資　料

熱量測定および熱分析用標準物質（I）

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標準物質は物性標準物質と組成標準物質とに区分されるが，表題の熱量測定および熱分析用標準物質は前者の範ちゅうのものである。後者の範ちゅうには化学分析用標準試料があるが，さらに本会に関係の深い高純度物質も純度が確定されれば組成標準物質である。一般に物性標準物質は高純度物質を用いて物質値が定められることに留意すべきである。次の表1の定義を参照していただきたい。

表1　標準物質の分類と定義**

標準物質　特性（**物性**あるいは**組成**）の確定された物質

物性標準物質　熱力学的，分光学的，またはその他の物性値がそれぞれ定められた精度（精密度および正確度）で確定された物質

組成標準物質　組成値が定められた精度（精密度および正確度）で確定された物質

a）**高純度標準物質**　組成標準物質のうち，主成分がある一定値以上の含有率を有し，主成分以外の特定成分含有率がある一定値以下の物質

b）**標準試料**　組成標準物質のうち，目的とする構成各成分の含有率の確定された物質

本稿で表形式で記載した標準物質は各国国立研究機関で物性の確定されたものである。この表2，3は筆者の所属するIUPAC物理化学部 Commission on Physicochemical Measurements and Standards でまとめたものであるが，近く刊行される予定のものから筆者が熱関係だけを抜き出して転載したものである。***

上記の委員会からは，同じ形式のものが筆者も編集に参加してすでにCatalogue of Physicochemical Standard Substances (Pure and Applied Chemistry, 1972, 29, 597) として刊行されているが，物性値の範囲をひろげて今回Catalogue of Reference Materials for Physicochemical Measurements from National Laboratories の表題で改訂版を出そうというのである。

この他同委員会の分科会である Sub-Commission on Calibration and Test Materialsから Recommended Reference Materials for the Realization of Physicochemical Properties が表形式で出版されるがこれは膨大なものである。

次回以降，上記の Sub-Commission のもの，米国NBSのもの，その他を資料として連載する予定である。

表2　Index to Contents (Property Certified)****

1. **Acidimetric standards**

○ **2.** **Calorimetric standards**
- **A.** **Heat capacity**
- **B.** **Heat of transition and fusion**
- **C.** **Heat of combustion**
- **D.** **Solution calorimetry**

3. **Color standards for spectrophotometers and tristimulus colorimeters**

○ **4.** **Density standards**

5. **Dielectric constants (Permittivity)**

○ **6.** **Differential thermal analysis**

7. **Magnetic susceptibility**

8. **Molar conductance**

9. **Molecular weight polymers**

10. **Mössbauer differential chemical shift**

11. **pH standards**

12. **pD standards**

13. **Polarimetric saccharimetric standards**

14. **Redox standards**

○ **15.** **Refractive index standards**

16. **Relative humidity**

17. **Specular spectral reflectance**

18. **Surface area**

19. **Surface tension**

○ **20.** **Thermal conductivity standards**

○ **21.** **Thermal emissivity**

○ **22.** **Thermal expansion**

○ **23.** **Thermometric fixed points**

○ **24.** **Vapour pressure standard**

25. **Viscosity standards**
- **A.** **Liquids**
- **B.** **Glasses**

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** JIS K0501 化学標準物質通則

*** わが国からのものは東工試篠田博士らの測定によるものである。

**** ○印のものだけを転載した。4.と15.とは関係が深いので同じく転載した。

表 3 Reference materials certified with respect to a particular physical property.
(Units are given as reported by issuing Laboratory.)

