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Role of reference materials for the realization of physicochemical properties. Past, present, and future*

Kenneth N. Marsh†

Department of Chemical and Process Engineering, University of Canterbury, Christchurch, New Zealand

Abstract: Reference materials have long been considered essential for both calibration and checking the correct operation of equipment used for the determination of physicochemical properties. Up until the 1970s, the maintenance of pure reference materials and the means to verify their properties through measurement using state-of-the-art equipment was the prerogative of many national standards laboratories. Over the last 30 years, many of the standards laboratories have either limited or eliminated their activity in maintaining both reference materials and state-of-the-art measuring equipment. One reason is the ready availability of high-purity materials from commercial sources and the ease with which one can now determine purity. A second reason is the ready availability of instruments to measure digitally fundamental quantities such as time, temperature, length, frequency, and voltage accurately has enabled chemical calibration using reference materials to be replaced in many instruments by electrical calibration. At the same time, digitization has enabled the computerization of the whole measurement process. Such automated devices, if not checked with reference materials, can give highly reproducible results but have large systematic errors, leading to poor values. The role of physicochemical reference materials in the past and the present will be outlined, and their status in the future will be explored.

INTRODUCTION

Science and technology is maintained, in large part, through the availability of numerical data obtained by measurement. The uncertainty in the measured values depends, to a large extent, on the reliability of the measurements and the use of a common frame of reference. The common frame of reference for the base system of units that is recognized internationally is the Système International d'Unités (SI) [1]. The means to realize this system, the definition of units, and the methods used to realize them is the responsibility of the Comité International des Poids et Mesures (CIPM) working with international scientific bodies and unions and national standards laboratories. Properties of materials usually have units that are some combination of the base units, and it is necessary to be able to transfer these units from standards laboratories to working laboratories that contain the measuring systems and instruments. Certain measuring devices for properties such as density, viscosity, and some thermal properties often yield results whose uncertainty of measurement and limits of error cannot easily be established without the employment of materials of known properties to calibrate the instrument. In other cases, materials of known properties are used to check the correct operation of an instrument. Materials used for both purposes are called reference materials.

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† E-mail: k.marsh@cape.canterbury.ac.nz

HISTORY OF THE ROLE OF REFERENCE MATERIALS WITHIN IUPAC

In the early years of IUPAC, reference materials or standards were of major concern, as shown in Table 1, which shows the IUPAC Commission structure in 1922 [2]. At the inception, there were two Commissions involved with reference materials for physicochemical properties. The reasons for that emphasis during this period included known difficulties in the purification of materials and, in particular, in establishing their purity. Indeed, in 1922, the only Commission to offer a persuasive case for funding was Physicochemical Standards and they were allocated 9000 francs on the understanding that this was not a precedent. However, their work was held in such high standing that they were given a further 7500 francs in 1923, and funding by IUPAC continued intermittently into the 1940s [3]. A major achievement of the Thermochemical Standards Subcommission (later a full Commission) in 1921 was the adoption of their recommendations for the publication of thermochemical results by the IUPAC Council and the adoption of benzoic acid as the primary thermochemical standard [2].

Rapid changes followed. The changes of significance to physical chemistry and reference materials was the establishment of a Commission on Physicochemical Symbols in 1923, and Commission 5 changed its scope with a name change to Thermochemical Data in 1926. Some of the other founding Commissions were abolished in subsequent years. It is interesting to note that the founders of IUPAC regarded Commissions as having limited lifetimes, with Commission 2.1, 2.2, and 2.3 and 5 to complete their work by 1930. In 1930, it was decided that Commission 4.1, Physicochemical Standards, would become one of the few permanent Commissions. Interestingly, the Commission on Thermochemical Data, scheduled to finish in 1930, produced such a strong case for its continuation that the IUPAC Council had to agree.

The major emphasis of the Commission on Physicochemical Standards in the early days was on physicochemical methods used to determine purity. They gave detailed recommendations on the use of thermal methods (including heat capacity measurements in the vicinity of the melting point), density, vapor pressure, and refractive index, to determine purity. Reference materials or standards were recommended for calibrating and testing the correct operation of these instruments. In addition, the Commission (many of its members being from national standards laboratories) worked with the nation-

Table 1. Commission structure, 1922.

