Understanding Uncertainty in Viscosity Measurement

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This Application Note provides information relating to measurement precision in general, and the precision of kinematic viscosity measurements in particular. It provides a brief history and discussion of primary concepts relating to measurement uncertainty. The information was drawn primarily from the National Institute of Standards and Technology (NIST) Reference on Constants, Units, and Uncertainty and the NIST Technical Note 1297 1994 Edition. The Application Note concludes with a practical example of uncertainty calculation for a CANNON viscosity reference material.

Over the years, many different approaches to evaluating and expressing the uncertainty of measurement results have been used. Because of this lack of international agreement on the expression of uncertainty in measurement, in 1977 the International Committee for Weights and Measures (CIPM, Comité International des Poids et Measures), the world's highest authority in the field of measurement science (i.e., metrology), asked the International Bureau of Weights and Measures (BIPM, Bureau International des Poids et Mesures), to address the problem in collaboration with the various national metrology institutes and to propose a specific recommendation for its solution. This led to the development of Recommendation INC-1 (1980) by the Working Group on the Statement of Uncertainties convened by the BIPM, a recommendation that the CIPM approved in 1981 and reaffirmed in 1986 via its own Recommendations 1 (CI-1981) and 1 (CI-1986):

Recommendation INC-1 (1980) Expression of experimental uncertainties

1. The uncertainty in the result of a measurement generally consists of several components which may be grouped into two categories according to the way in which their numerical value is estimated. Type A measurements are those which are evaluated by statistical methods. Type B measurements are those which are evaluated by other means There is not always a simple correspondence between the classification into categories A or B and the previously used classification into "random" and "systematic" uncertainties. The term "systematic uncertainty" can be misleading and should be avoided. Any detailed report of uncertainty should consist of a complete list of the components, specifying for each the method used to obtain its numerical value.

2. The components in category A are characterized by the estimated variances s_i^2 (or the estimated "standard deviations" s_i) and the number of degrees of freedom v_i. Where appropriate the covariances should be given.

3. The components in category B should be characterized by quantities u_j^2, which may be considered approximations to the corresponding variances, the existence of which is assumed. The quantities u_j^2 may be treated like variances and the quantities u_j like standard deviations. Where appropriate, the covariances should be treated in a similar way.

4. The combined uncertainty should be characterized by the numerical value obtained by applying the usual method for the combination of variances. The combined uncertainty and its components should be expressed in the form of "standard deviations."

5. If for particular applications, it is necessary to multiply the combined uncertainty by an overall uncertainty, the multiplying factor must always be stated.

The Guide to the Expression of Uncertainty in Measurement (GUM)

The above recommendation, INC-1 (1980), is a brief outline rather than a detailed prescription. Consequently, the CIPM asked the International Organization for Standardization (ISO) to develop a detailed guide based on the recommendation because ISO could more easily reflect the requirements stemming from the broad interests of industry and commerce. The ISO Technical Advisory Group on Metrology (TAG 4) was given this responsibility. It in turn established Working group 3 and assigned it to develop a guidance document based upon the recommendation of the BIPM Working Group on the Statement of Uncertainties which provides rules on the expression of measurement uncertainty for use within standardization, calibration, laboratory accreditation, and metrology services; The end result of the work of ISO/TAG 4/WG 3 was the 100-page Guide to the Expression of Uncertainty in Measurement (or GUM as it is now often called). It was published in 1993 (corrected and reprinted in 1995) by ISO in the name of the seven international organizations that supported its development in ISO/TAG 4:

BIPM	Bureau International des Poids et Mesures
IEC	International Electrotechnical Commission
IFCC	International Federation of Clinical Chemistry
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
IUPAP	International Union of Pure and Applied Physics
OIML	International Organization of Legal Metrology

GUM Acceptance

GUM methods have been adopted by various regional metrology and related organizations including:

NORAMET	North American Collaboration in Measurement Standards
EUROMET	European Collaboration in Measurement Standards
EUROLAB	A focus for analytic chemistry in Europe
EA	European Cooperation for Accreditation

The GUM has been adopted by NIST and most of NIST's sister national metrology institutes throughout the world, such as the National Research Council (NRC) in Canada, the National Physical Laboratory (NPL) in the United Kingdom, and the Physikalisch-Technische Bundesanstalt in Germany. The GUM is the standard reference used by CANNON Instrument Company in the determination of uncertainties associated with our equipment and calibration procedures.

Determination of Uncertainties

Type A Uncertainty (variance that is capable of measurement by statistical means) determination may be made by any valid statistical method for treating data. Examples are calculating the standard deviation of the mean of a series of independent observations using the method of least squares to fit a curve to data in order to estimate the parameters of the curve and their standard deviations; and carrying out an analysis of variance (ANOVA) in order to identify and quantify random effects in certain kinds of measurements.

