10,000 times?

Answer (Yasusei Yamada)

For durability, there was a major progress recently, and we are finding out that we may be able to develop a switchable mirror material with hardly any deterioration. By developing this technology, we have the prospect of creating a material with durability of about 10,000 times within this fiscal year.

7 Efforts for achieving practical use of the switchable mirror glass

Question (Norimitsu Murayama)

You quantitatively demonstrated the energy-saving effect of the switchable mirror glass at the Environment Friendly Experiment Building. As a result, how did the way the industry look at switchable mirror glass change? Also, do you have any plans such as setting up some corporate consortium as the scenario for achieving practical use of the switchable mirror glass?

Answer (Kazuki Yoshimura)

For the switchable mirror, the people of the glass manufacturers have been paying attention to it since 2003 as a new switchable material. However, due to the historical progress as described in this paper, they decided to sit and wait to see whether this material could actually be put to use. In such a situation, fabricating the switchable mirror windowpane that can be actually installed in a building and demonstrating the large cooling load reduction effect compared to other energy-saving glass materials were regarded with great enthusiasm. The glass manufacturers are specifically considering joint research.

To take the switchable mirror glass to the stage of an actual product that can be used as the windowpane for buildings, the developments of parts other than the switchable mirror thin film, such as the switching system that can be used in actual windowpanes and its power supply system are necessary. Currently, the research is being continued, and the prospect for practical use is good if these issues are solved. At that point, we plan to make powerful appeals to the glass manufacturers and accelerate the practical use research by perhaps forming a consortium.

Standardization of environmental analysis methods of hazardous chemicals

— Contribution to international control of hazardous chemicals by using advanced technologies —

Sachi Taniyasu[1], **Nobuyasu Hanari**[2], **Yuichi Horii**[3] **and Nobuyoshi Yamashita**[1] *

[Translation from *Synthesiology*, Vol.5, No.4, p.261-276 (2012)]

The development and dissemination of reliable analysis methods and reference materials, and the accumulation of high-quality analytical data are important to: (1) understand the environmental impact of hazardous chemicals; (2) evaluate the safety and effectiveness of international treaties regarding these chemicals; and (3) formulate policies accordingly. We published an international standard method for analysis of hazardous chemicals, using recent data on hazardous chemical usage and environmental persistence, before international regulations came into force. Here, we describe the development of our method, its adoption as ISO and JIS standards, and the significance of these achievements.

Keywords **:** ISO 25101, PFOS, environmental analysis, Stockholm convention on persistent organic pollutants (POPs), hazardous chemicals

1 Introduction

Many chemical substances are manufactured and used to support our life in a convenient and efficient way. However, some of the chemical substances may affect humans or the ecological system even if they are present in the environment in small amounts. The nonylphenol (NP, Fig. 1), perfluorooctanesulfonic acid (PFOS, Fig. 2), and perfluorooctanoic acid (PFOA, Fig. 2) that are subjects of this research are recognized as endocrine disrupting chemicals (EDCs) and persistent organic pollutants (POPs), respectively. For NP, the environmental standard for water quality was set in 2012 in consideration of its effect on aquatic organisms. To take appropriate measures against the environmental issues that may be caused by such chemical substances, it is mandatory to understand the environmental load capacity and to clarify the global environmental dynamics. In order to prevent pollution and understand the distribution of such chemical substances in the environment, it is necessary to develop the analysis method which allows high sensitivity and precise detection. Particularly, in the measurement of ultra-trace substances, erroneous measurement may unnecessarily inflate social anxiety and may result in wrong countermeasures. Therefore, the accumulation of reliable analysis data for hazardous chemical substances in the environment is extremely important.

In fact, many literatures and reports are gathered for the risk assessment (document that summarizes the risk outline) of hazardous substances which becomes the basis for the discussion in the Stockholm Convention on Persistent Organic Pollutants (hereinafter, POPs Convention). However, the individual analysis methods and the quality assurance and quality control (QA/QC) of each chemical are rarely discussed in detail, and presently, the quality and reliability of these analyses are not thoroughly considered.

In the global environmental issue, it is essential that any value, such as the concentration of CO_2 in the atmosphere causing global warming, measured in any part of the world, can be considered reliable and mutually comparable. To achieve this goal, we aimed to develop an analysis method with high reliability, and establish the international standard for the analysis method for the environmental researchers and analysts around the world. We also aimed to create a certified reference material (CRM), so the analysis value will be traceable to the SI unit. As a reference concerning the standardization of the environmental analysis method, the system of ISO and JIS will be briefly explained below.

The ISO standardization is conducted by the technical

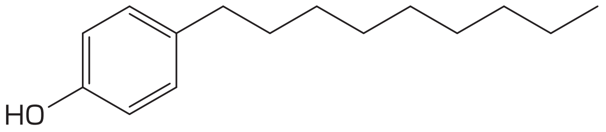


Fig. 1 Structural formula for linear nonylphenol (NP)

---

1. Research Institute for Environmental Management Technology, AIST 16-1 Onogawa Tsukuba 305-8569, Japan
＊ E-mail: nob.yamashita@aist.go.jp
2. National Metrology Institute of Japan, AIST Tsukuba Central 3, 1-1-1 Umezono, Tsukuba 305-8563, Japan,
3. Center for Environmental Science in Saitama 914 Kamitanadare, Kazo 347-0115, Japan

Original manuscript received June 27, 2012, Revisions received September 21, 2012, Accepted September 25, 2012

committees (TC) of each field. There are two TCs for environmental measurement: TC146 (Atmosphere) and TC147 (Water quality). Each TC is divided further into subcommittees (SC) and working groups (WG), and each WG has an appointed convener who organizes the international meetings and writes the standardization draft. The NP (ISO 24293:2009[1]) and PFOS/PFOA (ISO 25101:2009[2]) were handled in the subcommittees ISO/TC147 (Water Quality) / SC2 (Physical, Chemical and Biochemical Methods). They were discussed and standardized in the working groups WG17 (Phenols) and WG56 (PFOS/PFOA), respectively.

The JIS for environmental measurement includes: K 0101 and K 0102 for environmental indices, inorganic ion and metals, etc; K 0125 for volatile organic compounds; K 0128 for agrochemicals; and K 0312 for dioxins. The NP (K 0450-60-10:2007[3]) and PFOS/PFOA (K 0450-70-10:2011[4]) that were standardized in this research were established in the K 0450 series. The K 0450 series were originally started in 1998 to standardize the measurement of organic chemical substances that may affect humans or the ecosystem at trace amount in irrigation water and wastewater, when the endocrine disrupting substances started to raise attention. Bisphenol-A (K 0450-10-10), alkylphenols (K 0450-20-10[5]), phthalate ester (K 0450-30-10), bis (2-ethylhexyl) adipate (K 0450-40-10), and benzophenone (K 0450-50-10) were also standardized in the K 0450 series. The JIS standardization of NP was started at about the same time as the ISO, and the JIS standardization of PFOS/PFOA was set after ISO standardization as a MOD (partially modified standard).

In this report, the discussion on the environmental behavior of hazardous chemical substances and the development of their analysis method, as well as two case studies of ISO standards[1][2] and JIS standards[3][4] are described to illustrate the research process for standardization and the significance of such research.

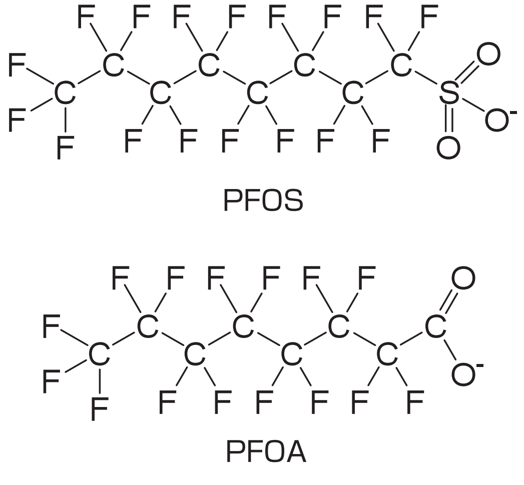


Fig. 2 Structural formulae for perfluorooctanesulfonic acid (PFOS), and perfluorooctanoic acid (PFOA)

2 Necessity and standardization of the environmental analysis technology that addresses the international regulation of hazardous chemical substances

In the international standardization for global environmental issues, the role of the public sectors, such as the international organizations and national research institutes, is important. Here, we engaged in the international standardization activities from this perspective. On the other hand, aside from international contribution, environmental analyses of the hazardous chemicals are useful in grasping the actual emissions from the Japanese industry and in executing appropriate environmental measures. Taking measures in response to the international regulation of chemical substances may become particularly essential for the continuation of a company. Hence, demands for standardization of environmental analyses were urged in Japan, and JIS standardization was promoted.

2.1 Necessity and standardization of the environmental analysis technology for NP

4-nonyphenol (NP, Fig. 1) is used as raw industrial material of nonylphenol ethoxylates (used as a nonionic surfactant in various industrial fields such as the rubber and plastic, textile, and metal processing industries), but it is strongly suspected to have an endocrine disrupting effect. Also, NP is produced by the successive breakdown of the ethoxy group of nonylphenol ethoxylate through the aerobic and anaerobic degradation in the sewage treatment process and aquatic environment. Therefore, the use of nonylphenol ethoxylate in household products was banned by the self-imposed regulation of industry. In recognition of this practice, the environmental standard pertaining to water pollution was revised in August 2012, and NP was newly added to the water quality environmental standard for the preservation of the aquatic organisms. We reported the vertical distribution of NP in outer seawater for the first time in 1998,[6] and commenced the research to determine the environmental fate and toxicity, such as developing the analysis method for NP isomers and clarifying the estrogen-like activity of various isomers.[7][8] In 2002, the necessity of the international standardization of the water analysis method for NP was explained to the Ministry of Economy, Trade and Industry. The research was selected as the Standard Certification Project (FY2002-2004) "Standardization of NP Analysis Method," and we were able to start the research for the ISO and JIS standardizations for this analysis method.

NP is a type of alkylphenol. In 2002, JIS K 0450-20-10:2002[5] existed, and for ISO, it was being drafted with Germany as the convener as ISO/CD 18857-1 (currently ISO 18857-1[9]). Both analysis methods involved the total measurement of NP as a single compound, and there was no information on the isomer composition. However, the ISO

24293 developed and standardized in this research was a method that, for the first time, separated and measured NP into 13 types of isomers with varying degrees of endocrine disrupting effect. This is equivalent to the individual measurement and selection of 17 highly hazardous isomers with different hazardous levels among the 210 isomers of dioxins (collective name for polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran). Since the NP isomers showed different estrogen-like activities, it was necessary to understand the concentrations of each isomer in the environment for accurate risk assessment, and the accumulation of the concentration data for each isomer in the environmental samples was necessary.

To standardize the developed analysis method as ISO, it was necessary to make adjustments with Germany, who was acting as the convener and was working on the total measurement method for NP (ISO 18857-1[9]) in ISO/TC147/SC2/WG17 (Phenols). Therefore, a meeting was set up for a preliminary discussion with the chairman of ISO/TC147 (Germany) and the convener for WG17 (Germany). We explained the necessity for the detailed analysis of individual isomers that enabled accurate assessment of hazards in the environment. The significance of such analysis was shared, and the new proposal by Japan on the analysis for individual isomers was approved at the ISO/TC147 meeting in 2003. As a result, the new analysis method was selected as the ISO New Work Item Proposal (NWIP) in 2005 before starting the JIS standardization,[3] and international standardization was started by the the working group for phenols (WG17). In the ISO proposal, the analysis method proposed by Japan was generally accepted in the process of discussion with the TC members, but there were several arguments about the reference material and the suspended solids (SS) in the environmental water samples. The focus was placed on the effect of analysis precision due to the amount of SS in the environmental water sample. Hence, agreement was made to conduct the quality control studies using the environmental water samples with different amounts of SS and adding this result in the Annex (Informative). For the reference material, it was necessary for the measurers themselves to evaluate the commercially available mixtures. Therefore, measurements for the mixture of commercially available materials from the five manufacturers were listed in the Annex (Informative). The details will be described in subchapters 3.1 and 4.1. After the above discussion, the working draft (WD) was submitted in 2005, followed by the committee draft (CD) in 2006, the draft international standard (DIS) in 2009, and the final draft international standard (FDIS) in 2009. Finally, the ISO 24293 was issued as the international standard in July 2009.

