International Journal of Thermophysics, Vol. 5, No. 1, 1984

Reference Materials and Evaluation of Thermophysical Properties Data

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Received February 8, 1984

This paper presents a general review of the governmental activities in Japan on reference materials and evaluation of thermophysical properties data and then describes recent developments at the National Research Laboratory of Metrology (NRLM) in the field of thermophysical properties and related standards. As for reference materials, the past and present activities organized by the government and a few related associations are reviewed from the point of view of establishing traceability systems, whereas, on the evaluation of thermophysical properties, the framework of collaborative research for establishing data base systems by network sharing is mentioned. Then the recent studies of NRLM on the measurements and standards of thermophysical properties as well as its calibration services are summarized.

KEY WORDS: data evaluation; measurement techniques; reference materials; standards; thermophysical properties data.

1. INTRODUCTION

As is well recognized, reference materials play an important role in examining the variability and deviation of measurement, test, and analysis, and in ensuring their exactness through calibrations. In that sense, it is expected that the use of reference materials would be a great help to attain the compatibility of physical and chemical data. The essential characteristics required for reference materials are (a) uniformity or homogeneity, (b) stability, and (c) exactness of assessed values. All of these conditions are realized by the deliberate preparation of materials, precise and accurate measurement, and pertinent evaluation in terms of statistical data treatment.

Presented at the Japan–United States Joint Seminar on Thermophysical Properties, October 24–26, 1983, Tokyo, Japan.

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Just the same remarks can be applied to the determination of thermophysical properties. The certification of reference materials and the determination of thermophysical properties require rather involved experimental and numerical procedures, which have much in common with the establishment of metrological standards. As the national standards laboratory of Japan, the National Research Laboratory of Metrology (NRLM) has been taking part in the calibration of several kinds of materials and in the determination of some thermophysical properties. In the following, the activities on reference materials and evaluation of thermophysical properties data in progress at government facilities in Japan are reviewed, and then the recent contributions of NRLM in these fields are summarized.

2. ACTIVITIES ON REFERENCE MATERIALS IN JAPAN

2.1. Supply and Certification of Reference Materials

A growing demand for a wider variety of reference materials is found in correspondence to developments in science and industry. During the period of evolution of industries in Japan after the Second World War, a number of reference materials have been prepared and provided by government laboratories, academic institutions, or private companies. Their specifications are different case by case. Some reference materials are specified by Japan Industrial Standards, while others are prepared according to the manufacturers' specifications. The systems of certification are also diverse as they are established in response to the use of reference materials and to the level of requirements for them. Good examples of reference materials certified by government laboratories are standard viscosity liquids, standard hardness testing blocks, standard reference gases, metal standard solutions, and so on. Most of the reference materials for composition standards are certified by respective associations or institutions.

2.2. Promotion of Traceability on Reference Materials

The need to establish standards and calibration systems of reference materials on a nationwide basis was first pointed out in Japan in the 1960s by the Research Liaison Conference for International Metrology organized by the Agency of Industrial Science and Technology (AIST) of the Ministry of International Trade and Industry (MITI). According to the recommendation of the conference, a Joint Committee of Industrial Measurements and Standards, consisting of committees in each field of standards, was established by the Japan Industrial Technology Association (JITA) in 1971 in order to exchange information on standards and calibration services and to promote the establishment of traceability systems, aiming at the same function as the National Conference of Standards Laboratories in the U.S.A. The Committee on Standard Reference Materials, formed as a member of the Joint Committee, started its activity in October of that year. However, it was difficult for the committee to systematize traceability in this field as the members were mainly concerned with chemical reference materials. The concept of a primary standard and transfer of standard values, which were familiar in the field of physical metrology, was not immediately acceptable to them.

In the meantime, AIST commissioned JITA to make a survey on a plausible traceability system for Japan in 1974. An *ad hoc* committee consisting of six subcommittees for specified fields submitted a report in 1975 recommending the introduction of a system of legally authorized intermediate standards laboratories which would transfer national standards to users through their calibrations. Unfortunately, the Joint Committee of Industrial Measurements and Standards was dissolved in 1978 for financial and other reasons, but the above mentioned recommendation was realized in the formation of the Traceability Promotion Committee in MITI, which stands at present.

2.3. Role of the Standards Department of AIST

Throughout the activities for promoting the establishment of traceability systems, it has been pointed out that there are some special problems in the field of reference materials, as follows:

1. Lack of a unified approach for determining the standard values;
2. Lack of a central certifying organization;
3. Lack of an administrative authority which is responsible for reference materials.