Type B Uncertainty (variance that is determined by other means) may include use of previous measurement data, general knowledge of relevant materials or instruments, manufacturer's specifications, and data provided in calibration and other reports.

Combination of Uncertainties

Most measurements involve several different actions, all of which may introduce an element of uncertainty into the final measurement. The combined standard uncertainty (u_C) is taken to represent the estimated standard deviation of the result. It is obtained by combining the individual standard uncertainties, using the usual method for combining standard deviations. This method is often called the law of propagation of uncertainty and in common parlance as the "root-sum-of-squares" (square root of the sum-of-the-squares) or "RSS" method of combining uncertainty components estimated as standard deviations.

It is assumed that a correction factor is applied to compensate for each recognized systematic effect that significantly influences the measurement result and that every effort has been made to identify such effects. The relevant uncertainty to associate with each recognized systematic effect is then the standard uncertainty of the applied correction. The correction may be either positive, negative, or zero, and its standard uncertainty may in some cases be obtained from a Type A evaluation while in other cases by a Type B evaluation.

Expanded Uncertainty

Although the combined standard uncertainty is used to express the uncertainty of many measurements, some commercial, industrial and regulatory applications may require a measure of uncertainty that defines an interval about which the measurement value will lie with a certain level of statistical certainty. This type of measure is termed expanded uncertainty, and is determined by multiplying the combined standard uncertainty by a coverage factor, *k*. The coverage factor is usually in the range of 2 to 3. In keeping with practices adopted by a variety of national standard laboratories and several metrological organizations, the stated National Institute of Standards and Technology (NIST) policy is to use expanded uncertainty *U* to report the results of all NIST measurements other than those for which combined standard uncertainty has traditionally been employed. To be consistent with current international practice, the value of *k* to be used at NIST for calculating *U* is, by convention, *k* = 2. Values of k other than 2 are only to be used for specific applications dictate by established and documented requirements. When the normal distribution applies and U_C (the combined standard uncertainty) has negligible uncertainty, $U = 2U_C$ (coverage factor of 2) defines an interval having a level of confidence of approximately 95 percent. $U = 3U_C$ defines an interval having a level of confidence of greater than 99 percent.

Harmonizing NIST and ASTM terminology on uncertainty

One difficulty in understanding and determining uncertainty is a lack of standardization of language used in discussion of uncertainty. As previously stated, CANNON reports the uncertainty according to the NIST Technical Note 1297 Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results. However, our customers may also frequently reference ASTM publications, as we do at CANNON. It is important to understand the relationship of the terminology on uncertainty. The following table may be useful:

CANNON publishes the expanded uncertainty with a k = 2 coverage factor.

A practical example of uncertainty calculation

NIST Terminology	ASTM Equivalent Terminology
Combined standard uncertainty (U_C)	Standard error (SE)
Coverage factor (*k*)	Coverage factor (*k*)
Expanded uncertainty (*U*)	Combined Extended Uncertainty (CEU)
$U = k * U_C$	CEU = *k* * SE

ASTM D 445-07, the current method for determination of kinematic viscosity using glass capillary viscometers, specifies an acceptable tolerance band (zone) for the acceptability of kinematic viscosity test results. The procedure for ascertaining the tolerance zone (TZ) is described in Annex A4, summarized as follows:

1) Determine the standard deviation for site uncertainty ($\sigma 2_{site}$). If unknown, use the value 0.19 percent.

2) Determine the combined extended uncertainty (CEU) of the accepted reference value (ARV) of the certified viscosity calibration standard.

3) Calculate the standard error of the accepted calibration, using the following equation:

$$TZ = \pm 1.44\sqrt{\sigma^2_{site} + SE^2_{ARV}}$$

In the example certificate, assuming a test temperature of 25°C and the recommended value for site uncertainty, substituting 0.19 for the site uncertainty variable and substituting the appropriate value from the Certificate of Calibration for the viscosity standard (see next pages), divided by 2 to account for the coverage factor, yields the following result, expressed as a percentage:

$$TZ = \pm 1.44\sqrt{0.19^2 + (\frac{0.22}{2})^2} \quad \text{or} \quad TZ = \pm 1.44\sqrt{0.0361 + 0.0121}$$

$$TZ = \pm 1.44\sqrt{.0482} \quad \text{or} \quad TZ = \pm 0.32$$

In this example, the tolerance zone will be ±0.32 percent of the certified viscosity value on the certificate/bottle label. With the certified value of 33.98 centistokes, **TZ = 33.871 - 34.089 cSt** with 95 percent certainty. Viscosity measurements made with that standard at that site should fall within that tolerance zone 19 out of 20 times.

REPORT OF CALIBRATION

This report of calibration shall not be reproduced except in full, without the written approval of Cannon Instrument Company.