2.2 Necessity and standardization of the environmental analysis technology for PFOS/PFOA

PFOS and PFOA are types of perfluoroalkyl substances (PFASs) that have fluoroalkyl groups as shown in Fig. 2. Because PFOS/PFOA-related substances have extremely strong carbon-fluoride covalent bond, in addition to both hydrophobic groups (fluoroalkyl groups) and hydrophilic groups (sulfonate groups or carboxyl groups), they have excellent, diverse physical and chemical properties, such as chemical and thermal inertness, low surface energy and special surface active properties. Therefore, they have been used widely as functional industrial materials of fluororesin, state-of-the-art electronic device, semiconductors, coating, etching, photograph, emulsifiers, water repellents, soil release agents, firefighting foams, and their intermediary materials. Figure 3 shows the social and research trends of the PFOS/PFOA-related substances. The manufacturing method of the PFOS/PFOA-related substances was developed in the 1940s, and they became commercially available in the 1950s. However, PFOS was detected in high concentration in wild animals in February 2000, and the 3M Company of the United States announced the phase-out of the production of related materials in May 2000. Hence, the environmental issues due to PFOS-related substances have became widely studied and known. Thereafter, their environmental persistence, high accumulation in organisms, and concerns of the effects on humans and organisms became apparent, and they were even detected in high concentration from wild animals in the polar region.[10] In such situations, international regulations on their use and treatment of their waste were considered, and PFOS and PFOA became “Type II Monitoring Chemical Substances” under the Act on the Evaluation of Chemical Substances and Regulation of Their Manufacture, etc. of Japan (CSCL) in December 2002. In January 2006, the US Environment Protection Agency (EPA) requested the major manufacturers voluntary reduction and elimination of PFOA and PFOA precursors by year 2015, and efforts on waste reduction started by setting up guidelines for drinking water around the water treatment plant. The considerations for regulations by the POPs Convention were started in June 2005 for PFOS. In 2010, PFOS and perfluorooctane sulfonylfluoride (PFOSF) that is its raw material became the substances subject to the POPs Convention, and were designated “Type I Monitoring Chemical Substances” under the CSCL in Japan. Their production and use were banned worldwide except for certain essential use. However, measures would be delayed if the analysis method were standardized after the regulations. To execute measures efficiently in industry and society, it is necessary to ensure the appropriate risk profile by establishing a reliable analysis method before the danger of a new chemical substance becomes widely known in society. Figure 4 shows the scenario of the standardization of the PFOS/PFOA analysis method. The procedures taken in the standardization will be described below.

The Potential Pollutants Group, Research Institute for Environmental Management Technology, AIST, conducts basic researches on various potential pollutants based on the findings and results obtained from numerous international joint researches using advanced analytical devices and technology. It has been engaged in researches focused on PFOS and its related chemicals before the international regulations were enforced. As part of the international joint research with the Wadsworth Center, USA, started in 1995, our group has conducted the development of the PFOS and PFOA analysis method from 1999, and in 2000, we started the PFOS project for the first time in Japan, through the Grant for Industrial Technology Research of the New Energy and Industrial Technology Development Organization (NEDO).

In 2001, the environmental concentration of PFOS and PFOA were surveyed for the surface water and fish in Japan, and the bioconcentration factor (transfer of chemical from water to the organism), which is an important factor in risk evaluation in the actual environment, was reported for the first time in the world.[11] However, to understand the environmental fate such as long-range transport, it was mandatory to analyze the outer atmosphere and outer seawater with low concentration of 1,000 times less than the high-concentration samples of coastal water and organisms. The greatest issue in establishing the analysis method for the extremely low concentration level was the reduction of background contamination. This was because the target substance was used in various commercial products like water repellents, soil resisting agents, resin additives, and others. To reduce the contamination, contamination sources must be identified and quantified systematically from our experimental environment, analysis equipment, device, and reference material. After elimination of all possible contamination sources, the level of contamination of PFOS and PFOA were reduced by over 1,000 times.[12] The weak anion exchange solid phase extraction column (Oasis®WAX) was also deployed as the extraction method with high precision and high recovery rate.[13] As a result, the establishment of the analysis technology at several pg/L level that could be applied to the outer seawater was achieved.

The measurements of outer surface seawater and deep seawater were started using this analysis method. Unlike the method where the PFOS/PFOA research was conducted from the perspective of hazardous chemical substances, we started this research by looking at their usability as chemical tracers in global material circulation satisfying the three requirements: persistence, water solubility, and detectability in ultra-trace analysis. In 2004, the outer seawater survey data was published for the first time in the world, and showed that the substances persisted in seawater at depth of 5,000 m.[12] Through the joint collaboration with the world's top level research institutes, such as the Leibniz Institute of Germany and Wadsworth Center of the US that realized the importance of this research, international joint survey cruises were conducted to measure the vertical distribution from surface to deep seawater in the Sea of Japan, the Atlantic, the South Pacific, and the Labrador Sea. Particularly in the

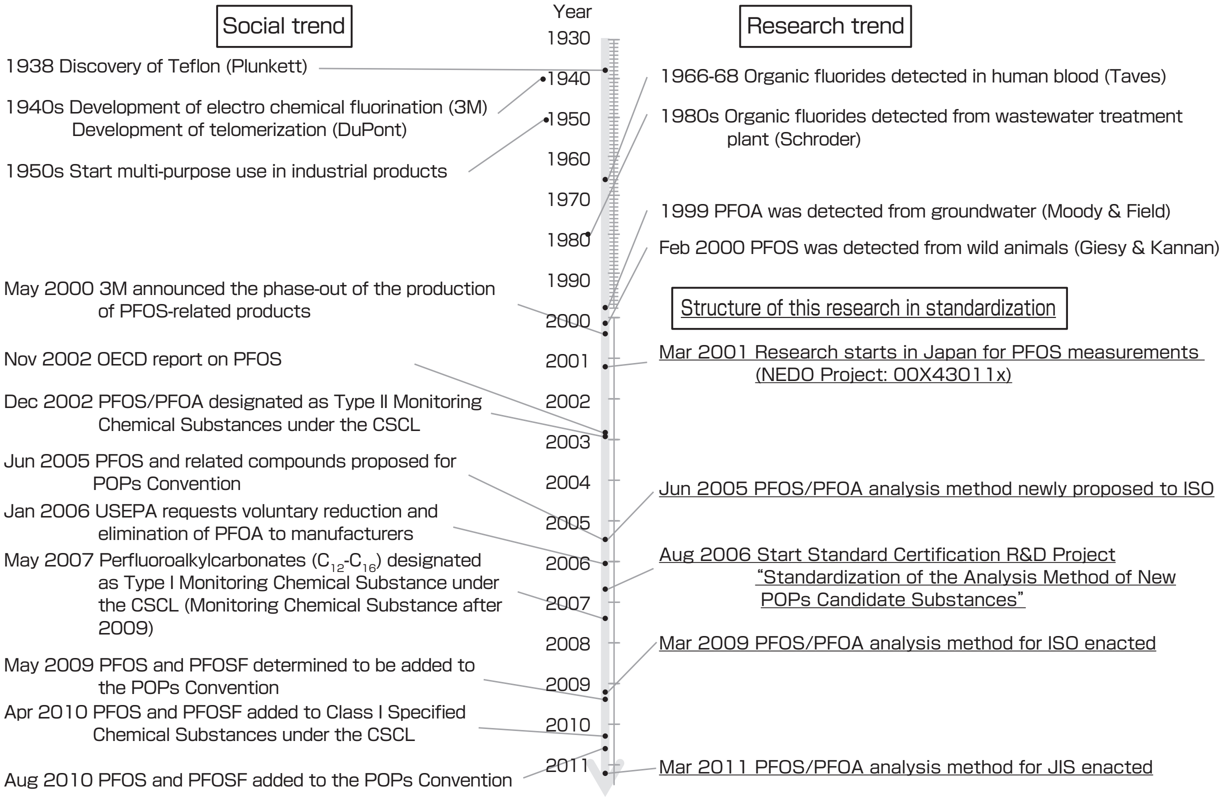


Fig. 3 Social and research trends of the PFOS/PFOA-related substances and their relationship to this research

Labrador Sea where the surface water dove straight into the depth and the surface and deep seawaters were mixed thoroughly, the vertical distribution at constant concentration was observed. It was found that PFOS was supplied to the deep seawater by the global general circulation mechanism of outer seawater by thermohaline convection.[14][15] While the conventional long-range transport mechanism of POPs was discussed only in terms of atmospheric transportation, the importance of global long-range transport mechanism by ocean current was indicated in our study. Currently, this mechanism is under investigation mainly by the oceanographers of Europe and the United States. The outer sea survey method developed by AIST is now being used worldwide, such as, the report of the surface seawater distribution of the entire Atlantic by AIST and Environment Canada, which is the leading research institute for PFOS/PFOA study in Canada, in 2012.[16]

The research accomplishments were highly evaluated in the international standardization of the analysis method, and Japan started up the working group WG56 (PFOS/PFOA) as the convener in the ISO/TC147 meeting held in June 2005, and commenced the international standardization process. The PFOS and 96 related substances were proposed as the substances subject to the POPs Convention in 2005. For standardization, research and development (R&D) (development of analysis method, improvement of analysis performance, maintenance of reliability by quality control study, etc.) and draft standard was written in the Standard Certification R&D Project (FY 2006-2008) "Standardization of the Analysis Method of New POPs Candidate Substances." Almost all of the analysis technologies proposed by Japan were accepted, but there were a few issues raised in the discussion with the TC members. First issue was the selection of the analytical device. Initially, at the start of the environmental measurement of PFOS and PFOA, liquid chromatograph mass spectrometer (LC-MS) or the so-called single MS was used instead of the liquid chromatograph tandem mass spectrometer (LC-MS/MS) that is generally used today, hence, the appropriateness of using the LC-MS was discussed. The British TC member proposed that the LC-MS should be included in the regulation in the draft process. However, LC-MS had lower selectivity compared to the LC-MS/MS and the separation from the interfering substances may be insufficient in some kinds of environmental samples. Since only one institute among the 23 institutes used it for international quality control study, the LC-MS method was only described in the Annex (Informative). Wastewater sample was proposed as a subject of analysis, but it was removed since the variation of analysis value was out of the guideline values in the international quality control study. For the related substances other than PFOS and PFOA, it was indicated that measurements could be done using the same analysis method, but only PFOS and PFOA were set as the subjects initially in the ISO standardization. The standardization would be delayed greatly if other related substances were added, and the subject substances were limited to PFOS and PFOA considering the demand for quick standardization. With the above deliberation, the WD was submitted in 2005, CD in 2006, DIS in 2007, and the FDIS in 2008. ISO 25101[2] was established as the international standard in March 2009. PFOS was added to the international POPs Convention in 2010, and was also added to the "Class I Specified Chemical Substance" under the CSCL in Japan in 2010. The international standardization was completed before the regulations for the hazardous chemical substances.

Upon the establishment of the ISO standard, the JIS

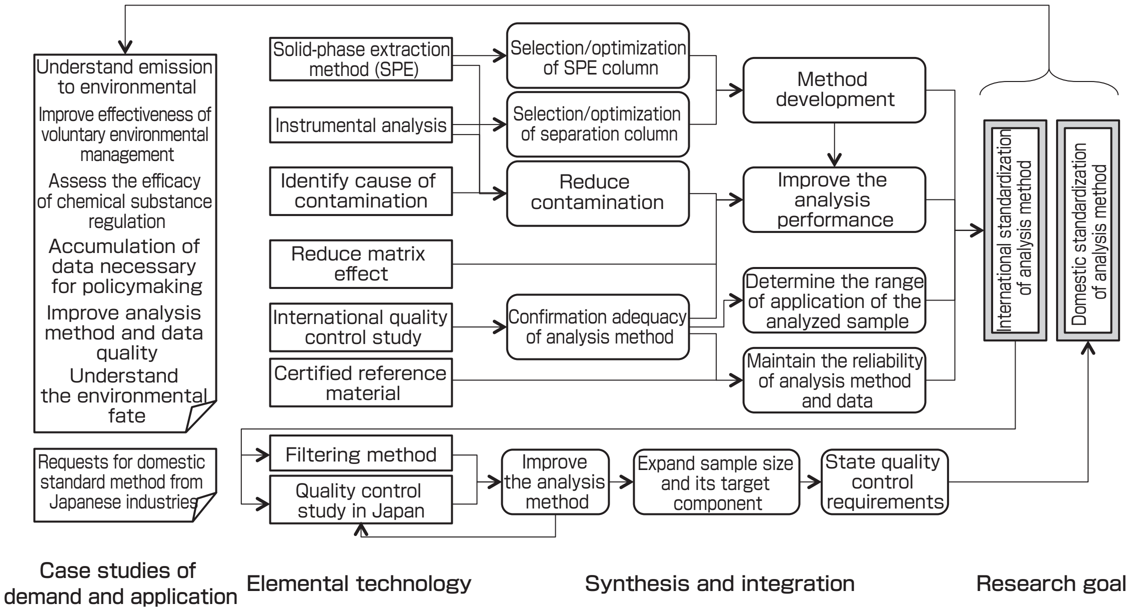


Fig. 4 Scenario for the standardization of PFOS/PFOA analysis method

standardization (in effect from March 22, 2011[4]) was done to meet the international compliance according to the principle of domestic standardization (WTO/TBT Agreement) based on the international standard, and in response to the demands from the Japanese analysis laboratories for the establishment of the Japanese standard to ensure quality control and collaborative systems in Japan. The JIS standard is the addition, removal, and modification of the rules (MOD) based on the ISO standard. The modified points of the ISO standard include: not to use the LC-MS (written in Annex (Informative) of ISO 25101), addition of filtering procedures of samples that can be applied to SS rich water such as wastewater in JIS Appendix (Informative), and the addition of possible measurements of related substances other than PFOS and PFOA in JIS Appendix (Informative). For these modifications, quality control studies were conducted twice to check the adequacy of the new analysis method.