1. Chemical elements
1.1 Atomic Weights
1.2 Isotopes
1.3 Radioactive Substances
2. Reform of Nomenclature
2.1 Inorganic Chemistry
2.2 Organic Chemistry
2.3 Biological Chemistry
3. Bibliographic Documentation
4. Institute of Chemical Standards
4.1 Physicochemical Standards
4.2 Pure Substances for Research
4.3 Documentation Services
5. Thermochemical Standards
6. Tables of Constants
7. Fuels and Ceramics
8. Preservation of Foodstuffs
9. Scientific and Industrial Property (Ownership)
10. Industrial Hygiene
11. Finance

al standards laboratories with respect to supply and certification of reference materials for combustion, viscosity, density, and other physicochemical properties.

There was minimal activity in IUPAC from the middle 1930s until the early 1950s. In 1952, the Physical Chemistry Division was reconstituted with three Commissions of general interest:

(a) Physicochemical Symbols and Terminology
(b) Fundamental Constants (subsequently, it became a working group in CODATA)
(c) Physicochemical Measurements and Standards

and six Commissions with specific interests including Chemical Thermodynamics.

In 1953, the then Commission on Physicochemical Measurements and Standards adopted terms of reference that included the promotion and encouragement of "the use of standard substances for calibrating and checking in physicochemical measurements". However, in the years that followed the Commission remained primarily concerned with the determination of purity, a prerequisite for the establishment of satisfactory reference materials. In 1971, this work culminated in the publication of *The Characterisation of Chemical Purity Organic Compounds*, edited by L. A. K. Staveley [4]. As the project on chemical purity came to a conclusion the Commission turned its attention to the preparation of a catalog of reference materials available from national laboratories. This work lead to the publication in 1972 of *Physicochemical Measurements: Catalogue of Reference Materials from National Laboratories* [5] with a second edition in 1976 [6]. No further catalog was published by IUPAC as a more comprehensive catalog was subsequently published by ISO-REMCO. In 1969, a Task Group on Standard Calibration Substances was formed and proceeded to develop recommendations for calibration and testing of various thermophysical properties. This was a very active group, and in 1976 this work became the primary work of the Commission.

From 1974 to 1981, a series of 16 recommendations were published, and these recommendations were collected, updated, and extended in *Recommended Reference Materials for Physicochemical Measurements and Standards*, edited by K. N. Marsh [7]. In 1981, some members felt that, since much of the cataloguing work of the Commission was now undertaken by ISO-REMCO, the Commission had completed its work while other members sort new directions. No new directions were sufficiently persuasive, so in 1983 it became one of the few Commissions to voluntarily disband and become a Subcommittee of the Physical Chemistry Division. There was a proviso in disbanding that its work would be reactivated after a determination that either new recommendations were required or the previous ones required updating.

Throughout the long history of the Commission, the majority of its members were either representatives of national standards laboratories or were associated with the International Standards Organisation (ISO) or the International Organisation for Legal Metrology (OIML). This representation ensured the authority of its recommendation. Prior to publication, the Commissions' recommendations were circulated widely and in particular to the appropriate experts in national laboratories for verification of the correctness of the information given on their reference materials and on their calibration and validation procedures.

HIERARCHY OF REFERENCE MATERIALS

In the meteorological hierarchy there are different types of reference materials termed primary, secondary, and working. A primary reference material has the highest meteorological quality in a specified field while a secondary reference material is one whose value is fixed by comparison with the primary reference. A secondary reference material is not necessary of inferior quality to a primary reference material. Working reference materials are used for the following four purposes:

- to calibrate instruments
- to check the performance of the instrument or its operator

- provide a means of quality control
- to ensure consistency of the quantity of materials exchanged intrastate, interstate, and internationally in commerce

A working reference material may be a primary or secondary reference material. In addition, some materials have their properties certified by, or their certification is traceable to, an authoritative national or international body, and these are called certified reference materials.