Purity moles %	Chemical Name (Identification #)	Certified Value and Accuracy	Source	Remarks
		2. CALORIMETRIC STANDARDS. A. Heat capacity		
99.95±	α-Aluminum oxide (720)	See Remarks	I	Enthalpy and heat capacity certified from 273 to 2250K. Enthalpy accurate to ±0.1 percent heat capacity from ±0.01 percent at lowest temperature to ±0.3 percent at 1200K. See certificate for full explanation of accuracy and precision.
99.99	Heptane	See Remarks	I	These materials are not certified as NBS Standard Reference Materials, but are held by the Calorimetry Conference, and are available to qualified users from E. J. Prosen at NBS. Heat capacity data are reported by Ginnings and Furukawa, *J. Am. Chem. Soc.* 75, 522(1953).
99.99	Benzoic acid	See Remarks		
99.99	α-Aluminum oxide	See Remarks		
		2. CALORIMETRIC STANDARDS. B. Heat of transition and fusion		
99.99±	Neopentane	(628.7±0.3)cal·mol^{-1} at (140.49±0.05)K (740.0±0.3)cal·mol^{-1} at Trip. Pt 256.75K	E	Purified by using a spinning band type distillation tower of 3m height and an adsorption column packed with molecular sieve.
		2. CALORIMETRIC STANDARDS. C. Energy of combustion		
99.99	Benzoic acid	Certified for each batch	F	Purity derived from temperature/enthalpy curves.
	Benzoic acid	Certified for each batch	H	Value certified by NPL, but samples prepared, purified and sold by firms, e.g., BDH and Bureau of Analyzed Samples.
99.997	Benzoic acid (39i)	(26.434±0.003)kJ·g^{-1}	I	Value certified when burned under, or corrected to the specific conditions described on the certificate.
99.993	2,2,4-Trimethylpentane (217b)	47.713 kJ·g^{-1}±0.02%	I	Value certified when burned under or corrected to the specific conditions described on the certificate.
		2. CALORIMETRIC STANDARDS. D. Solution calorimetry		
99.94	2-Amino-2-(hydroxymethyl)-1,3-propanediol [Tris(hydroxymethyl) aminomethane] (724a) (THAM or TRIS)	245.76±0.26 J·g^{-1} (with HCl)	I	Certified as to purity and homogeneity. This compound is intended to serve as a uniform material for checking calorimeters in different laboratories. See certificate for exact conditions.
		141.80±0.19 J·g^{-1} (with NaOH)		
Natural Brazilian Quartz	α-Quartz	-2362.2±1.1 J·g^{-1} at 353.15k in 24.4 wt% HF	I	See certificate for full details, also M. V. Kilday and E. J. Prosen, NBS Tech. Report 10 561(1971).

4. DENSITY STANDARDS

(Confidence level 99%)

99.95	Cyclohexane	$(0.77854 \pm 0.000005)\ g \cdot cm^{-3}$ (20°C)		
Unknown	Kerosene (a)	$(0.81016 \pm 0.000005)\ g \cdot cm^{-3}$ (20°C)		
Unknown	Kerosene (b)	$(0.86188 \pm 0.000005)\ g \cdot cm^{-3}$ (20°C)		
97.5	Methylcyclohexane	$(0.77037 \pm 0.000005)\ g \cdot cm^{-3}$ (20°C)	G	Temperature flotation method and pyknometric method. Density for these materials are given also at 10, 30, 40, 50 and 60°C.
>99.9	Toluene	$(0.86668 \pm 0.000005)\ g \cdot cm^{-3}$ (20°C)		
99.5	2,2,4-Trimethylpentane	$(0.69194 \pm 0.000005)\ g \cdot cm^{-3}$ (20°C)		
99.993 ±0.003	2,2,4-Trimethylpentane (217b)	$(0.69183 \pm 0.000002)\ g \cdot cm^{-3}$ (20°C)	I	Also certified for heat of combustion and refractive index and at 25 and 30°C.
99.72	n-Hexane	$659.378 \pm 0.005\ kg \cdot m^{-3}$ at 20°C		Also certified at 25, 30, 35, 40 and 45°C.
99.75	Isooctane	$691.959 \pm 0.005\ kg \cdot m^{-3}$ at 20°C		Also certified at 25, 30, 35, 40, 45 and 50°C.
99.40	n-Octane	$702.597 \pm 0.005\ kg \cdot m^{-3}$ at 20°C		
97.20	n-Nonane	$717.682 \pm 0.005\ kg \cdot m^{-3}$ at 20°C		
99.80	Methylcyclohexane	$769.323 \pm 0.005\ kg \cdot m^{-3}$ at 20°C	G	Also certified at 25, 30, 35, 40, and 45°C.
99.98	Cyclohexane	$778.583 \pm 0.005\ kg \cdot m^{-3}$ at 20°C		
99.74	Toluene	$866.762 \pm 0.005\ kg \cdot m^{-3}$ at 20°C		
97.00	Transdecahydronaphthalene	$869.623 \pm 0.005\ kg \cdot m^{-3}$ at 20°C		