2.3 Timing of the standardization

The common points of ISO 24293 and ISO 25101 are that they started from scientific research on the environmental behavior, internationally acclaimed results published after developing a new analysis method, and the international standardization started at the stage when de facto standard was established as a consensus among the research community. This is in opposition to the conventional flow where the domestic standardization was done after the economic and social demands manifest and then fine adjustments are made with the international standard. In other words, the public sector decided that an environmental analysis method from a global viewpoint was necessary for the appropriate international use of chemical substances and for the global environmental protection. Furthermore, to ensure that the international chemical substance regulation could be done effectively, the awareness was raised among the research community by releasing the research results as soon as possible, and efforts were made to obtain a highly reliable analysis method by providing the international standard at the same time as the enforcement of the standard. The research was conducted with the point of view that “reliable analysis value and standard analysis technologies that ensure reliability are essential in the control of hazardous chemical substances.”

3 Development of the analysis method

3.1 Development of the analysis method for nonylphenol

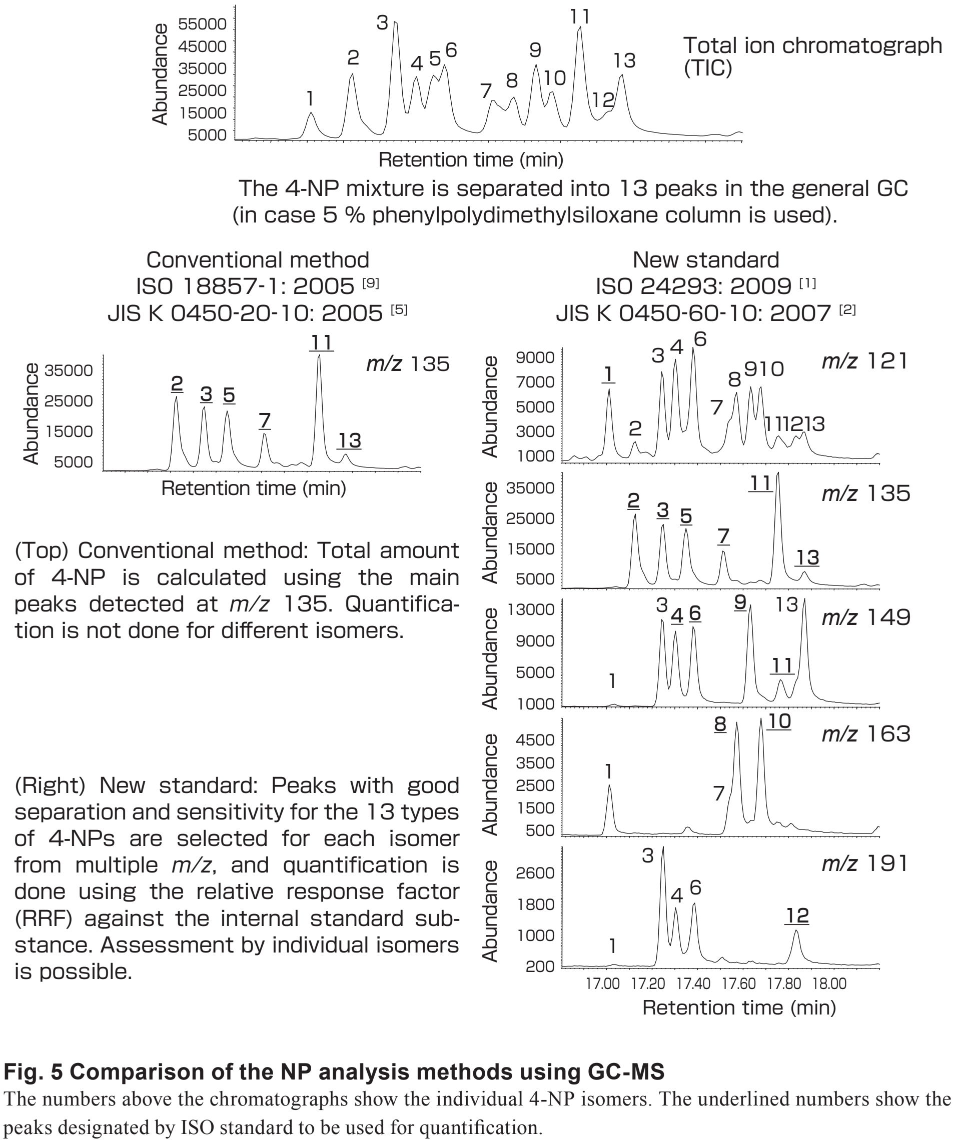
The total analysis method for NP already existed in 2002 as JIS K 0450-20-10, and the analysis of general water samples could be done.[5][9] However, other than the linear 4-NP shown in Fig. 1, there were theoretically 211 isomers of NP by different side chains and substitution sites,[17] and dozens of isomers were detected with different environmental degradability and hazardousness from the environmental samples.[18][19] Therefore, it was necessary to develop a method to accurately quantify each isomer in order to conduct a highly reliable risk assessment. Using the gas chromatograph/preparative fraction collector (GC-PFC)Term 1 that was uncommonly used in Japan at that time, the NP isomers in the mixture were separated and refined. Individual isomers were collected in the glass tube cooled by liquid nitrogen, and this procedure was repeated about 100 times until six fractions were obtained for the amount necessary for a hormone activity test. It was confirmed that the endocrine disrupting activity differed greatly for different individual isomers.[6][7][18] Next, the various commercially available capillary columns were compared to establish the optimal analysis condition for the advanced separation of the NP isomers. The method for maximum separation analysis of NP in the complex mixture was investigated using the two-dimensional gas chromatographTerm 2 mass spectrometry (GC×GC-MS), and we succeeded in separating 102 components in an NP product.[20]

While it was possible to separate NP into multiple components if such state-of-the-art analysis technology was used, from the perspective of quality control, it was necessary to have a standard where the majority of the users could obtain the same data. Therefore, for the analysis of individual NP isomers in the ISO standard, 13 NP isomers that could be separated by general GC were set as the subjects of analysis. The styrene-divinylbenzene solid phase extraction method was used as the extraction method, since it could be used universally for water analysis. Since NP was used as the raw material of nonylphenol ethoxylate, which is a nonionic surfactant that can be detected from almost all water environments, utmost care was needed for contamination control. There were possibilities that NP might be present in the silica gel column cartridge and the anti-clogging agent (glass beads) in the solid phase extraction.

The selective ion monitoring (SIM) method of the gas chromatograph mass spectrometer (GC-MS) was used, and quantification was done using ions with good sensitivity and separability for each isomer (Fig. 5). Normally, five to six peaks were detected at m/z 135 (m/z is mass-to-charge ratio, or the value obtained by dividing the charge z with mass m), but in this analysis method, the assessment for individual isomers became possible by selecting an optimal monitor ion for each of the 13 isomers, and then calculating the relative response factor (RRF) of each NP isomer and the internal standard Term 3. For the investigation of the ion selection for the NP isomer, refer to Horii *et al*. (2004).[21] The reasons for the complicated quantification of individual NP isomers are because NP is a complex mixture, the commercially available standards for their isomers are limited, and the fragmentation patternsTerm 4 differ greatly by isomers. In the situation at that time where the standards for individual isomers were not available, the only way was to use the NP mixture as a standard for quantification, and it was necessary to investigate the isomer composition in the NP mixture before hand, using the gas chromatograph flame ionization detector (GC-FID)[Term 5]. For the method development of NP, isomer compositions of the mixtures supplied by five reagent manufacturers were analyzed, and their coefficient of variation (value obtained by dividing the standard deviation by arithmetic mean; indicates relative variation) was 14 % (slightly different by isomers). To use the mixture for which the valuation of the isomer composition is done by the measurer him/herself as the quantifying standard substance is exceptional in the ISO standard. This point was discussed thoroughly in the DIS stage, and it was confirmed that there was hardly any variation in the composition among the reagent manufacturers,[22] and the information for the composition of mixtures from the five commercial companies were included in the Annex (Informative).

3.2 Development of the analysis method for PFOS/PFOA

At the time when general research for PFOS/PFOA was started in 2000, most analysis was conducted in blood samples which were considered as high concentration samples, and the analysis of environmental water was barely done. The reported analysis values had high detection limit due to background contamination, and there was no highly reliable analysis technology for low concentration environmental water. Therefore, research was done from 2001 in cooperation with the Wadsworth Center of the United States based on the solid phase extraction (SPE) [23] method using the existing octadecyl group (C18). [11] Until the new proposal of ISO 25101 in June 2005, we conducted the research to clarify the quality control condition to obtain highly reliable analysis data, by applying the developed PFOS/PFOA analysis method to various environmental samples.[11][12][14][24]-[29] The first issue in PFOS/PFOA analysis was the reduction of background contamination.[12] This was because the fluororesins such as the polytetrafluoroethylene (PTFE) that were used in various places around us as functional materials has became the contamination source, and also, system blank (contamination arising from the analysis device) tended to



The 4-NP mixture is separated into 13 peaks in the general GC (in case 5 % phenylpolydimethylsiloxane column is used).

(Top) Conventional method: Total amount of 4-NP is calculated using the main peaks detected at *m/z* 135. Quantification is not done for different isomers.

(Right) New standard: Peaks with good separation and sensitivity for the 13 types of 4-NPs are selected for each isomer from multiple *m/z*, and quantification is done using the relative response factor (RRF) against the internal standard substance. Assessment by individual isomers is possible.

Fig. 5 Comparison of the NP analysis methods using GC-MS

The numbers above the chromatographs show the individual 4-NP isomers. The underlined numbers show the peaks designated by ISO standard to be used for quantification.

be high because the state-of-the-art analysis devices had fluororesin components. To solve this issue, the system blank was reduced to tens of fg (1 fg = 10^{-15} g) by eliminating parts such as the degassing device and switching valve that were not essential for measurement by the LC-MS/MS. Because the SPE cartridge[23] that contained the existing octadecyl group (C18) was highly contaminated and not suitable for low concentration analysis, we developed the PFOS/PFOA analysis method using the Oasis®HLB cartridge that had both the hydrophilic and lipophilic properties, manufactured by the Waters Corporation. This was confirmed to have less contamination compared to the C18 SPE cartridge[23] and could be applied to low concentration samples such as the outer seawater.[26][28] However, the Oasis®HLB cartridge with excellent low contamination and high recovery rate is only limited to the measurement of PFOS/PFOA, and it was not suitable for the extraction of short-chain compounds such as perfluorobutanoic acid (PFBA). Therefore, we focused on the property of PFOS/PFOA as organic acids, and by reducing the contamination to a minimum by using the Oasis®WAX cartridge of Waters Corporation that had the anion exchange capability suitable for the adsorption and capture of acidic substance. We developed the analysis condition where carbonic acid with carbon chain length from C_2 to C_{18} and sulfonic acid from C_2 to C_{10} could be adsorbed and recovered, as well as PFOS and PFOA (Fig. 6).[13][30] The reduction of contamination and system blank of the equipment and reagents used[12][24][25] and its importance were also addressed in ISO 25101.

When an ordinary reverse phase HPLC column such as ODS (octadecylsilyl silica gel) column was used, elution occurred in the order of short to long chain, and the short-chain compound such as PFBA showed poor peak formation and the separation with the foreign substances was insufficient (Fig. 7a). On the other hand, in the separation column with ion exchange capacity, the order of elution reversed, and elution occurred from long to short chain, and the peak formation and foreign substance separation were improved (Fig. 7b).[30] Crosschecking by two types of separation columns with different separation principles by concurrent check of the ion strength ratio of the measured mass showed that the reliability dramatically increased compared to the conventional single column measurement. In both ISO 25101 and JIS method, the reverse phase column is used as the separation column since only PFOS and PFOA are subjects of analysis. However, it is written in the JIS Annex (Informative) that the measurement of related chemical substances with short-chain compound other than PFOS and PFOA can be measured, the reverse phase column and the separation column with ion exchange capacity are both described, and the importance of crosschecking using the two types of separation columns is discussed.