A complete solution of these problems has not been attained yet, but Standards Department of AIST has been taking an active part in this field for the last several years. The turning point was probably our participation in the ISO Council Committee on Reference Materials (REMCO) in 1978. The formation of ISO/REMCO itself in 1975 was a result of wavering negotiations since 1969 among such international organizations as the International Bureau of Weights and Measures (BIPM) and the International Organization of Legal Metrology (OIML), and it confines its activity now to providing a general guidance to ISO technical committees on reference materials and to enhancing the production, certification, and utilization of reference materials throughout the world [1].

Thanks to the efforts of ISO/REMCO members, good progress has been made in drafting international guides for terms and definitions (ISO

Guide 30), principle of certification (ISO/REMCO 74), etc., and in compiling the list of suppliers of reference materials. In order to contribute to these activities, the Standards Department of AIST arranged the formation of a Domestic REMCO Committee in the Japan Standards Association (JSA). The committee, consisting of experts from research and testing laboratories, academic institutions, and associations of manufacturers relevant to reference materials, started its activity in 1978 under the chairmanship of Y. Mashiko, ex-director of the National Chemical Laboratory for Industry, AIST. It is now a standing committee, making observations on ISO/REMCO documents, and is, at the same time, working as the leading group to review the general problems and to exchange information in this field.

AIST also commissioned JSA to make a survey on the establishment of a certification system of reference materials in 1981 and 1982. The survey was made by way of a questionnaire on the present status of reference materials, which was distributed among 475 organizations including manufacturing industries, research and testing laboratories, and various associations and institutions. The questionnaire comprises questions on the items and amounts of reference materials in use or in production, specifications adopted for them, and methods of certification. Two-hundred and fifty-eight organizations sent back their answers in which some 5000 species were included. Unfortunately, a greater portion of the species were not reference materials as defined but chemical reagents. However, a strong demand for inspection or certification by an authorized organization was expressed in nearly half of the answers. To our regret, reference materials for thermophysical properties were presented only in limited instances, since most of the destinations of the questionnaire were chosen among the list of manufacturers and laboratories related to chemical analysis.

At the same time, drafting and revision of the Japan Industrial Standards related to reference materials are going on. Some of them are standards for specifying the properties of reference materials themselves, while others are those for the measuring methods of their characteristics. Examples of the former are:

General Rule for Chemical Standards Materials (K 0501);
Standard Specimens from n-Hexane to n-Tridecane (K 0504-0511);
Primary Standard Substances for Volumetric Determination (K 8005);
Dusts and Aerosols for Industrial Testing (Z 8901);
Standard Reference Gases (K 0001–0007);
Metal Standard Solutions (K 0010–0015);
Standard Hardness Test Blocks (B 7730, 7731, 7735);
Standard Liquids for Calibrating Viscometers (Z 8809).

Examples of the latter are:

- Physical Testing Methods for Rubber (K 6300, 6301);
- Methods for Determining the Density and Specific Gravity of Plastics (K 7112);
- Testing Methods of Average Thermal Expansion of Glass (R 3102);
- Method of Testing for Thermal Conductivity of Insulating Fire Bricks by Hot Wire (R 2618).

2.4. Future Problems

The Standards Department of AIST has been investigating a possible scheme for a national information and certification system in Japan, taking the results of the above mentioned questionnaire into consideration. A crude plan has been proposed to establish a data bank and a special committee in the framework of the Japan Industrial Standards Committee (JISC), which is organized under the provisions of the Industrial Standardization Law and is responsible for the accreditation of certifying laboratories. The problems are under investigation again by a special group organized within JSA, which is to present its conclusions within a couple of years.

3. EVALUATION OF THERMOPHYSICAL PROPERTIES DATA

There are a few academic groups in Japan which have been involved with the evaluation or compilation of reference data on thermophysical properties for the past two or three decades. J. Osugi of Kyoto University (professor emeritus) has been working on a scheme for compiling physical and chemical data under high pressures, and T. Makita and his group have been establishing a data base for thermophysical properties of fluids at Kobe University, while K. Watanabe and A. Nagashima are continuing their work on the evaluation of thermophysical properties data at Keio University. Some efforts have also been made on the subject by a number of academic groups such as the Japan Society of Mechanical Engineers, the Chemical Society of Japan, the Society of Chemical Engineers, Japan, and the Society of Material Science, Japan. Probably the first national project on an extensive basis is the recent work entitled Studies on Advanced Use of Chemical Compounds Information by Network Sharing, financed by the Science and Technology Agency and initiated in 1981 [2]. Though we are not in a position to present details of the project, it would be helpful to give its outline here. The project is to be completed by 1985 and is being promoted in cooperation with various ministries, agencies, associations, and experts from universities. It consists of two parts:

1. Development of applied software to realize a shared computer network for the data base.
2. Development of a chemical compounds data base system, which comprises the following 10 bases:
    a. Dictionary of chemical compounds;
    b. Biochemical data base;
    c. Biological data base;
    d. Environmental data base;
    e. Medical and pharmaceutical data base;
    f. Safety data base;
    g. Spectral data base;
    h. Thermal properties data base;
    i. Agricultural chemicals data base;
    j. Acute poisoning data base.