REFERENCE MATERIALS FOR DENSITY

Examples of primary reference materials used for density are water, mercury, and silicon objects. The absolute density of water over a temperature range has not been well known until recently, and the present recommended value is still based on values of the maximum density of water measured at the beginning of the 19th century [8]. This value is probably not known to any better than $\pm 1 \times 10^{-2}$ kg·m^{-3}. The value taken for the uncertainty in the density of water and densities determined by using water as the calibrating fluid is a variable depending on the type of measurement being undertaken. We can compare densities with much greater precision, so, by international agreement, we have taken the density of standard mean ocean water (SMOW) at the maximum density of water as ρ_{max} = (999.975 ± 3×10^{-3}) kg·m^{-3}. We need to define water with a specific isotopic composition since the density of water can vary with its origin and change by distillation and other treatment. SMOW is a pure water sample that has been prepared in a defined way from a sample of deep ocean water and has known D/H and O^{18}/O^{16} ratios. There are formulas to calculate the density of water relative to SMOW from the measured isotopic ratio of a water sample. Water samples from different sources purified in different ways can have density difference up to $\pm 1.5 \times 10^{-2}$ kg·m^{-3}. In 1994, new density measurements were made on SMOW by CSIRO (Australia) [9] using the buoyancy effect on a hollow sphere made of ultra low expansion glass. They obtained give ρ_{max} = (999.9736 ± 0.0009) kg·m^{-3}. In 1996, NRML (Japan) [10] using a fused quartz sphere and purified tap water derived a density for SMOW of ρ_{max} = (999.9757 ± 0.0008) kg·m^{-3}. The relative difference of 2.1×10^{-6} is more than the combined uncertainties. A recent meeting of the Task Group on the Density of Water of CIPM recommended a value of ρ_{max} = (999.9749 ± 0.0008) kg·m^{-3} be promulgated in 2001 [11]. This value is in remarkable agreement with the original value. For measurements on aqueous solutions, where we use the same water sample and require a determination of density differences, we are at liberty to reduce the relative uncertainty in density differences to considerably better than $\pm 1 \times 10^{-3}$ kg·m^{-3}. The above values assume that the water is thoroughly degassed, as a saturated sample of water is less dense than degassed water by about $\pm 2.5 \times 10^{-3}$ kg·m^{-3}.

Despite all the above, most researchers habitually refer to the tables in various compilations that give the density of water at 298.15 K as 997.0480 kg·m^{-3} and take it as god-given without a second thought.

REFERENCE MATERIALS FOR VISCOSITY

A somewhat similar situation arises with the use of water as the primary reference material for the calibration of viscometers. There is an additional complexity. Because the viscosity of fluids varies over orders of magnitude no single reference material can be used for calibration. The present value of the viscosity of water is primarily based on a single set of measurements reported by Swindels, Coe, and Godfrey in 1952 [12] from measurements made at the then National Bureau of Standards (NIST) over a period of nearly 20 years.

They reported a value of (1.0019 ± 0.0003) mPa·s at 293.15 K and in 1958, ISO recommended a value of 1.002 Pa·s based on that work and on the fact that this value had been used rather widely over a period of time. The measurements by Swindells *et al*. were made with capillary viscometers, where

possible systematic errors could not be estimated. Nevertheless, an uncertainty of about ±0.0025 mPa·s was later assigned by ISO after careful reexamination of the measurements. The only other measurements on water considered to be made to metrological standards were those of Berstad *et al*. [13] using an oscillating cylinder, which is an absolute method. That value had an estimated uncertainty of ±0.0005 mPa·s and differed from the value of Swindels *et al.* by considerably more than the combined uncertainties estimated by the authors. ISO, in 1998, after reviewing all the measurements recommended an uncertainty of ±0.0025 mPa·s. At a recent meeting of the Commission 1.2 Subcommittee on Transport Properties it was reported that there exists an unconfirmed report that, after the completion of the Swindels *et al*. measurements, the capillaries were reexamined and the bore of the tube was found to be not as constant as initially assumed. NIST have been requested to reexamine any notebooks and documentation associated with those experiments. Thus, there is the possibility that the absolute viscosity of water could be uncertain by as much as ±0.3%. How important is such an uncertainty? In most cases, such a large uncertainty is not important as long as it is realized that the majority of viscosity values of dense liquids have, until recently, been reported relative to the viscosity of water. However, with the advent of various absolute methods, such as the vibrating wire, oscillating disk, and torsional crystal, this is no longer the case. At present, most of these absolute methods give viscosity values of liquids to, at best, ±0.7%.