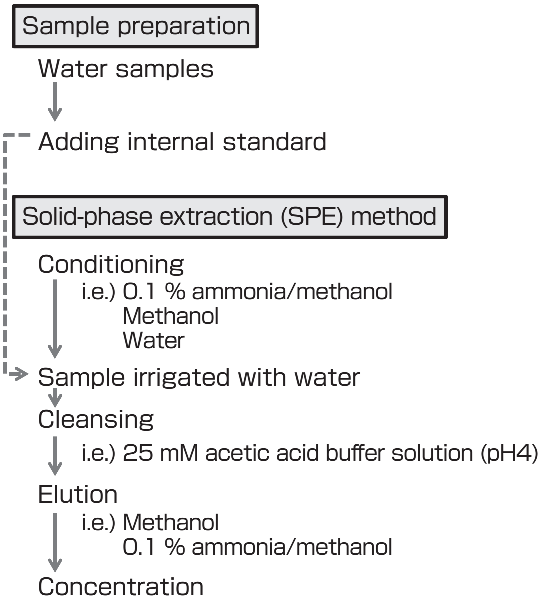


Fig. 6 Solid phase extraction method using the weak anion exchange cartridge (Oasis®WAX)

In general, when the detection sensitivity is insufficient, the amount of the sample is increased. However, in our case, by reducing the amount of the sample, the effect of coexisting substances on the analysis sensitivity (matrix effect) decreased,[12] and as a result, the measurement sensitivity was increased. With this technique, the limit of quantification can be increased by minimizing the contamination, even in the previous generation devices with low sensitivity. Since the latest measuring device uses a lot of fluororesin and has in general a higher system blank, what determines the methodological detection limit and precision for PFOS is, at present, not the sensitivity of the device, but how strictly the QA/QC is preformed. The highly sensitive analysis method is not truly necessary for rivers and coastal waters in Japan that are the usual monitoring targets. However, for outer sea environmental monitoring to understand the global dynamics, advanced QA/QC is essential in addition to high sensitivity. Such research papers were the basis of ISO 25101.

4 Reliability of the developed analysis method

In ISO /TC147 (water quality) /SC2 (physical, chemical and biochemical methods), the quality control studies (studies to determine whether the analysis method used is adequate) are conducted in multiple laboratories according to the standard operation procedure (SOP) for the analysis method to be used as a standard, and the performance data obtained must be comparable with the standard. On the other hand, in Japan, the performance data of the analysis method have not necessarily been released in the past. In the Research Project for Creating Standards to Meet Social Needs "Strategic Project to Build the JIS System for Environmental Measurement that Contributes to the Strengthening of

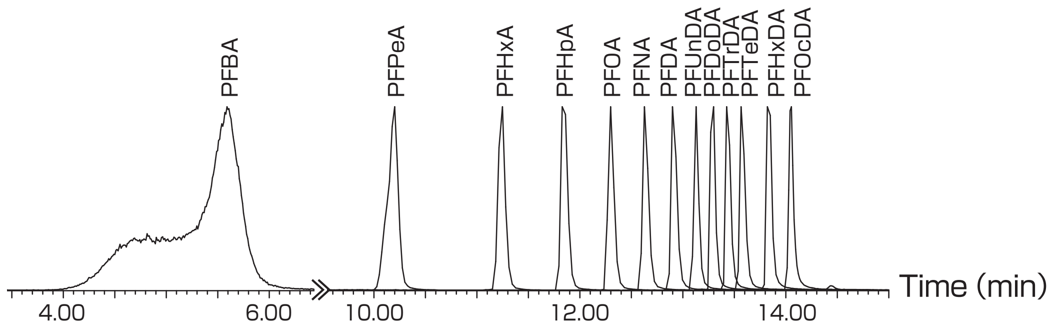
Industrial Competitiveness and Environmental Preservation," the necessity for describing the results of the quality control studies was indicated from the perspective of meeting the ISO standard that requires the inclusion of the performance data of the standardized analysis method. This was indicated as part of the revision of the conventional JIS system for the measurements of water quality and atmosphere.

4.1 Quality control study for nonylphenol

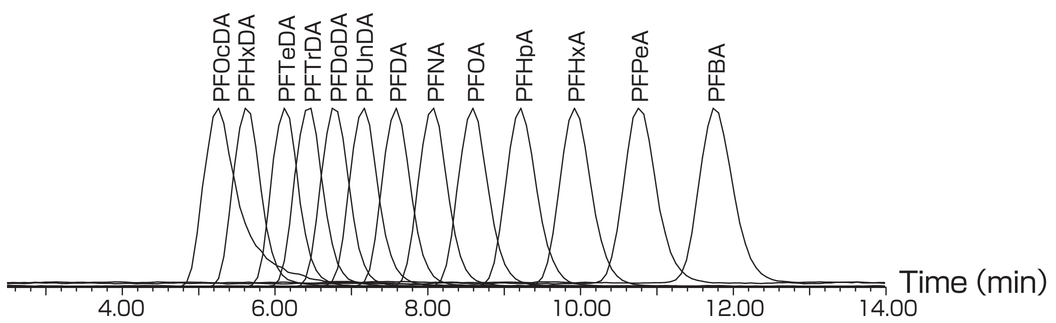
For NP, participation in the quality control study for the analysis of NP isomers in the water sample was solicited under the project leadership of Japan for ISO/TC147/SC2/WG17 (phenols) from July to September 2008. There were applications from 17 institutes from Japan and overseas. After conducting statistical analysis of the study results, the results were organized and reported to the participating institutes as an interim report, and a report was submitted to the ISO/TC147/SC2/WG17 as the performance data for the ISO/DIS 24293 (draft standard) in December 2008. The intermediate precision coefficient of variation (CVr) that looked at the variation of the analysis value within a laboratory was average of 10 % (minimum 4.4 % ~ maximum 21.6 %), and no difference was observed in intermediate precision due to the type of sample and difference in isomer composition. On the other hand, the reproducibility coefficient of variation (CV_R) that looked at the variation of the analysis results when the measurements were done among different laboratories was approximately 30 % or less, but it surpassed 50 % in some isomers. Particularly, there was large variation in the inter-laboratory variation of isomers with small composition among the NP mixtures (NP8 and NP12, refer to Fig. 5), and the reproducibility tended to be poor. It was reported that there were slight differences in the isomer separation by different column manufacturers or due to the deterioration of the column even when equivalent separation columns were used. In this analysis method where the NP mixture was used as the quantifying standard, the effect of the slight difference in the peak separation capacity on the quantitative value could not be prevented for some isomers.[22]

To check the effect on the analysis precision due to the difference of SS amount, river water (SS amount of 13 mg/L) and influx water of sewage treatment plant that contained large amount of SS (SS amount of 140 mg/L) were used as the quality control study samples. As described above, poor reproducibility was seen in some isomers (NP8 and NP12, refer to Fig. 5), but good results of CV_R within 30 % was obtained for other isomers.[22]

This analysis method was published as the ISO 24293:2009[1] in July 2009 after obtaining 15 votes of approval among 17 countries in the final vote. This analysis method was



a) Example of separation using the reverse phase column (Betasil C18)
(elution occurs in the order from short to long chain)



b) Example of separation using the multimode (reverse phase + anion exchange) column (JJ50 2D)
(elution occurs in the order from long to short chain)

Fig. 7 Example of the separation by chromatograph for perfluoroalkylcarbonic acid

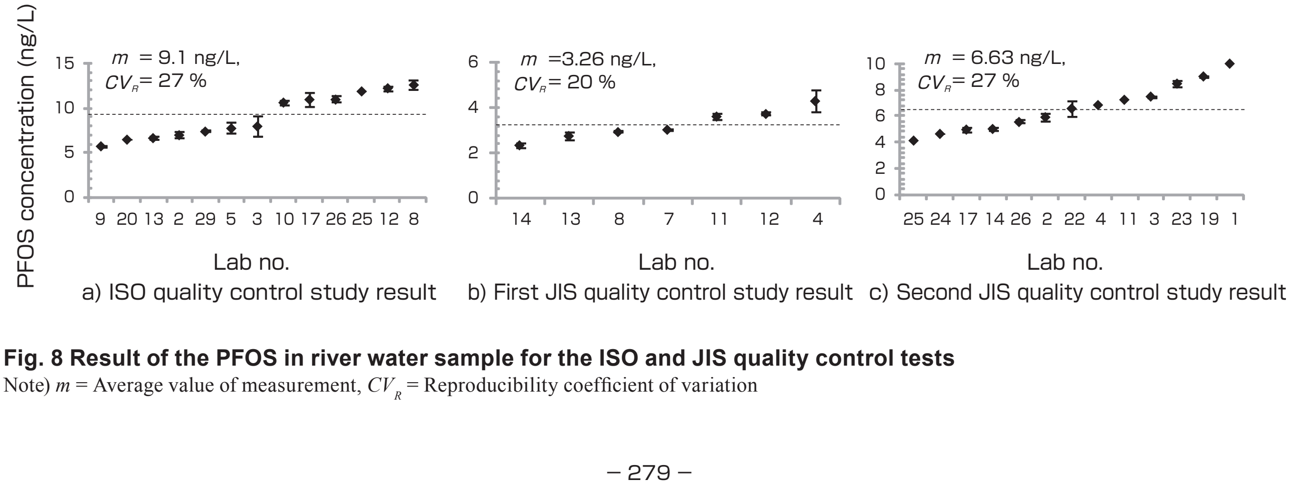
proposed as the ISO standard in February 2005. At that time, there were hardly any reference standards for the individual isomers of NP, but since the necessity of isomer analysis was recognized worldwide through the establishment of ISO 24293, several branched-chain isomers including the ^{13}C labeled standards are being sold by the reagent manufacturers today. Therefore, the improvement of reliability can be expected by using the commercially available standard materials in the next revision.

4.2 Quality control study for PFOS/PFOA

Before explaining the quality control performed in this research, the inter-laboratory study for the PFOS/PFOA-related substances conducted in early 2005 will be described. The inter-laboratory study was done using the in-house method (method that is not established as standard protocol) that each participant selected. The difference between the quality control study and the inter-laboratory study is that while the former is done for the purpose of assessing the analysis method and is conducted using a common SOP, the latter is done for the purpose of assessing the performance of laboratories on the analysis using in-house methods so there is no guideline for the analysis method used. The inter-laboratory study of 2005 was planned and managed by three organizations, Netherlands Institute for Fisheries Research, Örebro University, and Water Services Corporation. Thirty-seven international research institutes that have been working on the analysis technology development from the start of the PFOS problem, and five institutes from Japan (AIST, two companies, and two universities) participated. As a result, it was confirmed that the CV_R surpassed 100 % for the variation of analysis value. The reasons indicated were the use of standards with low purity, contamination by sample containers, and errors due to the difference in sensitivity and calibration curve of the measurement devices. It became apparent that the mutual comparison of the analysis values obtained by the in-house method was difficult, and there was a need for standardizing the analysis method.[31] In this study, our group supplied the measurement data for PFBA with carbon number 4 for the first time in the world.

The quality control study organized by AIST for checking the performance of ISO 25101 was done from November 2006 to February 2007 and 23 institutes from 9 countries participated. Since the quality control study was adopted to check the performance of the standard analysis method, the participants were required to use the draft of ISO 25101 as the SOP. The analyses were performed of river water, seawater, water containing low-concentration of the standard substance, water containing high-concentration of the standard substance, and the standard substance. The precision of CV_R of 27 % or less was successfully obtained for each sample, where the concentration of PFOS in the actual sample was 2.6-470 ng/L and PFOA was 9.4-4400 ng/L (Fig. 8a). Similar quality control study was conducted for wastewater samples, but the CV_R for PFOS reached 40 %, and the variation became greater than 30 % which was the guideline value set by ISO. Therefore, the wastewater sample was removed from the samples subjected to analysis in ISO 25101.