6. DIFFERENTIAL THERMAL ANALYSIS*

High-purity	Potassium nitrate (758)	Equilibrium value 127.7°C Extrapolated onset 128°C Peak 135°C		
High-purity	Indium (metal) (758)	Equilibrium value 157°C Extrapolated onset 154°C Peak 159°C	I	
High-purity	Tin (metal) (758)	Equilibrium value 231.9°C Extrapolated onset 230°C Peak 237°C		
Commercial grade	Potassium perchlorate (758) (759)	Equilibrium value 299.5°C Extrapolated onset 299°C Peak 309°C		
Analysed reagent	Silver sulphate (758) (759)	Equilibrium value-- Extrapolated onset 424°C Peak 433°C		The equilibrium value for the transitional temperature reported for this material is currently under review. A value of 430°C has been reported.
Natural quartz	Silica (759) (760)	Equilibrium value 573°C Extrapolated onset 571°C Peak 574°C	I	
Analysed reagent	Potassium sulphate (759) (760)	Equilibrium value 583°C Extrapolated onset 582°C Peak 588°C		
Analysed reagent	Potassium chromate (759) (760)	Equilibrium value 665°C Extrapolated onset 665°C Peak 673°C		
Analysed reagent	Barium carbonate (760)	Equilibrium value 810°C Extrapolated onset 808°C Peak 819°C	I	The equilibrium value for the transitional temperature reported for this material is currently under review. A value of 430°C has been reported.
Analysed reagent	Strontium carbonate (760)	Equilibrium value 925°C Extrapolated onset 928°C Peak 938°C		

*Note: These Standard Reference Materials are certified and issued jointly by NBS-ICTA (The US National Bureau of Standards and the International Confederation on Thermal Analysis). They are for use in calibrating the temperature scale on differential thermal analysis and related thermoanalytical equipment under the operating conditions, and are to be used only in the heating mode.

15. REFRACTIVE INDEX STANDARDS

99.95	2,2,4-Trimethylpentane	1.39139±0.00002 n_D (20°C)	G	95% confidence level.
99.993±0.002	2,2,4-Trimethylpentane (217b)	at 589.25nm and 20°C n = 1.39147	I	Certified for 7 wavelengths and at 20, 25, and 30°C. Uncertainty of all values less than 0.00002.
99.2	Methylcyclohexane	1.42382±0.00003 n_D (20°C)	G	All at 99% confidence level.
94.1	Cyclohexane	1.42622±0.00003 n_D (20°C)		
99.9	Toluene	1.49675±0.00003 n_D (20°C)		
97.8	1-Bromonaphthalene	1.6580±0.0002 n_D (20°C)		
--	Optical glass 'Crown'	1.51840±0.00002 n_D (20°C)	G	At 95% confidence level.
98.9	Chlorobenzene	1.52452±0.00003 n_D (20°C)	G	99% confidence level.
99.4	o-Netrotoluene	1.5462±0.0002 n_D (20°C)		
99.95	Trimethylpentane	1.39139±0.00003 n_D (20°C)		
--	Glass (1820)	At hydrogen C line (656.28nm), e.g., n = 1.48532±0.00001	I	n given for 13 different spectral source wavelengths

20. THERMAL CONDUCTIVITY ($W \cdot m^{-1} \cdot K^{-1}$)

					Water (mass%)
99.98	Platinum	(70.25 + 0.0075t)	±0.5%	C	0°C<t<100°C
99.0	Propyl alcohol	(0.1575 - 0.000230t)	±0.5%	C	10°C<t< 40°C---0.05
99.8	Isopropyl alcohol	(0.1395 - 0.000202t)	±0.5%	C	10°C<t< 40°C---0.1
99.5	Butyl alcohol	(0.1534 - 0.000211t)	±0.5%	C	10°C<t< 55°C---0.1
99.8	see Butyl alcohol	(0.1400 - 0.000203t)	±0.5%	C	10°C<t< 55°C---0.05
99.2	Isobutyl alcohol	(0.1353 - 0.000166t)	±0.5%	C	10°C<t< 55°C---0.05
99.9+	Electrolytic Iron (734)	λ certified from 6-280K		I	See J. G. Hust, et al, *J. Res. Nat. Bur. Stand.* 74A, 673(1970).
--	Austenitic Stainless Steel (735)	λ certified from 5-280K		I	Same reference as above.

21. THERMAL EMISSIVITY ε (Dimensionless)

--	Platinum - 13% Rhodium Alloy (1402-09)	Certified for ε at 800, 1100, 1400 and 1600K and wavelengths from 1 to 36μm.	I	See W. N. Harrison, et al, Report AD426846 (1963), National Technical Information Service.
--	Oxidized Kanthal (1420-28)	Certified for ε at 800, 1100, and 1300K from 1 to 15μm.	I	Same reference as above.
--	Oxidized Inconel (1440-47)	Same as above.	I	Same reference as above.