Another concern is with the methods used to calibrate viscometers over the wide range of viscosities of fluids encountered in practice. Such calibrations can be made with certified reference materials distributed by national laboratories or traceable to national laboratories. These laboratories do not use pure materials as certified reference materials because they have found that the viscosity of such materials can depend significantly and indeterminately on their purity. Usually, the reference materials used are commercial oils selected because they are nonhygroscopic and stable over long time periods. Batches are calibrated using a series of master viscometers by a building-up principle, with the uncertainty in the viscosity value increasing with the number of inter comparisons. In addition to the uncertainty in the absolute viscosity of water, an uncertainty of up to ±0.6% is present for viscosity values from (10 to 100) Pa·s.

Capillary viscometers, unless carefully constructed, can have kinetic-energy and end-corrections factors as well as surface tension effects that result in a nonlinear relationship between flow time and viscosity. Figure 1, a calibration curve for a typical viscometer for use to measure viscosity below 1 mPa·s, shows that neglect of this correction can give rise to errors of up to 5%, particularly with low-viscosity fluids. It is surprising how many measurements on the viscosity of liquids and liquid mixtures

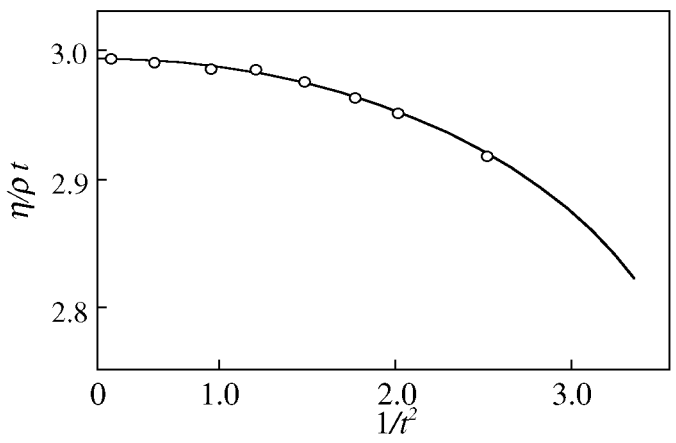


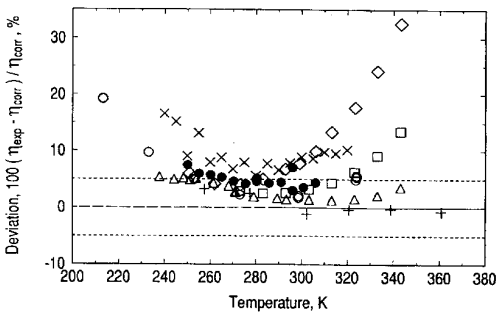
Fig. 1 Viscometer calibrated with water at temperatures T from 283.15 K to 343.15 K.

fail to make any comment about the kinetic and end corrections or indicate in a vague sentence that the correction is negligible.

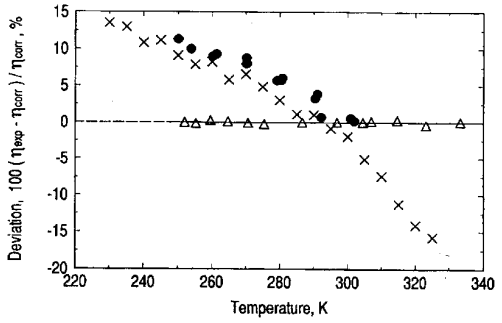
The viscosity of pure fluids can vary indeterminately with small amounts of impurity. If no effort is made to purify a material, measurements on different commercially available, common, pure organic fluids can vary between laboratories by well over 2%. Hence, it is surprising how many publications report the use of such fluids for the calibration of viscometers and claim uncertainties in their viscosity values of better than ±0.5%, often some claiming ±0.1%. When asked to justify such claims it is clear that the claims are made on the basis of the repeatability of the measurements and assume no error in the value of the various "reference" materials they have used. Except for water, these materials are usually of ill-defined impurity straight from a bottle, and their value will often differ considerably from a purified sample.