After the establishment of ISO 25101, two quality control studies organized by AIST were conducted for JIS standardization, as requests were made by the Japanese laboratories for the compliance of the standard according to the principle of domestic standardization based on the international standard. In the first study conducted from March to July 2008, studies were conducted for tap water, seawater, river water, water containing low-concentration of the standard substance, water containing high-concentration of the standard substance, and the standard substance, using the same analysis method as ISO 25101. There were 13 participating institutes, and the study results were analyzed using the reports submitted by 11 institutes. In most samples, good results were obtained where CV_R of PFOS/PFOA and their related substances was within 30 % (Fig. 8b), and it was confirmed that ISO 25101 could be used in the Japanese analytical laboratories. However, some points had to be reviewed, such as, the variation of the study results for low-concentration water samples and the low recovery rate of long-chain compounds. In the second quality control study conducted from September 2009 to January 2010, the industrial water and plant wastewater were used as the main subjects of measurement for the JIS standardization. There



a) ISO quality control study result b) First JIS quality control study result c) Second JIS quality control study result

Fig. 8 Result of the PFOS in river water sample for the ISO and JIS quality control tests

Note) m = Average value of measurement, CV_R = Reproducibility coefficient of variation were 30 participating institutes, and the analyses of the study results were done for the reports submitted by 23 institutes. In this study, satisfactory results ($CV_R < 30$ %) were obtained for all samples of PFOS/PFOA (Fig. 8c). It can be thought that the analysis error due to the difference in the in-house method was controlled by using the SOP, including the reference standard for creating the calibration curve.

5 Feedback for the effort on the international regulation of hazardous chemical substances using the ISO standard

How are these international standards being utilized?

First, for ISO 24293, the necessity of individual NP isomer analysis was recognized internationally, and the sales of reference standards for individual isomers were started by reagent manufacturers. Germany added the measurement for individual isomers when standardizing ISO 18857-2[32] (analysis method for alkylphenols including NP using the solid phase extraction method and the derivatization method) that is the second part of ISO 18857-1[9] (analysis method for alkylphenols including NP using the liquid-liquid extraction method; NP is the total measurement).

As an example of the use of ISO 25101, Company S, which is a Japanese manufacturer of semiconductors and assembled products, requested AIST to assess the environmental load and the percentage of PFOS in the chemicals used in their plants from 2003. Company S took measures against the PFOS issue before other companies and regulations were implemented. It obtained the information on the amount of PFOS used and the environmental load in 2006, and shifted to alternative substances, and sufficient safety measures were achieved by the time interviews and surveys were conducted by METI in 2008. On the other hand, the companies that did not take measures against PFOS by 2009 had to struggle to take action in a short period, as they had to determine the usage amount and shift to alternative substances while facing the countdown for regulations. If this was done by a private analytical laboratory without strict quality control, there might have been questions about the reliability of the values reported. The survey results in compliance with the ISO 25101 were readily accepted, and this helped the consideration of the exceptions and essential use according to the Chemical Substances Evaluation Act.

In the analysis, a reference material that has been accurately characterized is necessary to determine the measurement value. Previously, there was no choice but using the values provided by the chemical suppliers, but the National Metrology Institute of Japan (NMIJ), AIST, developed the certified reference material (CRM)$^{\text{Term 6}}$ appropriate for ISO 25101 that is traceable to the SI . To strengthen the linkage of the reference material and the standards inside and outside Japan as much as possible, the development of the reference material was performed concurrently with the international standardization for PFOS, and as a result, quick provision was possible for the CRM related to PFOS. For the development of CRM, NMIJ conducts a management system in compliance to the ISO Guide 34[33] and ISO/IEC 17025[34] which are the guidelines for the production of reference materials, and our CRM is produced accordingly. To ensure the traceability to the SI, the application of the primary method of measurement$^{\text{Term 7}}$ [35] is recommended. The freezing point depression method, one of the primary methods, is often chosen in the purity assessment of the organic reference materials. However, since the raw material used was potassium salt of PFOS (K-PFOS) that could be readily refined, the melting point was extremely high (about 300 °C), and it was difficult to obtain accurate results using the purity assessment by the freezing point depression method[36]-[39] (about 150 °C or less) developed by NMIJ. The reproducibility of measurement was improved by using the high- pressure sample crucibles and by applying the reference material for the high-temperature melting point calibration to the freezing point depression method. Hence, it was possible to determine the purity traceable to the SI for the high melting point material such as the K-PFOS (Fig. 9). Therefore, it is expected that the purity assessment of many hazardous materials will become possible by combining this method with the conventional method.[40] The preparation of solution of this reference material was applied to the

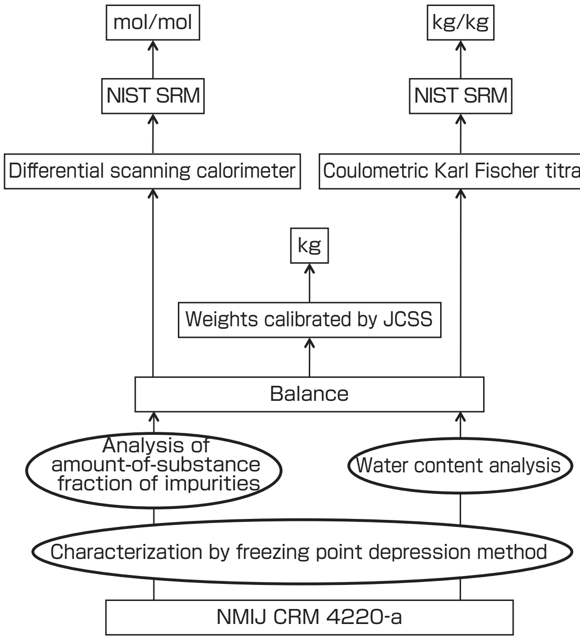


Fig. 9 Traceability diagram of potassium perfluorooctanesulfonate in methanol (NMIJ CRM 4220-a)

Note) JCSS = Japan Calibration Service System; NIST SRM = Standard Reference Material from the National Institute of Standards and Technology (USA).

Table 1. Factors of uncertainty on potassium perfluorooctanesulfonate in methanol

Factors of uncertainty	Relative standard uncertainty(%)
Purity assessment	0.059
Preparation of solution	0.515
Homogeneity	0.474
Stability	0.066
Solvent blank	0.001

Note) Relative standard uncertainty: The relative amount where the uncertainty arising from measurement result expressed by measurement standard deviation etc. (so-called standard uncertainty) is divided by the measurement result.

gravimetric blending method (one of the preparation methods used frequently by the national metrology institutes[41]), and the concentration of the reference material was calculated by multiplying the dilution ratio and purity of K-PFOS. This concentration (certified value) is traceable to the SI. As described above, upon determining the certified value and uncertainty (Table 1), the development of the reference material of K-PFOS in methanol was completed in FY 2009[42] (Fig. 10). The ISO international method (March 2009) and the world's first CRM (2010) became available at almost the same time as the addition of PFOS to the POPs Convention (August 2010).

On the other hand, we would like to point out the use of Oasis®WAX cartridge as the problem indirectly generated in this standardization. The analysis of the PFOS/PFOA-related substances by ISO 25101 assumes basic knowledge of the analysis method and strict quality control conditions, and the reliability and reproducibility of the analysis value may decrease when such conditions are insufficient. The Oasis®WAX cartridge used frequently in SPE can produce excellent results for the various PFOS/PFOA-related substances from C2 to C18, if the appropriate buffer solution is used as the cleansing fluid for low-concentration samples, as described in the original paper,[13] which has become the basic technology for ISO 25101 and JIS K 0450-70. However, when the simplified elution method using formic acid (described in guidelines such as Guideline for Wastes Containing PFOS (2010)) was used, we found that the recovery varied greatly depending on the matrix. Therefore, reliability could not be maintained unless the elution condition was optimized sufficiently when the formic acid was used. The reasons for the decrease in the recovery and reproducibility of the short-chain (PFBA) were the same when the SPE cartridge that had similar property as the Oasis®WAX cartridge was used. Moreover, in recently conducted research, it was confirmed that particularly strict desalinization and elution condition controls were necessary in cases where the SPE cartridge was used for seawater analysis. If limited to the PFOS/PFOA measurement of carbon chain 8 in the high-concentration sample, the SPE for simple C18 or polymers was easier for less experienced people to use, although there were problems such as the contamination and low recovery of related compounds other than PFOS/PFOA. In the ISO 25101 and JIS K 0450-70, the C18[23] and polymer SPE (such as the Oasis®HLB cartridge[26][28]) were given as examples where SPE cartridges other than the Oasis®WAX cartridge could be used in the ISO Annex (Informative) and the JIS Annex (Informative).

Fig. 10 Potassium perfluorooctanesulfonate in methanol (NMIJ CRM 4220-a)

At this point, there may be insufficient understanding for the most important essence of QA/QC of how to confirm the reliability of the "PFOS analysis technology using the solid phase extraction and liquid chromatograph tandem mass spectrometer" that is the basic concept of ISO 25101. The problem of ISO is that there is no "explanation" at the end like JIS, and there is hardly any detailed explanation such as the reasons and background for conducting a certain analysis procedure. JIS documents the items that were discussed in the process of JIS standardization and the detailed explanation of the reasons and background of standardization, not just the performance data, so the user can thoroughly understand each procedure. It is necessary to enforce the good laboratory practice (GLP)[Term 8] by returning to the fundamentals of analytic chemistry; to obtain high quality study data and to ensure that the study data are of the same level and therefore allowing the mutual acceptance of the study data among different countries and laboratories.

6 Conclusions

The CSCL is controlled by three ministries: the Ministry of Environment; Ministry of Economy, Trade and Industry; and the Ministry of Health, Labour and Welfare. The POPs Convention is handled in the same framework. If the sharing of appropriate information and trans-ministry support for international standardization can be achieved, the establishment of several international standards in the environmental analysis field can be expected based on the valuable findings and technologies of the Japanese environmental pollution science. This covers not only the environment in a narrow sense, but will become the basis for the international solutions for hazardous chemical substance issues including the hazardous substances in products, trans-boundary pollution, and the Basel Convention, etc. To create the risk and dynamic models and to establish policies, it is mandatory to obtain objective and reliable measurement values.

There are three ISO international standards on water quality measurement recently established with Japan as the convener, including ISO 24293[1] and ISO 25101[2] that were discussed in this paper, as well as ISO 22719.[43] Moreover, the international standardization of pH measurement of seawater is in progress. It should be noticed that these are all international standards closely related to the global environmental problem that is one of the most important issues in the international community, including global warning and pollution. This is one of the examples where the ISO's main concept "to solve the international issues through international standards" is expanded to the global environmental issues, and where issues concerning domestic industry and environment policies as well as the international economy are being addressed. In the future, Japan must be responsible as an "advanced nation in environmental issues" for making international contributions by seeking solutions for the environmental issues through realizing the international standardization of many environmental measurements across the framework of different ministries. Also, standardization activity is needed to strengthen the industrial competitiveness through the advance acquisition of problem-solving technologies for environmental issues. In the future, standardization in close collaboration with industries will become essentially important.

Acknowledgement

In this R&D, we are deeply grateful to the cooperation and advice we received from the following people and organizations: Akira Miyazaki, chairman of ISO/TC147 of Japan; ISO/TC147 members of Japan; Yoshiteru Tsuchiya, chairman and member of Standardization Steering Committee for NP and PFOS/PFOA in Japan; Jun'ichi Nakagawa, member of Standardization Steering Committee for NP and PFOS/PFOA in Japan; Japan Environmental Management Association for Industry (JEMAI); Japan Environmental Measurement and Chemical Analysis Association (JEMCA); and the people of the institutes and laboratories that participated in the quality control study.

Terminology

Term 1. GC-PFC: Gas chromatograph with the preparative fraction collector system where trace target substance in complex matrix is collected, concentrated, and purified using the high separation capacity of the GC capillary column.

Term 2. Two-dimensional gas chromatograph: Method of separating and purifying the interfering substance or the target compound that co-elutes using two capillary columns. The separation capacity is determined by the length and diameter of the capillary column used and the combination of the liquid phase. This method enables advanced separation of the compounds, and also enables highly sensitive analysis by reducing the background of the detector by removing the organic compounds other than the ones subject to analysis from the analysis.

Term 3. Internal standard: Substance added for the preliminary treatment of sample, the correction of yield in the analysis procedure, or for the confirmation of the recovery. Substance with similar chemical structure as the target substance can be used.

Term 4. Fragmentation patterns: Pattern of ions produced by the cleavage of molecular ions. The fragmentation patterns reflect the chemical structure of the compound.

Term 5. Flame ionization detector (FID): Standard detector used in gas chromatography. The backbone carbon of the organic compound is ionized using the combustion heat of hydrogen, and the change in ion current is measured.

Term 6. Certified reference material (CRM): The reference material (standard substance) for which one or more property values have been certified using the procedure with established traceability (comes with a certificate). Each certified value has uncertainty of certain confidence level.

Term 7. Primary method of measurement: The method defined as the "method that has the highest quality, of which the procedures are completely explained and understood, its uncertainty can be completely described using the SI unit, and the measurement result can be used as a standard without referring to other standards." The primary methods of measurement in chemical analysis include the gravimetric, titration, coulometric titration, isotope dilution mass spectrometry, and freezing point depression methods.