The development of the thermal properties data base mentioned above is allocated to the Japan Information Center of Science and Technology (JICST), which is now compiling thermophysical and some thermochemical data by organizing an *ad hoc* committee for the project with J. Osugi as chairman.

As for the position of AIST on this project, it should be mentioned that the National Chemical Laboratory for Industry, one of our sister laboratories in AIST, is undertaking the compilation of a spectral data base system (item g) in the AIST central computer (RIPS). Six kinds of spectra, infrared, Raman, ^{1}H and ^{13}C nuclear magnetic resonance, mass, and electron-spin resonance, on about 10,000 compounds, will be filed by 1984. Bilateral access to spectral data is under development: display of spectra by the name of compounds and identification of compounds from spectral data. It is planned to establish, finally, a mutual use system accessible from anywhere in Japan using the software to share the network.

4. NRLM ACTIVITIES ON THERMOPHYSICAL PROPERTIES

The following descriptions are outlines of the NRLM research activities and calibration services on thermophysical properties and related standards for measurements.

4.1. Temperature Standards

It is true and generally known that the concept of absolute temperature can be introduced independently of the nature of materials. However, it should be noted that the real temperature scales we have are entirely based on the thermodynamic and thermophysical properties of materials as described below.

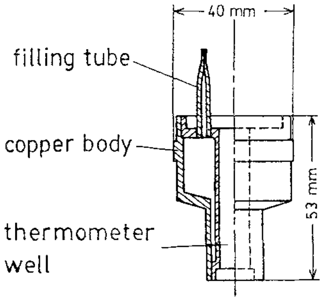


Fig. 1. Sealed copper cell for the realization of triple point temperatures of gases.

4.1.1. Fixed Points

Figure 1 shows a sealed copper cell filled with pure argon or neon with which their triple points are realized [3]. It has been shown by an international comparison that the sealed cell can transfer the triple point temperatures from one place to another with a reproducibility better than 0.1 mK [4]. The triple point of indium has been realized with a sealed glass cell as an alternative to the steam point [5]. The temperature of the triple point of indium has been determined to be 156.6296°C with an uncertainty of 0.0003°C on the International Practical Temperature Scale of 1968 (IPTS-68). From the necessity of a fixed point in the range 660 to 960°C, the realization of the silver-copper eutectic point has been investigated [6]. The melting temperature has been determined to be 779.46°C on the IPTS-68 with a reproducibility better than 0.02°C.

4.1.2. Gas Thermometry

A thermodynamic temperature measurement of the triple point of oxygen (about 54 K) is in progress by means of gas thermometry using helium as a working gas. The preliminary experiments indicate that a measurement accuracy of about 1 mK can be obtained at the final determination [7]. The gas thermometry will be extended to the lower temperature range from 30 to 4.2 K.

4.1.3. Resistance Thermometry

High temperature platinum resistance thermometers (HTPRTs) have been developed since the 1960s aiming at use up to the gold point (1064°C). An acceptable level of reproducibility of the resistances at 0°C has been obtained after long term use at 1000°C. The effect of use at 1100°C is under investigation. The HTPRTs will replace the standard platinum/

rhodium thermocouples for improvement of the IPTS-68 in the range from 630°C at least up to the silver point (960°C), and hopefully up to the gold point.

4.1.4. Radiation Thermometry

The high temperature standards above the gold point were established using a visual pyrometer in the late 1960s and using a photoelectric pyrometer in the late 1970s. For calibration of industrial radiation thermometers below 1100°C, a new traceability system has been developed to permit industrial calibration laboratories to achieve acceptable levels of accuracy with the least effort. The system is based on a standard silicon photocell radiation thermometer calibrated at the freezing points of copper, silver, and aluminum using practical fixed point blackbody furnaces [8, 9].

A measurement apparatus having a blackbody cavity has been constructed for determining the resistance-to-temperature relation of the HTPRTs on the thermodynamic temperature scale. The method is such that a multiplicative comparator of spectral radiances measures radiometrically the temperature of the blackbody cavity into which an HTPRT is inserted. The apparent emissivity of blackbody cavities has been investigated comprehensively at the NRLM. Details are given below.

4.2. Pressure Standards

NRLM has established pressure standards in the range from 1 Pa to 2 GPa. The primary standards are realized by the following three kinds of instruments corresponding to the pressure ranges:

1. Interferometric standard barometers from 1 Pa to 120 kPa.
2. Gas-operated deadweight piston gauges from 0.05 to 1 MPa.
3. Deadweight piston gauges from 0.2 MPa to 2 GPa.