Measurements made at reputable laboratories using equipment that has been demonstrated to give the highest quality results does not guarantee the quality of new measurements. The Subcommittee on Transport Properties [14] has documented discrepancies in the measurements of the viscosity and thermal conductivity of R-125 and R-134a. Differences of the order of 25% were noted as shown in Fig. 2. The causes for the differences were ascribed to either impurities or measurement errors. The Subcommittee organized a round-robin with a standard sample of R-134a distributed to the participating laboratories, with facilities to reanalyze the samples after the completion of the measurements.

The new measurements on the viscosity of a standard sample of R-134a reduced the discrepancies to a maximum value of 6% with a mean deviation about 3% [15]. Combined with the earlier measurements, the results from the four main methods (capillary, rolling ball, vibrating wire, and oscillating disc) are now in good agreement and within the combined uncertainties of the various methods. The torsional crystal results remain as outliers. The reasons for the major discrepancies in the earlier results are not fully understood, but effects due to particles in the sample, reaction of the refrigerant with pressure seals, residual water, and inappropriate technique or analysis have been suggested. Similar discrepancies in the earlier measurement on the thermal conductivity of R-134a have also been resolved [15]. Again, some of the differences resulted from using inappropriate techniques. Such results illustrate that significant errors can occur when making measurements on new materials under new conditions even in laboratories that have special skills in such measurements.



Deviations of the viscosity of R134a in the liquid phase at saturation available in 1992 from the correlation of the results of Krauss et al. [9]. ×, Diller et al. [2]; ◇, Fellows et al. [3]; △, Oliveira and Wakeham [4]; ●, Ripple and Matar [5]; □, Kumagai and Takahashi [6]; +, Ruvinski et al. [7]; ○, Okubo et al. [8].



Deviations of the viscosity of R125 in the liquid phase at saturation available in 1992 from the correlation of Oliveira and Wakeham [12]. △, Oliveira and Wakeham [12]; ●, Ripple and Matar [5]; ×, Diller and Peterson [13].

Fig. 2 Deviations in the viscosity of R-134a and R-125 in the liquid phase at saturation available in 1992 from the correlations of Krausse *et. al*. and Olivera and Wakeham respectively. Reprinted with permission from *Int. J. Thermophys.* **16**, 63 (1995).

REFERENCE MATERIALS USED IN CALORIMETRY

Reference materials are used extensively in all areas of calorimetry and the chapter on enthalpy [16] contains an extensive list of reference materials recommended for the calibration and testing in measurements concerned with heat capacity, enthalpies of phase change, enthalpies of reaction and mixing, and enthalpies of combustion. Within each group, specific compounds, reactions, or mixtures were recommended depending on the phases or phase changes under study. In some cases definitive recommended values with their estimated uncertainties were given, while for other materials, only values and their uncertainties as given by the various investigators were reported. During the preparation of the series of recommendations, two major points of view were held concerning materials that were not provided with certified values from standards laboratories. One view was that the Commission should analyze all the measurements that had been made for the particular property and, after assigning weighting for the estimated uncertainties, provide definitive recommended values. The other view was that all the measured values, along with the authors' uncertainties, should be listed and the reader be invited to make his or her own conclusions when using that material. In the chapter on enthalpy both these views are expressed, depending on the preference of the various contributors. I have argued that definitive values derived from careful analysis of the all the data would have made the publication much more valuable.

ENTHALPY OF COMBUSTION

For combustion studies it is rare to use electrical calibration, and most calorimeters are calibrated using reference materials. By international agreement, benzoic acid is the principal reference material for measuring the energy equivalent of oxygen-bomb calorimeters. NIST, through its Office of Standard Reference Materials, provides certified benzoic acid. The Physical and Chemical Properties Division within NIST appears to be the only standards laboratory now capable of determining the enthalpy of combustion of a benzoic acid sample using a calorimeter calibrated by means of electrical energy. Because calibration with electrical energy is excessively time-consuming and requires special care, only every third batch of thermochemical-grade benzoic acid is now determined in an electrically calibrated combustion calorimeter. The other samples are determined by inter-comparison with a standard sample whose value was determined in a calorimeter calibrated by means of electrical energy. It should be noted that benzoic acid used for calibration purposes is not necessarily pure, and the certified value can differ considerably from the value for pure benzoic acid. The uncertainty in the value of the enthalpy of combustion of a standard sample of benzoic acid is of the order of ±0.004%.