Term 8. Good laboratory practice (GLP): The quality control system for the organizational procedures and the condition in planning, execution, monitoring, recording, storage, and reporting, for the purpose of maintaining the reliability and quality of the test performance and for ensuring the test data at certain level in various safety tests. It was established by the Organization for Economic Cooperation and Development (OECD) in 1981, and was revised in 1997. In the Chemical Substances Evaluation Act, the GLP was introduced in March 1984, and it is in compliance with the GLP principle of OECD.

References

[1] ISO 24293:2009, Water quality -- Determination of individual isomers of nonylphenol -- Method using solid phase extraction (SPE) and gas chromatography/mass spectrometry (GC/MS) (2009).

[2] ISO 25101:2009, Water quality -- Determination of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) -- Method for unfiltered samples using solid phase extraction and liquid chromatography/mass spectrometry (2009).

[3] Japan Industrial Standards: JIS K 0450-60-10:2007, Testing method for individual 4-nonylphenol isomers in industrial water and wastewater (2007) (in Japanese).

[4] Japan Industrial Standards: JIS K 0450-70-10:2011, Testing methods for perfluorooctanesulfonate (PFOS) and. perfluorooctanoate (PFOA) in industrial water and wastewater (2011) (in Japanese).

[5] Japan Industrial Standards: JIS K 0450-20-10:2005, Testing method for alkyl phenols in industrial water and wastewater (2005) (in Japanese).

[6] N. Kannan, N. Yamashita, G. Petrick and J. C. Duinker: Polychlorinated biphenils and nonylphenols in the Sea of Japan, *Environ.Sci. Technol*., 32 (12), 1747-1753 (1998).

[7] N. Yamashita, K. Kannan, S. Hashimoto, A. Miyazaki and J. P. Giesy: Estrogenic potency of individual nonylphenol congeners isolated from technical mixtures, *Organohalogen Compd*., 42, 121-125 (1999).

[8] Y-S Kim, T. Katase, T. Inoue, S. Sekine, Y. Fujimoto and N. Yamashita: Variation of estrogenic activity in a commercial nonylphenol preparation fractionated by HPLC, *Organohalogen Compd*., 53, 61-64 (2001).

[9] ISO 18857-1:2005, Water quality -- Determination of selected alkylphenols -- Part 1: Method for non-filtered samples using liquid-liquid extraction and gas chromatography with mass selective detection (2005).

[10] J. P. Giesy and K. Kannan: Global distribution of perfluorooctane sulfonate in wildlife, *Environ. Sci. Technol*., 35 (7), 1339-1342 (2001).

[11] S. Taniyasu, K. Kannan, Y. Horii, N. Hanari and N. Yamashita: A survey of perfluorooctane sulfonate and related perfluorinated organic compounds in water, fish, birds, and humans from Japan, *Environ. Sci. Technol*., 37 (12), 2634-2639 (2003).

[12] N. Yamashita, K. Kannan, S. Taniyasu, Y. Horii, T. Okazawa, G. Petrick and T. Gamo: Analysis of perfluorinated acids at parts-per-quadrillion levels in seawater using liquid chromatography-tandem mass spectrometry, *Environ. Sci. Technol*., 38 (21), 5522-5528 (2004).

[13] S. Taniyasu, K. Kannan, M. K. So, A. Gulkowska, E. Sinclair, T. Okazawa and N. Yamashita: Analysis of fluorotelomer alcohols, fluorotelomer acids, and short- and long-chain perfluorinated acids in water and biota, *J. Chromatogr. A*, 1093 (1-2), 89-97 (2005).

[14] N. Yamashita, K. Kannan, S. Taniyasu, Y. Horii, G. Petrick and T. Gamo: A global survey of perfluorinated acids in oceans, *Mar. Pollut. Bull*., 51 (8-12), 658-668 (2005).

[15] N. Yamashita, S. Taniyasu, G. Petrick, S. Wei, T. Gamo, P. K. S. Lam and K. Kannan: Perfluorinated acids as novel chemical tracers of global circulation of ocean waters, *Chemosphere*, 70 (7), 1247-1255 (2008).

[16] J. P. Benskin, D. C. G. Muir, B.F. Scott, C. Spencer, A. O. De Silva, H. Kylin, J.W. Martin, A. Morris, R. Lohmann, G. Tomy, B. Rosenberg, S. Taniyasu and N. Yamashita: Perfluoroalkyl acids in the Atlantic and Canadian Arctic Oceans, *Environ. Sci. Technol*., 46 (11), 5815-5823 (2012).

[17] K. Guenther, E. Kleist and B. Thiele: Estrogen-active nonylphenols from an isomer-specific viewpoint: a systematic numbering system and future trends, *Anal. Bioanal. Chem*., 384 (2), 542-546 (2005).

[18] Y-S. Kim, T. Katase, M. Makino, T. Uchiyama, Y. Fujimoto, T. Inoue and N. Yamashita: Separation, structural elucidation and estrogenic activity studies of the structural isomers of 4-nonylphenol by GC-PFC coupled with MS and NMR, *Aust. J. Ecotoxicol*., 11, 137-148 (2005).

[19] M. Makino, T. Uchiyama, H. Saito, S. Ogawa, T. Iida, T. Katase and Y. Fujimoto: Separation, synthesis and estrogenic activity of 4-nonylphenols: two sets of new diastereomeric isomers in a commercial mixture, *Chemosphere*, 73 (8), 1188-1193 (2008).

[20] T. Ieda, Y. Horii, G. Petrick, N. Yamashita, N. Ochiai and K. Kannan: Analysis of nonylphenol isomers in a technical mixture and in water by comprehensive two-dimensional gas chromatography-mass spectrometry, *Environ. Sci. Technol*., 39 (18), 7202-7207 (2005).

[21] Y. Horii, T. Katase, Y-S Kim and N. Yamashita: Determination of individual nonylphenol isomers in water samples by using relative response factor method, *Bunseki Kagaku*, 53 (10), 1139-1147 (2004) (in Japanese).

[22] Y. Horii, S Taniyasu, Y. Tsuchiya, J. Nakagawa, T. Takasuga, N. Yamashita and A. Miyazaki: Interlaboratory trial on the analysis of individual isomers of nonylphenol in water samples according to ISO 24293:2009, *Bunseki Kagaku*, 59 (4), 319-327 (2010) (in Japanese).

[23] K. J. Hansen, H. O. Johnson, J. S. Eldridge, J. L. Butenhoff and L. A. Dick: Quantitative characterization of trace levels of PFOS and PFOA in the Tennessee River, *Environ. Sci. Technol*., 36 (8), 1681-1685 (2002).

[24] S. Taniyasu, K. Kannan, Y. Horii and N, Yamashita: The first environmental survey of perfluorooctane sulfonate (PFOS) and related compounds in Japan, *Organohalogen Compd*., 59, 311-314, (2002).

[25] S. Taniyasu, N. Yamashita, Y, Horii, K, Kannan and T. Gamo: Perfluorooctane sulfonate and related compounds in the South China Sea, Sulu Sea and Japanese environmental samples, *Organohalogen Compd*., 62, 339-342, (2003).

[26] M. K. So, S. Taniyasu, N. Yamashita, J. P. Giesy, J. Zheng, Z. Fang, S. H. Im and P. K. S. Lam, Perfluorinated compounds in coastal waters of Hong Kong, South China, and Korea, *Environ. Sci. Technol*., 38 (15) 4056-4063 (2004).

[27] N. Yamashita, K. Kannan, S. Taniyasu, Y. Horii, N. Hanari, T. Okazawa and G. Petrick: Environmental contamination by perfluorinated carboxylates and sulfonates following the use of fire-fighting foam in Tomakomai, Japan, *Organohalogen Compd*., 66, 4013-4018 (2004).

[28] E. Sinclair, S. Taniyasu, N. Yamashita and K. Kannan: Perfluorooctanoic acid and perfluorooctane sulfonate in Michigan and New York waters, *Organohalogen Compd*., 66, 4019-4023 (2004).
[29] K. S. Guruge, S. Taniyasu, N. Yamashita, S. Wijeratna, K. M. Mohotti, H. R. Seneviratne, K. Kannan, N. Yamanaka and S. Miyazaki: Perfluorinated organic compounds in human blood serum and seminal plasma: a study of urban and rural tea worker populations in Sri Lanka, *J. Environ Monit*., 7 (4), 371-377 (2005).
[30] S. Taniyasu, K. Kannan, L. W. Y. Yeung, K. Y. Kwok, P. K. S. Lam and N. Yamashita: Analysis of trifluoroacetic acid and other short-chain perfluorinated acids (C2-C4) in precipitation by liquid chromatography-tandem mass spectrometry: comparison to patterns of long-chain perfluorinated acids (C5-C18), *Anal. Chim. Acta*, 619 (2), 221-230 (2008).
[31] S. P. J. van Leeuwen, A. Karrman, B. van Bavel, J. de Boer and G. Lindstrom: Struggle for quality in determination of perfluorinated contaminants in environmental and human samples, *Environ. Sci. Technol*., 40 (24), 7854-7860 (2006).
[32] ISO18857-2:2009, Water quality -- Determination of selected alkylphenols -- Part 2: Gas chromatographic-mass spectrometric determination of alkylphenols, their ethoxylates and bisphenol A in non-filtered samples following solid-phase extraction and derivatisation (2009).
[33] ISO Guide 34:2009, General requirements for the competence of reference material producers (2009).
[34] ISO/IEC 17025:2005, General requirements for the competence of testing and calibration laboratories (2005).
[35] M. J. T. Milton and T. J. Quinn: Primary methods for the measurement of amount of substance, *Metrologia*, 38 (4), 289-296 (2001).
[36] Y. Shimizu, Y. Ohte, X. Bao, S. Otsuka, Y. Kitamaki, K. Ishikawa, T. Ihara and K. Kato: Development of certified reference materials of high-purity volatile organic compounds: purity assay by the freezing-point depression method, *Accred. Qual. Assur*., 13 (7), 389-396 (2008).
[37] N. Hanari, K. Ishikawa, Y. Shimizu, R. Iwasawa, S. Otsuka and T. Yarita: Certified reference material for determination of *p-n*-nonylphenol and *p-n*-heptylphenol from the National Metrology Institute of Japan, *Organohalogen Compd*., 70, 1349-1352 (2008).
[38] N. Hanari, K. Ishikawa, Y. Shimizu, R. Iwasawa, S. Otsuka, N. Fujiki, X. Bao, T. Yarita, K. Kato and N. Yamashita: Certified reference materials for determination of phthalates and alkylphenols from the National Metrology Institute of Japan, *Organohalogen Compd*., 71, 1605-1609 (2009).
[39] N. Hanari, K. Ishikawa, S. Otsuka, K. Higuchi, R. Iwasawa and T. Yarita: Certified calibration solution reference material for the determination of benzo[*a*]pyrene from the National Metrology Institute of Japan (NMIJ), *Polycyclic Aromat. Compd*., 28 (4-5), 302-319 (2008).
[40] N. Hanari, N. Itoh, R. Iwasawa, M. Numata, S. Taniyasu and N. Yamashita: Purity evaluation of potassium perfluoroalkylsulfonate using differential scanning calorimetry, *Organohalogen Compd*., 72, 271-274 (2010).
[41] ISO 6142:2001, Gas analysis -- Preparation of calibration gas mixtures -- Gravimetric method (2001).
[42] National Metrology Institute of Japan, AIST: NMIJ Certified Reference Materials (NMIJ CRM), http://www.nmij.jp/service/C/ (in Japanese).
[43] ISO 22719:2008, Water quality -- Determination of total alkalinity in sea water using high precision potentiometric titration (2008).

Authors

Sachi TANIYASU

Completed the doctor’s course at the Graduate School of Natural Science and Technology, Kanazawa University in March 2006. Joined the Potential Pollutants Group, Research Institute for Environmental Management Technology, AIST in April 2006. Engages in the development of the analysis method for persistent organic halogen compounds and the research on the environmental fate. In this paper, was in charge of the development of analysis method, ISO standardization, and JIS standardization of PFOS and PFOA.

Nobuyasu HANARI

Completed the doctor’s course in Agricultural Technology and Sciences at the Graduate School of Life and Environmental Sciences, University of Tsukuba in March 2001. Joined the Potential Pollutants Group, Research Institute for Environmental Management Technology, AIST in July 2004, and engaged in the development of the analysis method for dioxin analogs. Transferred to the Organic Analytical Chemistry Division, National Metrology Institute of Japan in October 2005. Engaged in the development of the national standard (NMIJ CRM) of organic reference material (particularly for persistent organic pollutants). Developed the reference materials essential for the operation of JCSS to ensure traceability, as well as general CRM. In this paper, was in charge of the development of potassium perfluorooctanesulfonate reference liquid (NMIJ CRM 4220-a).