The accuracies of the primary standards are shown in Fig. 2. The performance of the interferometric standard barometer has recently been improved, for example, in the automatic correction for the effect of the refractive index of the working gases. A gas-operated piston gauge having a nonrotating piston-cylinder system has been developed with an accuracy of 9 ppm [10]. In the range above 200 MPa, controlled-clearance piston-cylinder assemblies associated with precision weights ranging from 400 to 1000 kg are used for the deadweight piston gauges. The primary standards up to 2 GPa are realized by those deadweight piston gauges of four different ranges [11]. Commercially available precision manometers and manganin resistance manometers used as transfer standards are calibrated against those primary standards.

The phase transitions of carbon dioxide, mercury, ammonium fluoride, and water have been investigated for the fixed points of pressure, and the

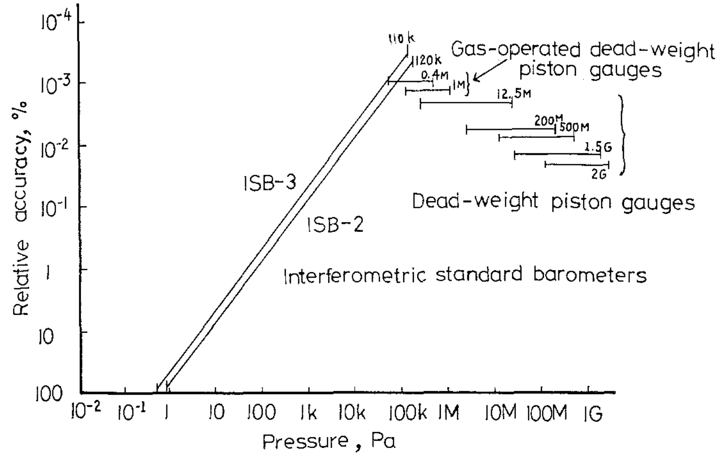


Fig. 2. Accuracy and measuring range of the primary pressure standards.

pressure values and phase diagrams have been determined. For example, the vapor pressure of carbon dioxide at 0°C was found to be 3.48433 ± 0.00045 MPa [12]. This is in good agreement with literature values.

4.3. Density

4.3.1. Density of Water

In the response to the recommendation of IUPAC to the national standards laboratories, NRLM started in 1973 a research project to redetermine the density of water having the same isotopic abundance as that of the Standard Mean Ocean Water (SMOW). The buoyancy method has been employed because of its simplicity and accuracy wherein the density is determined from the buoyancy of a body (called a sinker) having a well-defined volume that is immersed in the sample water. Fused quartz spheres of 85 mm diameter have been prepared as sinkers. The diameters of spheres have been measured interferometrically with an accuracy of 0.1 ppm [13], and the correction for sphericity (about 0.2 μm) has been made to determine the volume [14].

The measurement apparatus (Fig. 3) consists of a balance (upper part) and a sample water cell (lower part). This apparatus actually measures the density of distilled city water. The density of distilled sea water, which is close to SMOW in the isotopic abundance, is determined by comparing it with the sample water using a special pycnometer with a relative accuracy of 2×10^{-7} [15]. The effect of differences of isotopic abundance between

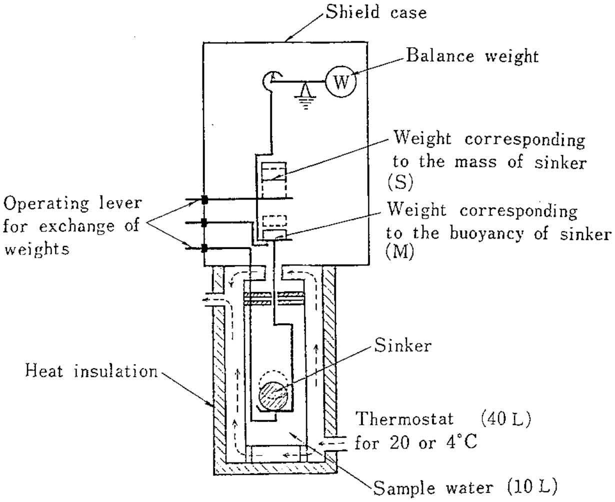


Fig. 3. Apparatus for the measurement of the density of water.

distilled sea water and the sample water, and any other effect from contamination of the sample water during the measurement procedures, are corrected for at this comparison stage. The above measurements are now being replicated to derive the final result. The effect of dissolution of air on the density of water has also been studied [16].