Methane is the reference material used for calibrating calorimeters used for measuring the calorific value of fuels. Its reference value is based on the measurements by Prosen and Rossini in 1945 [17] and Pittam and Pilcher in 1972 [18]. The various measurements are shown in Fig. 3. Various national and international groups have been involved in the reanalysis of the two sets of measurements and derived different recommended values. The difference revolves around the treatment of the outlier point initially rejected by Prosen and Rossini. A detailed evaluation by Garvin *et al*. [19] of all the values reported in the two papers concluded that the rejection of the outlier was not justified, leading to a considerably higher uncertainty in the heating value of methane. Some groups did not agree with this reassessment. Since the recommended heating value of methane is used in calculating the commercial value of natural gas, it is essential that we have international agreement. New designs of commercial flow calorimeters have a precision considerably better than the uncertainty with which the value for methane is now known, and there has been a recent call for a redetermination of the heating value of methane. In the early 1990s, Sayer measured a value of (890.63 ± 0.20) $J \cdot mol^{-1}$ at 298.15 K [20]. No details of the measurement method and number of measurements have been published. The Physikalisch Technische Bundesanstalt, Braunschweig (PTB), in conjunction with a number of gas sup-

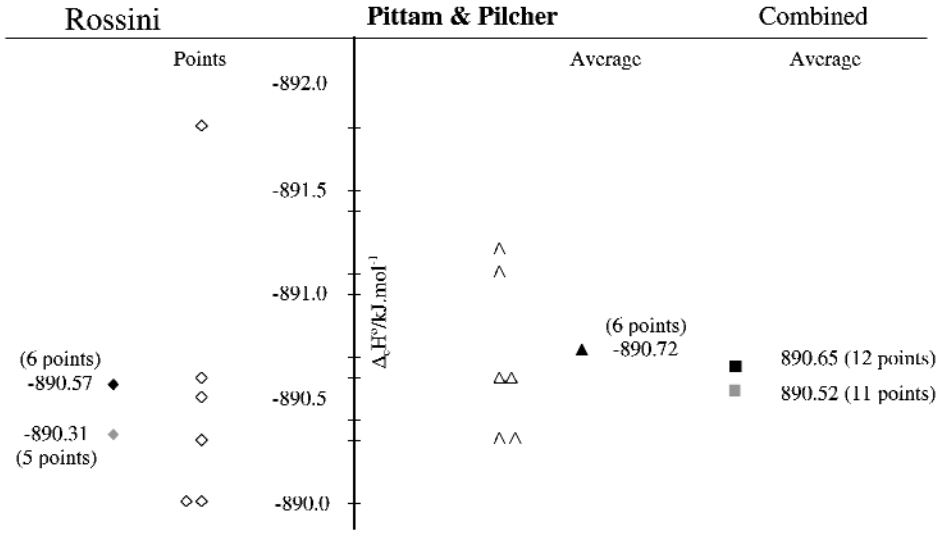


Fig. 3 Comparison of the measurements of the enthalpy of combustion of methane made by Rossini and by Pittam and Pilcher and average values using different number of points.

ply companies, are preparing a feasibility study on the design of a reference calorimeter having an uncertainty of better than ±0.05% on the basis of two standard deviations [21].

RECENT HISTORY OF STANDARDS LABORATORIES, REFERENCE MATERIALS, AND MEASUREMENT DEVICES FOR PHYSICOCHEMICAL PROPERTIES

From the mid 1970s, many national measurement laboratories have either limited or eliminated their activity in both reference materials and state-of-the-art methods to measure the properties of reference materials, particularly in the area of thermochemistry. At the same time, commercial suppliers began to provide chemicals of high purity and the methods of determining purity based on gas–liquid chromatography (GLC) and high-performance liquid chromatography (HPLC) became readily available. Such advances eliminated the need for many reference materials used for purity determinations. In addition, instrument manufacturers moved rapidly to provide automated instruments that gave a digital readout of the property value directly, often with minimal human intervention. Such instruments, which include densimeters, viscometers, thermal conductivity meters, and calorimeters, can give digital outputs that often have more significant figures than many early experimentalists ever dreamt. Such devices lull the unsuspecting experimentalist into a false sense of security and appear to eliminate the need for reference materials since they require minimal or no calibration. How can the experimentalist be certain that the square of the natural vibration period of an oscillating tube is linear in the density and independent of the viscosity of the fluid? Does the automated viscometer have an in-built correction for kinetic and end effects? Some instruments do not allow such corrections to be incorporated, on the basis that the manufacturer knows best. With such instruments, the user should be obliged to check the performance with reference materials to ensure confidence in at least some of the many significant digit numbers that are transmitted electronically to the computer to await further digital analysis, often to provide unrealistically small standard deviations, reinterpreted as uncertainties, which have no relation to the known uncertainties expected from the technique.