Yuichi HORII

Completed the doctor’s course at the Graduate School of Science and Engineering, Ibaraki University in March 2006. Post-doctorate researcher at the New York State Department of Health (Wadsworth Center) for two years from May 2006. Joined the Center for Environmental Science in Saitama in October 2008, and engages in the environmental monitoring and fate study of persistent organic pollutants. Current interest is the natural production of dioxin in kaolin clay. In this research, was in charge of the development of the analysis method for individual NP isomers.

Nobuyoshi YAMASHITA

Completed the doctor’s course in Environmental Chemistry at the United Graduate School of Agricultural Sciences, Ehime University in 1992. Joined the National Institute for Resources and Environment, Agency for Industrial Science and Technology (current AIST) in 1992. Has been involved in the development of new technologies and their applications in the environmental analytic chemistry field. Has supervised various tests and researches on international quality control to improve the reliability of analytical chemistry technologies both in Japan and overseas, as well as being various standardizing committee member and TC147/SC2/WG56 convener. Also contributed to the councils of chemical substance management policy such as the member of New POPs Review Committee. Highly Cited Author Award in 2010 (2 articles). Was the supervisor of this research.

Discussions with Reviewers

1 Overall evaluation

Comment (Akira Ono, AIST)

This paper is based on the authors' excellent research results on the analysis technology for hazardous chemical substances in the environment, and the effort was brought to international standardization through international joint collaboration. It can be seen that the synthetic and integrated researches were conducted based on a clear scenario that aims for international standardization, and this research is appropriate as a paper to be published in *Synthesiology*.

It should be noted that in this paper the authors conducted the research and standardization as a set. These standards have been used widely by people in the society after the international standard was published, and that should also be highly evaluated.

2 Expressions in consideration of the general readers

Comment (Akira Ono)

It is hoped that the papers of *Synthesiology* are read not only by specialists of certain technological fields, but also by researchers and engineers of wide-ranging fields. I think the intents of this paper are to introduce the thinking on international standardization, to present some case studies of environmental analysis to a wide range of readers, and to widely share this information.

From this perspective, I see some expressions that may be hard to understand for people whose specialties are not analytical chemistry, so please work on the written expression to ensure better communication.

Answer (Sachi Taniyasu)

As you indicated, there are many terminologies and expressions that may be hard to understand for the researchers and engineers outside the environmental analysis technology specialty, and I also realize that this may prevent understanding of the reader. I have added descriptions to the text and added explanations in "Terminology" to enhance the understanding of the standardization process in this research.

3 Composition of the paper (1)

Comment (Akira Ono)

Synthesiology requires the paper to have the following composition, so please consider revising.

(1) First, how the research goal is linked to "social values" is explained,

(2) next, the "research scenario" showing how the authors achieve the research goal is drawn, and then

(3) the "synthesis process" of how elemental technologies were integrated to achieve the research goal is described.

I think the readers will have better understanding if you summarize the "research scenario" of (2) into a diagram that gives an overview of the entire research. The reviewer suggests a diagram of the "research scenario" within his understanding of this paper, so please consider it as a reference if it is useful.

Answer (Sachi Taniyasu)

(1) The research goal of this paper is the "standardization of the analysis method." Therefore, the main objective is to explain the four cases where the international and domestic standards such as ISO and JIS were established using the technological ideas developed by AIST. The chemical substances studied in this research began to be recognized as environmentally hazardous chemical substances when this research started. However, there was no analysis method for which reliability was assured, and it was difficult to understand the environmental load of the chemicals that was important in taking appropriate environmental measures. The need for standardization of the analysis method in such environmental analysis and the social background of the subject compounds were described specifically in chapters 1 and 2. The ISO and JIS systems for environmental analysis and the positioning of this report were described, and texts were added to enhance the understanding of this research.

(2) In achieving the standardization, unlike the flow of "industrial demand → development of analysis method → quality control → JIS standardization → ISO standardization" that is commonly seen in ordinary standardization, the research was conducted in the flow of "understanding the environmental behavior and environmental loadings necessary to manage the chemical substances → development of analysis method → quality control → industrial demand → JIS standardization." Based on the diagram that you provided for us, we created Fig. 4 as the scenario of this research.

(3) Details were described about the problems that were discussed in the process of ISO and JIS standardizations and the measures that were taken to solve them. Also, we added some points which were determined to be the normative items (rules to comply) and informative items (information provided for reference).

4 Composition of the paper (2)

Comment (Hiroaki Tao, Research Institute for Environmental Management Technology, AIST)

The composition of this paper is introduction, development of the analysis method, standardization, contribution to chemical substance management, and conclusion. I think the part on the clarification of environmental behavior is lacking. The reason this standardization was successful was because you published the paper on the clarification of environmental behavior and were highly evaluated internationally for conducting such excellent research. Therefore, I think you should add a chapter on the subject of clarification of environmental behavior.

Answer (Sachi Taniyasu)

I have added the text on the discussion of the environmental behavior, in the process of explaining the research elements and scenario in "Chapter 2 Necessity and standardization of the environmental analysis technology that addresses the international regulation of hazardous chemical substances."

5 Necessity of the standardization

Comment (Hiroaki Tao)

I think it will become easier to understand if you explain the chemical formula, properties, use, and what kind of environmental problem it is causing for each compound (such as nonylphenol), as well as the reasons why the existing standardization method cannot help solve the problem and the reasons why you proposed the new standardization.

Answer (Sachi Taniyasu)

I have added the background information on the use, environmental issues, and environmental fate for each compound because they are important in explaining the necessity of the environmental analysis technology, and modified the text so the readers can understand the process of "standardization."

6 Content of the standardization

Comment (Akira Ono)

In this paper, you describe how the international standard was created, but you do not describe details of the standard itself. Please describe what items were selected as "normative" and as "informative" respectively in the international standard. Also, please mention the reasons and background for those selections.

Answer (Sachi Taniyasu)

I have added the content of the standard and the background and process of the standardization, in addition to the response to comment 3 of discussion 3.

7 Necessity of the standardization and the standardization process

Comment (Hiroaki Tao)

In the international standardization, I think you should explain the role played by the Standard Certification R&D Project, as it may help the people who are trying for standardization using this system. This time, ISO standardization was first and JIS followed. I think if you explain this process and the problems in doing so, it will be helpful for people who are working on standardization by the reverse process.

Answer (Sachi Taniyasu)

I added the description of the work done in the Standard Certification R&D Project. As you indicated, in this research, the ISO standardization started before the JIS standardization. Also, for the ISO standardization of NP, Germany was investigating the standard for a similar analysis method, and it was necessary to do some preliminary adjustments with the convener country. Since such adjustments are important processes in standardization, I have added the description of this process. The points that were raised in the discussions in the process of ISO and JIS standardizations and the measures taken were described.

8 Relationship between the public institutes and private companies in standardization (1)

Question (Akira Ono)

I think it is often the case in the environmental field, but there is a reality that private companies (or related industrial organizations) are not very interested in the development of standards. The reviewer thinks that the public research institute should take action in the fields that private companies are not interested (or cannot be interested), and that the general public expects the public research institute to take on such a role. Considering such a role of the public research institute, what is the opinion of the authors about the relationship of public research institutes and private companies in the standardization in the environmental field?

Answer (Sachi Taniyasu)

In the standardization in the environmental field that is closely related to the global issues, it is often difficult to obtain support from the industry sector. The authors think that the role to be played by the public research institute is great, as you indicated, and we have engaged in the standardization activities from this perspective. On the other hand, seeking solution technology for the environmental issues will help strengthen industrial competitiveness. Therefore, in the future, I think it is important to develop standardizations in close collaboration with industries, to contribute to the development of industry as well as to environmental preservation.

9 Relationship between the public institutes and private companies in standardization (2)

Comment (Hiroaki Tao)

One of the reasons that it is difficult to obtain support from industry is because the development of an environmental analysis method may require new measures to prevent environmental pollution, or it may mean more expense for industry. However, recently, quick discovery of the solution to global issues is important in maintaining industrial competitiveness. The standardization to strengthen industrial competitiveness through advance acquisition of problem solving technology is a hope in gaining support from industry for the standardization of environmental analysis methods. I think you should emphasize this point.

Answer (Sachi Taniyasu)

As indicated, it was difficult to gain support from the industrial organizations due to the image that new measures may be needed after standardization. However, taking measures quickly before something becomes a major social issue will encourage seeking a solution for an environmental issue, and this will lead to strengthening of the industrial competitiveness and the healthy growth of industry in the long run. Therefore, I suggested that the standardization in collaboration with industry is necessary in the future.

10 Effect of standardization

Comment (Akira Ono)

The question "How are these international standards being utilized?" in the beginning of chapter 5 is important. That's because the important objective should not be making a standard, but how the standard is used.

It is important to investigate what aspects of society changed after the standards were delivered and used in the international community, and to compare the actual effect it brought about and the expected effect that was supposed to happen. Please address what were the actual effects in the society after the standards were enforced.

Answer (Sachi Taniyasu)

For the NP standards, two ISO standards were proposed by Germany and one was proposed by Japan. The first standard proposed by Germany (ISO 18857-1) is of total NP measurement, and the measurements of the individual isomers of NP were not described. However, in the Japanese proposed standard (ISO 24293), the necessity of analysis for individual isomers was widely recognized internationally, and the reagent manufacturers started the sales of reference standards for different isomers. The second Germany-proposed standard (ISO 18857-2) was also of total measurement of NP as in Part 1, but because the standards for individual isomers have become available and also because of the importance of the analysis for individual isomers, the measurements for different isomers were added and this enabled more detailed risk assessment using the analysis method. Most private analytical laboratories that subcontract the PFOS/PFOA analysis are in compliance with ISO 25101 and JIS K 0450-70-10, and this enables the provision of high quality and mutually comparable data. I think progresses have been made through this standardization.

Editorial Policy

Synthesiology Editorial Board

Objective of the journal

The objective of *Synthesiology* is to publish papers that address the integration of scientific knowledge or how to combine individual elemental technologies and scientific findings to enable the utilization in society of research and development efforts. The authors of the papers are researchers and engineers, and the papers are documents that describe, using "scientific words", the process and the product of research which tries to introduce the results of research to society. In conventional academic journals, papers describe scientific findings and technological results as facts (i.e. factual knowledge), but in *Synthesiology*, papers are the description of "the knowledge of what ought to be done" to make use of the findings and results for society. Our aim is to establish methodology for utilizing scientific research result and to seek general principles for this activity by accumulating this knowledge in a journal form. Also, we hope that the readers of *Synthesiology* will obtain ways and directions to transfer their research results to society.

Content of paper

The content of the research paper should be the description of the result and the process of research and development aimed to be delivered to society. The paper should state the goal of research, and what values the goal will create for society (Items 1 and 2, described in the Table). Then, the process (the scenario) of how to select the elemental technologies, necessary to achieve the goal, how to integrate them, should be described. There should also be a description of what new elemental technologies are required to solve a certain social issue, and how these technologies are selected and integrated (Item 3). We expect that the contents will reveal specific knowledge only available to researchers actually involved in the research. That is, rather than describing the combination of elemental technologies as consequences, the description should include the reasons why the elemental technologies are selected, and the reasons why new methods are introduced (Item 4). For example, the reasons may be: because the manufacturing method in the laboratory was insufficient for industrial application; applicability was not broad enough to stimulate sufficient user demand rather than improved accuracy; or because there are limits due to current regulations. The academic details of the individual elemental technology should be provided by citing published papers, and only the important points can be described. There should be description of how these elemental technologies are related to each other, what are the problems that must be resolved in the integration process, and how they are solved (Item 5). Finally, there should be descriptions of how closely the goals are achieved by the products and the results obtained in research and development, and what subjects are left to be accomplished in the future (Item 6).

Subject of research and development

Since the journal aims to seek methodology for utilizing the products of research and development, there are no limitations on the field of research and development. Rather, the aim is to discover general principles regardless of field, by gathering papers on wide-ranging fields of science and technology. Therefore, it is necessary for authors to offer description that can be understood by researchers who are not specialists, but the content should be of sufficient quality that is acceptable to fellow researchers.

Research and development are not limited to those areas for which the products have already been introduced into society, but research and development conducted for the purpose of future delivery to society should also be included.

For innovations that have been introduced to society, commercial success is not a requirement. Notwithstanding there should be descriptions of the process of how the technologies are integrated taking into account the introduction to society, rather than describing merely the practical realization process.

Peer review

There shall be a peer review process for *Synthesiology*, as in other conventional academic journals. However, peer review process of *Synthesiology* is different from other journals. While conventional academic journals emphasize evidential matters such as correctness of proof or the reproducibility of results, this journal emphasizes the rationality of integration of elemental technologies, the clarity of criteria for selecting elemental technologies, and overall efficacy and adequacy (peer review criteria is described in the Table).