4.3.2. Density at High Pressures

The variable volume method has been investigated for the density measurement of liquids such as pressure-transmitting liquids and lubricants in the pressure range up to 1.5 GPa. In the method the volume change of the test liquid under high pressure is detected by a bellows piezometer installed in a high pressure vessel. The displacement of the bellows is measured by a differential transformer with an accuracy better than 5 μm. The effect of the volume change of the piezometer cell is corrected for using its compressibility measured separately. The compressions of selected liquids are shown in Fig. 4 in the pressure range up to 0.4 GPa. The total accuracy of the density measurement is estimated to be 0.05% [17].

4.3.3. Calibration Services

Considering that vibrating-tube densimeters are widely used in industrial communities, NRLM is investigating the possibility of providing standard liquids for density measurements. For selected organic liquids with different densities ranging from 0.7 to 1.5 $g \cdot cm^{-3}$, the long term

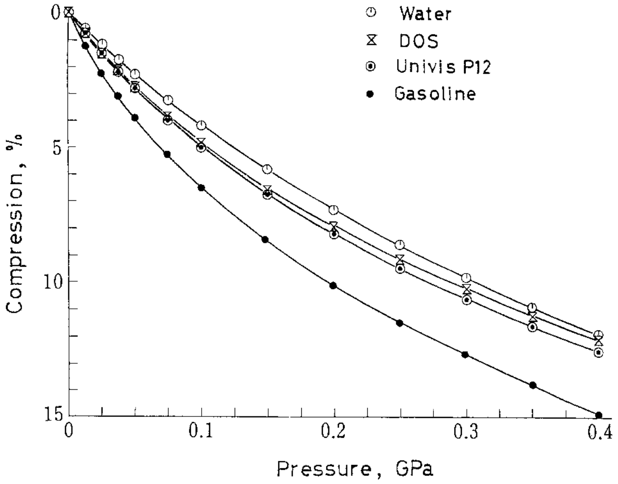


Fig. 4. Compressions of selected liquids at high pressures.

stability of the densities is studied when the liquids are kept in glass containers.

4.4. Thermal Expansion

4.4.1. Liquids

The thermal expansion measurements of pure water are in progress to obtain its density table. The buoyancy and the volumetric methods have been employed aiming at an accuracy better than 1 ppm in the ranges 0 to 44°C and 0 to 85°C, respectively. Figure 5 shows the measuring apparatus

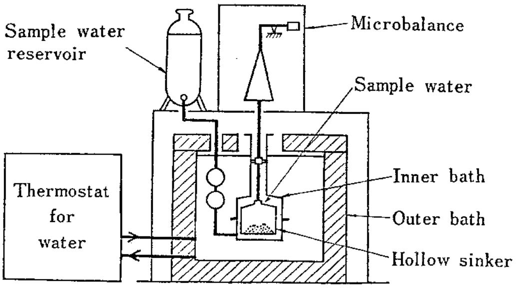


Fig. 5. Apparatus for the measurement of the thermal expansion of water (the buoyancy method).

for the buoyancy method wherein the density change due to temperature (this is equivalent to the thermal expansion) is obtained in the range 0 to 44°C by measuring the buoyancy change acting on the sinker of 300 cm^3 in volume immersed into the sample water [18]. The cylindrical hollow sinker, made of fused quartz, contains an amount of lead grains such that the apparent density of the sinker is nearly equal to the density of the sample water. The preliminary result for pure water is listed in ref. [18]. In the volumetric method the volume of mercury pushed out by the thermal expansion of the sample water in a constant volume cell is measured. Measurement is now under way in the range 0 to 85°C.

4.4.2. Solids

A versatile and accurate dilatometer for the thermal expansion measurement of solids has been developed using a parallel spring movement for supporting the specimen and reflecting mirrors and employing an optical heterodyne interferometer for the displacement measurement [19]. Figure 6 illustrates the optical and specimen-supporting systems. The use of the parallel spring movement requires no special finish to the specimen surfaces and extends the applicability of the dilatometer to specimens having different shapes and dimensions with no significant degradation of the measurement accuracy. The measured thermal expansion coefficients of the NBS Standard Reference Material 736 (copper) agree with the NBS and other calibrations within 1% in the range from 300 to 700 K [20].

The dilatometer is now under improvement by employing a multifold path interferometer, having a resolution higher than 0.05 nm and a long term stability better than 1 nm, which, at the same time, self-compensates the optical misalignment caused by thermal deformation of the components during the measurements [21].