RESPONSIBILITY FOR RECOMMENDED VALUES OF REFERENCE MATERIALS

The IUPAC recommendations on reference materials were finalized between 1983 and 1986. The major aim of these recommendations was to provide users advice as to the best materials and values to use when either calibrating or testing apparatus. Those requirements still exist. When the Commission on Reference Materials was disbanded, a mechanism was put in place to enable the update of the recommendations, but that mechanism has now been abandoned. I believe that the publication of a book with updated recommended reference materials and their values is not a feasible option without a concerted effort from interested parties in diverse areas of physical chemistry. However, it is essential that recommendations be promulgated from authoritative bodies and there not be competing recommendations. The IUPAC Commission on Electrochemistry has just published provisional recommendations on *Measurement of pH: Definition, Standards, and Procedures* [22] that is more comprehensive than the previous reference materials recommendation and will be a worthy successor. That recommendation was produced by 11 of the leading experts in the field and has been widely distributed as provisional recommendations for comment and criticism prior to being accepted by IUPAC. In 1991, the Subcommittee on Transport Properties of the Commission on Thermodynamics updated the recommendations on viscosity and thermal conductivity and added recommendations on diffusion coefficients in *Experimental Thermodynamics, Vol. III. Measurement of the Transport Properties of Fluids* [23]. The Subcommittee organizes collaborative projects whose aim is to provide reference type data on well-characterized materials. They have recently proposed the remeasurement of the thermal conductivity of butane, the reevaluation of the viscosity of liquid water, the determination of the viscosity of cyclopentane, and an investigation of a new high-viscosity standard. This subcommittee has the requisite mix of experts from national standards laboratories and leading academic researchers in the field and is eminently qualified to develop new authoritative recommendations on transport properties.

Recommendations do not need to follow strictly the format of the previous recommendations. The format adopted was a compromise between conflicting views and arrived at after considerable debate. While the listing of reference materials available from national standards laboratories and other certified distributors was regarded as essential at the time, this information is now readily available from the ISO-REMCO database. The section on enthalpy has recently been updated by the Thermochemistry Working Group of the International Confederation of Thermal Analysis and Calorimetry [24]. I do not know if the Commission on Thermodynamics was consulted and if they approved of the transfer of authority from IUPAC. I was not aware of the work until after its publication. There exist problems with these recommendations. The Thermochemistry Working Group has not addressed the previous problem of the uniformity of the recommendations. In addition, the heat capacity values were readjusted to ITS-90, with the authors making no comment on the correctness or otherwise of the method used. That method has been a subject of controversy, and, at present, there appears to be no consensus on the correct method for readjusting smoothed heat capacity values from different temperature scales. Further, some values reported, even allowing for the conversion to ITS-90, are not now the values recommended by the issuing standards laboratory. In addition, recent high-quality measurements and evaluations on a number of the reference materials have not been included, and some new results have added to the range of available reference materials. Of concern is that the recommendations do not appear to have been widely circulated as provisional recommendations to all interested parties for a suitable period of time to allow informed comments, corrections, and updates.

CONCLUSIONS

The founding fathers of IUPAC understood fully the importance of the role of reference materials in both the meteorological hierarchy and the measurement chain in ensuring that high-quality experimental data is reproducible between laboratories. The need for recommended property data on reference materials increases as we make different measurements on new materials under more adverse condi-

tions of temperature and pressure. I believe that recommendations are only authoritative if international bodies issue them after consultation with all interested parties. IUPAC must determine if they are to continue to be the body to encourage this work.

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