In general, the quality of papers published in academic journals is determined by a peer review process. The peer review of this journal evaluates whether the process and rationale necessary for introducing the product of research and development to society are described sufficiently well.

In other words, the role of the peer reviewers is to see whether the facts necessary to be known to understand the process of introducing the research finding to society are written out; peer reviewers will judge the adequacy of the description of what readers want to know as reader representatives.

In ordinary academic journals, peer reviewers are anonymous for reasons of fairness and the process is kept secret. That is because fairness is considered important in maintaining the quality in established academic journals that describe factual knowledge. On the other hand, the format, content, manner of text, and criteria have not been established for papers that describe the knowledge of "what ought to be done." Therefore, the peer review process for this journal will not be kept secret but will be open. Important discussions pertaining to the content of a paper, may arise in the process of exchanges with the peer reviewers and they will also be published. Moreover, the vision or desires of the author that cannot be included in the main text will be presented in the exchanges. The quality of the journal will be guaranteed by making the peer review process transparent and by disclosing the review process that leads to publication.

Disclosure of the peer review process is expected to indicate what points authors should focus upon when they contribute to this journal. The names of peer reviewers will be published since the papers are completed by the joint effort of the authors and reviewers in the establishment of the new paper format for *Synthesiology*.

References

As mentioned before, the description of individual elemental technology should be presented as citation of papers published in other academic journals. Also, for elemental technologies that are comprehensively combined, papers that describe advantages and disadvantages of each elemental technology can be used as references. After many papers are accumulated through this journal, authors are recommended to cite papers published in this journal that present similar procedure about the selection of elemental technologies and the introduction to society. This will contribute in establishing a general principle of methodology.

Types of articles published

Synthesiology should be composed of general overviews such as opening statements, research papers, and editorials. The Editorial Board, in principle, should commission overviews. Research papers are description of content and the process of research and development conducted by the researchers themselves, and will be published after the peer review process is complete. Editorials are expository articles for science and technology that aim to increase utilization by society, and can be any content that will be useful to readers of *Synthesiology*. Overviews and editorials will be examined by the Editorial Board as to whether their content is suitable for the journal. Entries of research papers and editorials are accepted from Japan and overseas. Manuscripts may be written in Japanese or English.

Required items and peer review criteria (January 2008)

	Item	Requirement	Peer Review Criteria
1	Research goal	Describe research goal ("product" or researcher's vision).	Research goal is described clearly.
2	Relationship of research goal and the society	Describe relationship of research goal and the society, or its value for the society.	Relationship of research goal and the society is rationally described.
3	Scenario	Describe the scenario or hypothesis to achieve research goal with "scientific words".	Scenario or hypothesis is rationally described.
4	Selection of elemental technology(ies)	Describe the elemental technology(ies) selected to achieve the research goal. Also describe why the particular elemental technology(ies) was/were selected.	Elemental technology(ies) is/are clearly described. Reason for selecting the elemental technology(ies) is rationally described.
5	Relationship and integration of elemental technologies	Describe how the selected elemental technologies are related to each other, and how the research goal was achieved by composing and integrating the elements, with "scientific words".	Mutual relationship and integration of elemental technologies are rationally described with "scientific words".
6	Evaluation of result and future development	Provide self-evaluation on the degree of achievement of research goal. Indicate future research development based on the presented research.	Degree of achievement of research goal and future research direction are objectively and rationally described.
7	Originality	Do not describe the same content published previously in other research papers.	There is no description of the same content published in other research papers.

Instructions for Authors

"Synthesiology" Editorial Board
Established December 26, 2007
Revised June 18, 2008
Revised October 24, 2008
Revised March 23, 2009
Revised August 5, 2010
Revised February 16, 2012

1 Types of contributions

Research papers or editorials and manuscripts to the "Readers' Forum" should be submitted to the Editorial Board. After receiving the manuscript, if the editorial board judges it necessary, the reviewers may give an interview to the author(s) in person or by phone to clarify points in addition to the exchange of the reviewers'reports.

2 Qualification of contributors

There are no limitations regarding author affiliation or discipline as long as the content of the submitted article meets the editorial policy of Synthesiology, except authorship should be clearly stated. (It should be clearly stated that all authors have made essential contributions to the paper.)

3 Manuscripts

3.1 General

3.1.1 Articles may be submitted in Japanese or English.
Accepted articles will be published in Synthesiology (ISSN 1882-6229) in the language they were submitted. All articles will also be published in Synthesiology - English edition (ISSN 1883-0978). The English edition will be distributed throughout the world approximately four months after the original Synthesiology issue is published. Articles written in English will be published in English in both the original Synthesiology as well as the English edition. Authors who write articles for Synthesiology in Japanese will be asked to provide English translations for the English edition of the journal within 2 months after the original edition is published.
3.1.2 Research papers should comply with the structure and format stated below, and editorials should also comply with the same structure and format except subtitles and abstracts are unnecessary. Manuscripts for "Readers' Forum" shall be comments on or impressions of articles in Synthesiology, or beneficial information for the readers, and should be written in a free style of no more than 1,200 words. Editorials and manuscripts for "Readers' Forum" will be reviewed by the Editorial Board prior to being approved for publication.
3.1.3 Research papers should only be original papers (new literary work).
3.1.4 Research papers should comply with various guidelines of research ethics.

3.2 Structure

3.2.1 The manuscript should include a title (including subtitle), abstract, the name(s) of author(s), institution/contact, main text, and keywords (about 5 words).
3.2.2 Title, abstract, name of author(s), keywords, and institution/contact shall be provided in Japanese and English.
3.2.3 The manuscript shall be prepared using word processors or similar devices, and printed on A4-size portrait (vertical) sheets of paper. The length of the manuscript shall be, about 6 printed pages including figures, tables, and photographs.
3.2.4 Research papers and editorials shall have front covers and the category of the articles (research paper or editorial) shall be stated clearly on the cover sheets.
3.2.5 The title should be about 10-20 Japanese characters (5-10 English words), and readily understandable for a diverse readership background. Research papers shall have subtitles of about 15-25 Japanese characters (7-15 English words) to help recognition by specialists.
3.2.6 The abstract should include the thoughts behind the integration of technological elements and the reason for their selection as well as the scenario for utilizing the research results in society.
3.2.7 The abstract should be 300 Japanese characters or less (125 English words). The Japanese abstract may be omitted in the English edition.
3.2.8 The main text should be about 9,000 Japanese characters (3,400 English words).
3.2.9 The article submitted should be accompanied by profiles of all authors, of about 200 Japanese characters (75 English words) for each author. The essential contribution of each author to the paper should also be included. Confirm that all persons who have made essential contributions to the paper are included.
3.2.10 Discussion with reviewers regarding the research paper content shall be done openly with names of reviewers

disclosed, and the Editorial Board will edit the highlights of the review process to about 3,000 Japanese characters (1,200 English words) or a maximum of 2 pages. The edited discussion will be attached to the main body of the paper as part of the article.

3.2.11 If there are reprinted figures, graphs or citations from other papers, prior permission for citation must be obtained and should be clearly stated in the paper, and the sources should be listed in the reference list. A copy of the permission should be sent to the Publishing Secretariat. All verbatim quotations should be placed in quotation marks or marked clearly within the paper.

3.3 Format

3.3.1 The headings for chapters should be 1, 2, 3…, for subchapters, 1.1, 1.2, 1.3…, for sections, 1.1.1, 1.1.2, 1.1.3.

3.3.2 The text should be in formal style. The chapters, subchapters, and sections should be enumerated. There should be one line space before each paragraph.

3.3.3 Figures, tables, and photographs should be enumerated. They should each have a title and an explanation (about 20-40 Japanese characters or 10-20 English words), and their positions in the text should be clearly indicated.

3.3.4 For figures, image files (resolution 350 dpi or higher) should be submitted. In principle, the final print will be in black and white.

3.3.5 For photographs, image files (resolution 350 dpi or higher) should be submitted. In principle, the final print will be in black and white.

3.3.6 References should be listed in order of citation in the main text.

Journal – [No.] Author(s): Title of article, Title of journal (italic), Volume(Issue), Starting page-Ending page (Year of publication).

Book – [No.] Author(s): Title of book (italic), Starting page-Ending page, Publisher, Place of Publication (Year of publication).

4 Submission

One printed copy or electronic file of manuscript with a checklist attached should be submitted to the following address:

Synthesiology Editorial Board
c/o Website and Publication Office, Public Relations Department, National Institute of Advanced Industrial Science and Technology(AIST)
Tsukuba Central 2 , 1-1-1 Umezono, Tsukuba 305-8568
E-mail: synthesiology@m.aist.go.jp

The submitted article will not be returned.

5 Proofreading

Proofreading by author(s) of articles after typesetting is complete will be done once. In principle, only correction of printing errors are allowed in the proofreading stage.

6 Responsibility

The author(s) will be solely responsible for the content of the contributed article.

7 Copyright

The copyright of the articles published in “Synthesiology” and “Synthesiology English edition” shall belong to the National Institute of Advanced Industrial Science and Technology(AIST).

Inquiries:
Synthesiology Editorial Board
c/o Website and Publication Office, Public Relations Department, National Institute of Advanced Industrial Science and Technology(AIST)
Tel: +81-29-862-6217 Fax: +81-29-862-6212
E-mail: synthesiology-ml@aist.go.jp

Vol.5 table of contents (2012)

Vol.5 No.1

Research papers

Report

Vol.5 No.2

Research papers

Round-table Talks

Vol.5 No.3

Research papers

Round-table Talks

Vol.5 No.4

Research papers

Letter from the editor

We deliver to you *Synthesiology* Volume 5 Issue 4. There are five research papers in this issue. One paper is about earthquakes and tsunamis; two papers are about international standardization, one for fuel cells and the other for hazardous chemical substances; one paper on the development of metrology standard; and one on the development of a new material. All the papers are written with focus on the synthetic approach that is the signature of this journal, on the products for which R&Ds were conducted after clearly visualizing the social values that the technology may bring forth. I think they are worthy papers that will bring satisfaction to the readers.

The paper (by Yukinobu Okamura) on the giant Jogan tsunami that occurred in AD 869 presents a major topic in the field of disaster prediction and prevention, as it drew social attention after the Great East Japan Earthquake. There are "problems in announcing study results to society" as stated in the subtitle. Pertaining to the scale of the Jogan tsunami, "the research results … were submitted by AIST to the Earthquake Headquarters in the spring of 2010," but the Great East Japan Earthquake occurred during the time when "the headquarters conducted the evaluations for about one year, for earthquakes along the entire Japan Trench," and the "the possibility that a giant tsunami might strike the Ishinomaki, Sendai, and the Fukushima coasts" was not communicated (quotes from the paper). Although the researchers may be confident about their research results, the common sense until now was that a result is not accepted as a scientific result unless it is objectively evaluated by some peer review process (and therefore, unreviewed result should not be released to society). On the other hand, considering that "in society, for society" is recognized as one of the objectives of science and technology R&D in the 21st century, efforts must be made to quickly release the research result that may have great impact on the society. After the Great East Japan Earthquake, there has been much mass media coverage of earthquakes and tsunamis, and this may reflect the fact that the researchers are working actively from the perspective of speed. The objective and thorough review of the research results and speedy announcement and publicity of the research results may be contradictory. At AIST where the social demonstration of technology is considered as part of the work of the open innovation hub, this contradiction is a major issue that must be overcome. This issue will be taken up again in *Synthesiology*. Please send us your comments and continue your support.

Editor in Chief
Shingo ICHIMURA

Synthesiology - English edition Vol. 5 No. 4, Mar. 2013
Edited by *Synthesiology* Editorial Board
Published by National Institute of Advanced Industrial Science and Technology (AIST)

Publishing Secretariat: Publication Office, Public Relations Department, AIST
Contact: *Synthesiology* Editorial Board
c/o Website and Publication Office, Public Relations Department, AIST
Tsukuba Central 2, Umezono 1-1-1, Tsukuba 305-8568, Japan
Tel: +81-29-862-6217 Fax: +81-29-862-6212
E-mail: synthesiology-ml@aist.go.jp
URL: http://www.aist.go.jp/aist_e/research_results/publications/synthesiology_e

Synthesiology Vol.5 No.4 March 2013
-English edition

"Synthesiology-English edition" is a translated version of "Synthesiology," which is published quarterly, ISSN 1882-6229, by AIST. Papers or articles published in "Synthesiology-English edition" appear approximately four months after the publication of the original "Synthesiology."

AIST11-A00005-7 Published by AIST

Synthesiology-English edition ❹ 2013

National Institute of Advanced Industrial Science and Technology (AIST)