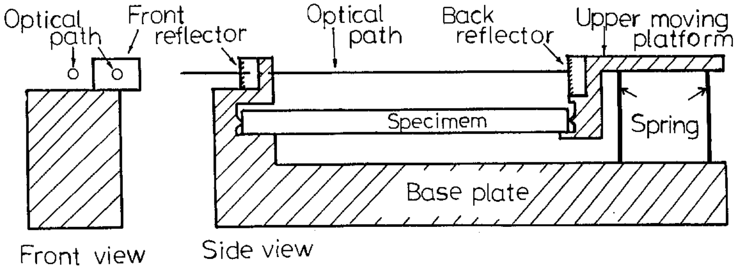


Fig. 6. Specimen holder with a parallel spring component for measuring the thermal expansion of solids.

4.5. Thermal Conductivity

The thermal conductivity measurements of liquids by the transient hot-wire method has been initiated. The accuracy of the method is under evaluation with the intention of determining the thermal conductivity of standard liquids such as water and toluene [22]. The steady-state hot-wire method has been applied to the thermal conductivity measurement of the standard liquids of viscosity to evaluate the heating effect in the precise measurement of viscosity [23].

4.6. Viscosity

4.6.1. Gases

An oscillating-disk viscometer having a suspension strand made of fused quartz has been constructed by which the viscosity is determined from the period and decrement of the disk oscillation. One of the features of this viscometer is the measurement of the angular velocity of the oscillating disk to obtain the logarithmic decrement of oscillation. In the application of the viscometer to low pressure ranges the effect of slip between the oscillating disk and the test gases has been investigated [24]. The viscosity of He, Ne, N_2, and CO_2 gases below 1×10^4 Pa has been determined by correcting the effect of slip.

A falling-piston viscometer has been developed for convenient and precise measurements of gas viscosity. Stable and reproducible falling of the piston through the cylinder is achieved by a tapered gap between the cylinder and the piston. This viscometer has been applied to Ne, C_3H_8, NO, and SO_4 gases [10, 25].

4.6.2. Liquids at High Pressures

A research project for viscosity measurements of liquids at high pressures up to 1.8 GPa has been under way since the late 1970s with application to industrial lubricants and pressure-transmitting liquids of low viscosity. A falling-sphere viscometer applicable up to 0.5 GPa has been developed for the absolute measurement of the viscosity of the reference liquids at high pressures (Fig. 7). The fall rate of the sphere is measured optically using laser beams through the windows on the high pressure vessel. By this method the viscosity of the reference liquid JS 200 (about 0.17 Pa · s at 20°C) has been measured using a precision ruby sphere in the range 20–60°C and up to 0.2 GPa with the coefficient of variation of 0.1 to 0.03% in the fall time measurements [26, 27].

Rolling-ball and falling-cylinder viscometers applicable up to 0.8 and 1.8 GPa, respectively, have been made for the relative measurements of

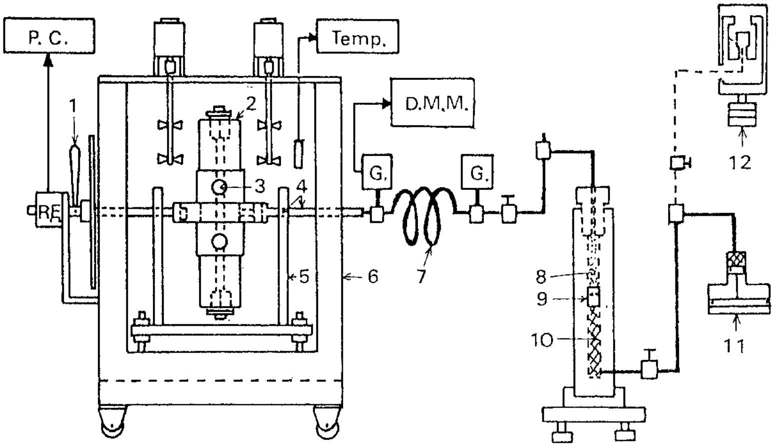


Fig. 7. Schematic diagram of the falling-sphere viscometer for high pressures. P. C., pulse counter; R. E., rotary encoder; Temp., temperature control and measuring system; D.M.M., digital multimeter; G., pressure gauge; *1*, handle; *2*, high pressure vessel; *3*, optical window; *4*, bearing and axis; *5*, stand; *6*, constant temperature bath; *7*, spiral tube; *8*, sample liquid; *9*, piston; *10*, pressure-transmitting oil; *11*, oil pump; *12*, deadweight pressure gauge.

high pressure liquids. The fall rates of the ball and the cylinder are measured by using differential transformers. By the rolling-ball method, the viscosity of synthetic lubricant (Univis P12) has been measured with an estimated accuracy of 1.2% [28].

4.6.3. Standard Liquids

At present 13 kinds of standard viscosity liquids are provided in the range from 2×10^{-3} to 150 Pa · s (at 20°C) according to JIS Z 8809. These have been developed under cooperative work between NRLM and the Central Research Laboratory of Showa Oil Co. Ltd. In 1960 ten kinds of standard liquids (JS 2.5 to JS 2000) were provided, and then three other kinds (JS 20H to JS 200H) were added for use in the higher viscosity range. NRLM is responsible for measuring the viscosity and kinematic viscosity of the standard liquids using normal flow U-tube master viscometers.