The Cannon Instrument Company certifies that the kinematic viscosities were determined by the Master Viscometer technique reported in the Journal of Research of the National Bureau of

Mfg. Date: **2/25/2004** CANNON® CERTIFIED VISCOSITY STANDARD

Viscosity Standard: **S20** Lot No.: **04101** Use before: 2/28/2006

Temperature		Kinematic Viscosity	Viscosity	Density	Saybolt Viscosity
°C	°F	mm^2/s, (cSt)	mPa·s, (cP)	g/mL	seconds
20.00	**68.00**	**43.49**	**37.53**	**0.8630**	
25.00	**77.00**	**33.98**	**29.22**	**0.8598**	
37.78	**100.00**	**19.65**	**16.73**	**0.8516**	**96.3 SUS**
40.00	**104.00**	**18.02**	**15.32**	**0.8501**	
50.00	**122.00**	**12.63**	**10.66**	**0.8437**	
98.89	**210.00**	**3.797**	**3.084**	**0.8124**	
100.00	**212.00**	**3.720**	**3.020**	**0.8117**	

All data are traceable to the National Institute for Standards and Technology

Standards, (Vol. 52, No. 3, March 1954, Research Paper 2479) and Cannon Laboratory Standard viscometer. The above data are based on the primary standard, water at 20°C (ITS-90), with a viscosity of 1.0016 mPa ·s or kinematic viscosity of 1.0034 mm^2/s as listed in ISO 3666. See also ASTM methods D2162, D445, D446, D2161, D2171 and ISO 3104 and 3105. This material ceases to be a standard after the date shown on this certificate. Manufactured in the U.S.A.

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R. E. Manning, Ph.D., P.E.
M. T. Zubler
K. O. Henderson

Results relate only to the sample tested.

[1] *The inclusion of the A2LA logo does not imply certification/approval of the products calibrated or tested*

REPORT OF CALIBRATION

Kinematic viscosity measurements at temperatures of 20°C through 40°C have been made using Cannon and Cannon-Ubbelohde (long-capillary) Master viscometers, as described in ASTM D 2162. Measurements at lower and higher temperatures have been made using Cannon-bbelohde Laboratory Standard viscometers. The expanded uncertainty of the measurements at 95% confidence over the temperature range of -40°C to +150°C is as follows:

K=2

Range of Kin Vis (mm^2/s)	Expanded Uncertainty* (%) at temperatures: <15°C	15 to 45°C	>45°C
<10	0.21	0.16	0.21
10-100	**0.26**	**0.22**	**0.26**
100-1000	0.32	0.29	0.32
1000-10,000	0.47	0.38	0.38
10,000-100,000	0.53	0.44	0.48

** An expanded uncertainty U is determined by multiplying the combined standard uncertainty u_c by a coverage factor k: $U = k\,u_c$ where k=2. See NIST Technical Note 1297, 1994 edition, Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results.*

The assigned accuracy of the primary viscosity standard at 20°C (ITS-90) is ± 0.17%. See ISO 3666.

The estimated precision of density measurements for liquids having a kinematic viscosity less than 1000mm ^{2}/s is ± 0.0001 g/mL. For liquids of kinematic viscosity from 1000 to 100,000mm ^{2}/s, the estimated accuracy of density is ± 0.0002 g/mL. Viscosity in mPa·s is the product of the measured kinematic viscosity in mm^2/s and density in g/mL, both at the same temperature.

Temperature measurements are traceable to the National Institute for Standards and Technology, Test No. 260470. Viscosity Standards

Viscosity Standards S3 through S600 and N35 through N600

CAS No.: 8012-95-1 FORMULATION: Mineral Oil (100%)
CHEMICAL HAZARD: Not applicable
HEALTH HAZARD: Contact may cause irritation of skin, eyes, and mucous membranes. Inhalation of vapor may cause irritation of respiratory passages.
FIRST AID PROCEDURES: Skin: Wash with soap and water. Eyes: Flush with water. Inhalation: Remove to fresh air. Ingestion: Get medical assistance. Do not induce vomiting.

DOT: Not regulated EPA: Not regulated

Viscosity Standards S2000 through 30000 and N2000 through N2700000

CAS No.:9003-28-5 FORMULATION:Poly (1-butene)(100%)
CHEMICAL HAZARD: Not applicable
HEALTH HAZARD: Contact may cause irritation of skin, eyes, and mucous membranes. Inhalation of vapor may cause irritation of respiratory passages.
FIRST AID PROCEDURES: Skin: Wash with soap and water. Eyes: Flush with water. Inhalation: Remove to fresh air. Ingestion: Get medical assistance. Do not induce vomiting.

DOT: Not regulated EPA: Not regulated

THIS PRODUCT WAS CALIBRATED WITHIN A QUALITY SYSTEM WHICH IS REGISTERED TO ISO 9001:2000.

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