Purity moles %	Chemical Name (Identification #)	Certified Value and Accuracy	Source	Remarks
99.99	Phenanthrene	Freezing point (100 C)[b]	F	Purity derived from temperature/enthalpy curves.
99.994	Silver metal	Freezing point (961.93 C)[a]	C	Thermodynamic temperatures.
>99.9	Silver-copper eutectic	Freezing point (779 C)[b]	C	Thermodynamic temperatures.
99.99	1,2,4,5-Tetrachloro-benzene	Freezing point (140 C)[b]	F	Purity derived from temperature/enthalpy curves.
99.99	Sodium	Freezing point (97 C)[b]	F	Purity derived from temperature/enthalpy curves.
99.999	Sulphur	Boiling point (444 C)[b]	C	Thermodynamic temperatures.
99.999+	Tin (741)	Freezing point (231.9681± 0.0007 °C)[a]	I	Primary fixed point on IPTS-68
99.999	Tin metal	Freezing point (231 C)[b]	C	Thermodynamic temperatures.
	Tin (42f)	Freezing point (231.940± 0.005 C)[b]	I	International Temperature Scale(1968).
99.999	Zinc metal	Freezing point (419.58 C)[a]	C	Thermodynamic temperatures.
99.9999	Zinc (740)	Freezing point (419.58 C)[a]	I	Fixed point on International Practical Temperature Scale of 1968.
--	Superconductive thermometric fixed point device (767)	Cadmium - 0.515±0.0025K Zinc - 0.844±0.0015K Aluminum- 1.1746±0.002K Indium - 3.416±0.0015K Lead - 7.201±0.0025K	I	Use of this device and discussion of how prepared and certified, see NBS Spec. Publ. 260-44(1972).

Note: Temperature of the primary fixed points for calibration on the International Practical Temperature Scale of 1968 (IPTS-68) are indicated by the superscript a. Secondary reference points carry a nominal temperature value for general information only, and are indicated by the superscript b. The temperature certified by the standardizing laboratory appears only on the certificate provided with the sample.

24. VAPOUR PRESSURE STANDARD

99.9968	Neopentane	35.793±0.017kN m^{-2} (256.750K)	E	Purified by using a spinning band type distillation tower of 3m height and an adsorption column packed with molecular sieve.
99.999+	Gold (745)	Certified for vapor pressure over range 1300 to 2100K. At 1338K (M.P.), P = 2.56×10^{-8} atm	I	1 atm = 101 325 $N \cdot m^{-2}$ See NBS Spec. Publ. 260-19(1970) for full discussion of data and uncertainties.
99.999+	Cadmium (746)	Certified for vapor pressure over range 350 to 594K. At 594K (M.P.), P = 1.51×10^{-4} atm	I	See NBS Spec. Publ. 260-21(1971) for full discussion of data and uncertainties.
99.999+	Silver (748)	Certified for vapor pressure over range 800 to 1600K at 1235K (M.P.), P = 3.71×10^{-6} atm		

Purity moles %	Chemical Name (Identification #)	Certified Value and Accuracy	Source	Remarks
--		**22. THERMAL EXPANSION (EXPANSIVITY, (α), K^{-1})**		
--	Borosilicate Glass (731)	Certified for expansion and expansivity from 80 to 680K.	I	See NBS Spec Publ. 303(1968)
99.99 at%	Copper	Certified for expansion and expansivity from 20 to 800K.	I	See T. A. Hahn, *J. Appl. Phys.* 41, 5096(1970).
99.8	Fused Silica	Certified for expansion and expansivity from 80 to 1000K.	I	
		23. THERMOMETRIC FIXED POINTS		
99.999	Aluminum metal	Freezing point (660 °C)[b]	C	
	Aluminum (44e)	Freezing point (660.3±0.2 °C)[b]	I	International Temperature Scale(1968).
99.9+	Aluminum Oxide (742)	Melting point (2053±5° °C)[b]	I	IPTS-68, Pyrometric standard
--	Benzene-Water	Freezing point certified for each batch	H	Used in STPTC Test Method RLB 24-67 and British Standard BS-135
99.99	Benzoic acid	Freezing point (122 °C)[b]	F	Purity derived from temperature/enthalpy curves.
99.99	Benzophenone	Freezing point (48 °C)[b]	F	
99.99	Dimethyl terephthalate	Freezing point (142 °C)[b]	F	
99.99	Biphenyl	Freezing point (70 °C)[b]	F	
99.999	Cadmium metal	Freezing point (321 °C)[b]	C	
99.999	Copper (45d)	Freezing point (1084.8±0.5 °C)[b]	I	International Temperature Scale(1968).
99.998	Gold metal	Freezing point (1064.43 °C)[a]	C	
	Lead (49e)	Freezing point (327.493± 0.005 °C)[b]	I	International Temperature Scale(1968).
99.99	Naphthalene	Freezing point (80 °C)[b]	F	Purity derived from temperature/enthalpy curves.
99.996	Neopentane	Transition point (-132 °C)[b]	E	Purified by using a spinning band type distillation tower of 3 m height and an adsorption column packed with molecular sieve.
		Triple point (-16 °C)[b]	E	

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