4.6.4. International Comparison

Under the auspices of the Subcommittee RDD VII-A of the ASTM Committee D-2, the ASTM Cooperative Kinematic Viscosity Measuring Program has been performed with more than 30 participants from 13 countries of the world. NRLM has participated in the program since 1969

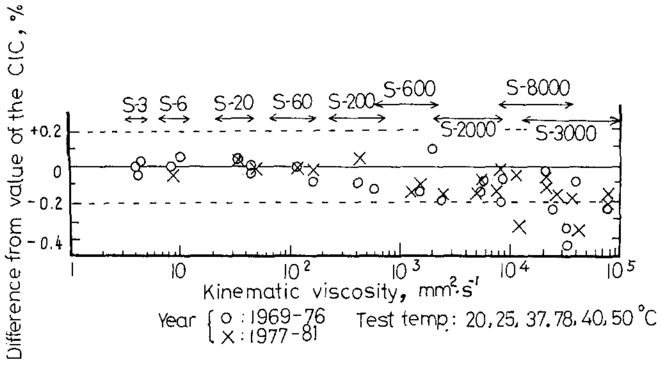


Fig. 8. Comparisons of the viscosity measurements between NRLM and CIC.

to establish international consistency of the viscosity standards. Figure 8 shows the result of the comparison between NRLM and Cannon Instrument Company of the U.S.A. The measurements were made using the U-tube master viscometers.

4.7. Thermal Radiative Properties

4.7.1. Emissivity

Two radiometric methods have been applied for the directional emissivity measurements; one is the separate blackbody method for good thermal conductors (metals or alloys), and the other is the hemispherical mirror method for poor thermal conductors. In the separate blackbody method, the sample emissivity is determined from the surface temperature measured by a thermocouple and the radiance temperature indicated by a monochromatic or total radiation thermometer. The emissivity of anodized, black aluminum surfaces having crossed V-grooves was evaluated to be greater than 0.99 in the spectral range 8–14 μm from 0 to 50°C [29]. Polished surfaces of stainless steel and aluminum surfaces partly covered with black coating have been investigated using a total radiation thermometer [30].

The hemispherical mirror method has been developed for the measurements of poor thermal conductors, the surface temperature of which is difficult to measure accurately by means of contact thermometers [31]. Figure 9 shows the experimental arrangement of a sample and a hemispherical mirror having an aperture on its top through which a radiometer views the sample surface. The mirror aperture approximates a blackbody at

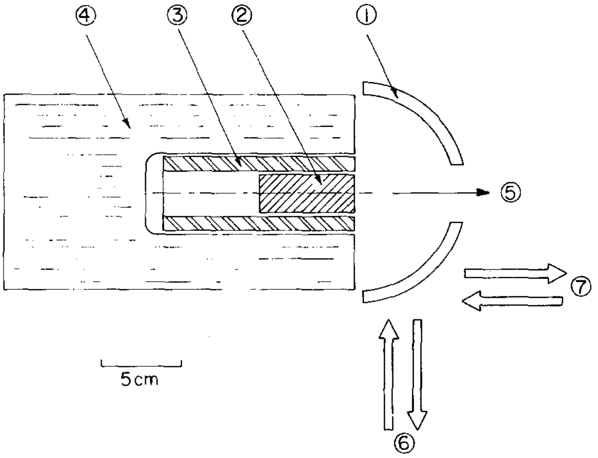


Fig. 9. Experimental arrangement of the hemispherical mirror method for measuring the directional emissivity. *1*, hemispherical mirror; *2*, sample; *3*, thermal guard; *4*, furnace; *5*, observation of radiation; *6* and *7*, directions for positioning a hemispherical mirror laterally and normally, respectively, to the sample surface.

the same temperature as that of the sample surface. The ratio of the radiances without and with the hemispherical mirror in place therefore provides the sample emissivity. This method has been applied to roughened, oxidized stainless steel, silicon carbide, graphite [31], and silicone rubber [30].

4.7.2. Reference Blackbodies

From the difficulty of preparing a surface with a stable and reproducible emissivity, the reference for the radiometric methods of emissivity measurement is always a blackbody having well-defined temperature and emissivity. The radiant characteristics of blackbody cavities have been investigated comprehensively at NRLM. Assuming lambertian surfaces, the apparent emissivities of cylinders, cones, double cones, and cylinders having conical bottoms have been numerically calculated using a series technique [32–34]. The emissivity calculation has been extended to such surfaces that the reflective character is intermediate between diffuse and specular by introducing the specular-diffuse model. The computations of apparent emissivities were performed by using random numbers (Monte Carlo method). This method has been applied to cylindrical cavities with conical bottoms [35, 36] and cavities formed by lateral holes on a metallic tube [37].

The concept of effective temperature of a cavity has been introduced to express the radiant characteristics of nonisothermal cavities. The effect of temperature gradients along a cylindrical cavity was clarified [38].

4.7.3. Reflectance

An apparatus for measuring the bidirectional reflectance distribution function in the spectral range from the visible to 15 μm has been constructed. The reflectance of specially prepared gypsum surfaces has been measured for use as a working standard of diffuse reflectance in aircraft remote sensing [39]. The as-received surfaces of cold rolled steel, hot rolled steel, stainless steel, and aluminum have been investigated to analyze an emissivity-free temperature measurement method in metal manufacturing processes [40].

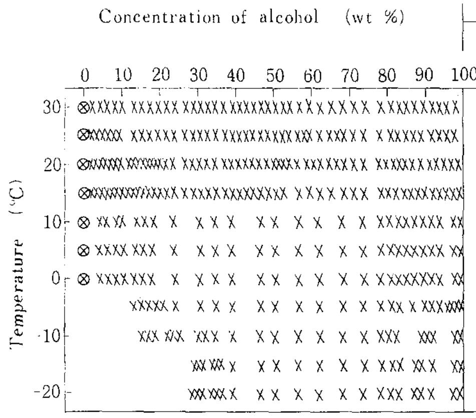
4.8. Heat Flux Density

NRLM has investigated the reliability of heat flow meters from the viewpoints of instrumental and operational errors. An apparatus for calibrating the responsivity of heat flow meters has been made on the basis of the guarded hot plate method to supply a given heat flux density to the heat flow meters. Calibrations have been made for commercial heat flow meters made by different manufacturers. The results were such that there were some heat flow meters for which the specifications of the manufacturers differed from the calibrations of NRLM by as much as 20% [41]. Operational errors of the heat flow meters have been studied using a vertical wall simulator supplying a given heat flux density through the wall [42].

4.9. Statistical Evaluation of Data

At NRLM, a number of statistical methods have been applied for investigating the effect of various conditions on measurements (design of experiment), for assessing the uncertainty of measurements (analysis of variance), and for deriving experimental formulas from observations (regression analysis). One of the typical examples of statistical analysis applied to the measurement of thermophysical properties is the derivation of specific gravity versus concentration and temperature table of alcohol-water mixtures (so-called alcoholometric table) [43].

As no theoretical prediction was available on the form of the formula correlating three variables, orthogonal polynomials were fitted to the observations by the method of least squares. The numerical procedure of orthogonal polynomials was extended to the case where there are two independent variables and the observations are distributed with random



Number n	Weight	Significant figures
47	0.227	5
55	0.444	5
55	0.277	5
55	0.250	5
30	0.309	4
30	0.119	4
30	0.160	4
29	0.025	4
25	0.052	4
23	0.059	4
23	0.027	4

Fig. 10. Distributions of the observations in the specific gravity measurements of alcohol-water mixtures (×) (the observation is duplicated for a few concentrations). The circled ×'s represent the data derived from the specific gravity table of distilled water.

intervals, including a lack of data below the freezing temperatures, as is shown in Fig. 10.

As the precision of the specific gravity measurement was dependent on temperature, a series of data at each temperature was weighted by the reciprocal of the residual variance in fitting a polynomial at respective temperatures. The weighting values are shown in Fig. 10. The total number of observations is 402, including the data for water derived from Chappui's table, which were given a weight of about 10 by assuming a standard error of 3×10^{-6}. As a result of the computation with the significant test of the sums of squares for the terms of respective orders, the specific gravity of an alcohol-water mixture was expressed by the polynomials with the 12th degree in concentration and the 5th degree in temperature, which are nearly equal to those for the OIML alcoholometric table [44].

5. CONCLUSIONS

The establishment of both systems of the traceability of reference materials and the thermophysical properties data base in Japan is still in its early stage, although the experiences of a wide variety of activities, including measurements, calibrations, certifications, and evaluations, have already been accumulated in these fields. As the exactness (precision and accuracy) of the measured values is most important in both systems, they must have international compatibility as their goal, and international cooperation is indispensable not only in scientific fields but also in industrial communities.

ACKNOWLEDGMENTS

The authors are pleased to acknowledge the help given to them by their colleagues in the National Research Laboratory of Metrology and Dr. O. Yamamoto of the National Chemical Laboratory for Industry during the preparation of this review and the encouragement by Dr. M. Kawata, Director-General of the Agency of Industrial Science and Technology.

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