National Institute of Standards & Technology

# Report of Investigation

# Reference Material 5

## Copper Heat Capacity

This Reference Material (RM 5) is intended primarily for the comparison of heat capacity results from different laboratories and as a test specimen for heat capacity measurements below 25 K, but it may also be useful at higher temperatures. It is available as a rod of high purity polycrystalline copper 19 mm (0.75 in) in diameter and 120 mm (4.75 in) in length. This reference material will serve the same purposes as the 1965 Calorimetry Conference Copper Standard (prepared and distributed by Argonne National Laboratory), the supply of which has been exhausted [1].

The copper from which RM 5 is made was obtained from the American Smelting and Refining Company (ASARCO). They also manufactured the material used in the 1965 Calorimetry Conference Copper Standard. Based on a spectrographic analysis made on similar material, ASARCO claims a purity of 99.999+%. The composition of material obtained at the same time as that used for RM 5, as determined by spectrochemical analysis at NIST, is listed in Table 1. The residual resistivity ratio, $\rho 273K/\rho 4K$, of RM 5 was determined to be approximately 2000.

Table 1. Approximate elemental concentration, mg/kg (ppm) composition

| | | | | | |
|---|---|---|---|---|---|
| Sn | 0.01 | Zn | 0.07 | K | <1. |
| Pb | 0.02 | Co | 0.02 | Li | <0.01 |
| Bi | <0.1 | Se | 0.02 | Mg | <0.01 |
| Ni | 0.05 | S | 0.5 | N | <0.2 |
| Sb | 0.3 | O | ~9. | Na | <1. |
| Fe | 0.1 | Al | <0.1 | P | <0.1 |
| Te | <0.5 | B | <0.01 | Si | <0.01 |
| As | 0.2 | Be | <0.01 | Ti | <0.01 |
| Au | <0.01 | C | <1. | V | <0.01 |
| Ag | 0.3 | Ca | <0.02 | Zr | <0.01 |
| Cr | 0.03 | Cd | 0.1 | | |
| Mn | 0.01 | Cl | <0.1 | | |

The rods were chemically etched and then annealed at 800 °C in high vacuum (~$10^{-6}$ Torr) for two hours [2]. Contamination of the specimen with transition metals, especially iron, manganese, or nickel, should be avoided. After machining, cutting or drilling, the specimen should again be etched to remove the contaminated material.

*This Report of Investigation has undergone editorial revision to reflect program and organizational changes at NIST and at the Department of Commerce. No attempt was made to reevaluate any technical data presented in this report.*

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William P. Reed, Chief
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(over)

Use a 1:1 solution of nitric acid, followed with a 1:1 solution of hydrochloric acid. Rinse with distilled water and dry in air on filter paper. This procedure should be followed especially before heating the specimen above room temperature. It is recommended that any machining, cutting, or drilling be carried out dry, to avoid enclosing lubricant in small pores or crevices in the specimen.

The procurement and technical advice associated with the issuance of this Reference Material were coordinated by D.W. Osborne and R.K. Kirby both formerly of NIST. The technical and support aspects involved in the review, update and issuance of this Reference Material were coordinated through the Standard Reference Materials Program by J.C. Colbert.

The National Institute of Standards and Technology does not certify values of the heat capacity of RM 5 but results obtained on the 1965 Calorimetry Conference Copper Standard and recent results on other high purity copper samples may be useful for comparison purposes. Workers who are new to the field of low temperature heat capacity measurements, as well as experienced workers with a new temperature scale or a new type of calorimeter, may wish to compare their results with these recommended (but uncertified) values. Below 25 K the "copper reference equation" given by Osborne, Flotow and Schreiner [1] is recommended:

$$C_P = \sum_{i=1}^{6} A_i T^{2i-1}$$

The coefficients for $C_p$ in $mJ \cdot K^{-1} \cdot mol^{-1}$(one mol = 63.54 g) are:

| | |
|---|---|
| $A_1 = 6.9434 \times 10^{-1}$ | $A_4 = 9.4786 \times 10^{-8}$ |
| $A_2 = 4.7548 \times 10^{-2}$ | $A_5 = -1.3639 \times 10^{-10}$ |
| $A_3 = 1.6314 \times 10^{-6}$ | $A_6 = 5.3898 \times 10^{-14}$ |

This copper reference equation was based on the measurements of Osborne et al. [1] and of Ahlers [3] on the 1965 Calorimetry Conference Copper Standard from 1.0 to 22.6 K and from 1.3 to 21 K, respectively, on the measurements of Martin [4] on vacuum cast ASARCO 99.999+% copper from 3 to 30 K, and on other results from the literature. The results cited in reference [1], as well as results obtained subsequently on the 1965 Calorimetry Conference Copper Standard and on other high purity copper [5-27], indicate that this copper reference equation gives the heat capacity of pure copper to better than 1% below 25 K. These values are also recommended by the Commission on Physicochemical Measurements and Standards of the Physical Chemistry Division, the International Union of Pure and Applied Chemistry [28].

Table 2. Heat capacity of copper.

| Temperature | $C_p$ | Temperature | $C_p$ |
|---|---|---|---|
| 25 K | 0.963 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ | 75 K | 11.89 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ |
| 30 | 1.693 | 80 | 12.85 |
| 35 | 2.638 | 90 | 14.56 |
| 40 | 3.740 | 100 | 16.01 |
| 45 | 4.928 | 125 | 18.70 |
| 50 | 6.154 | 150 | 20.51 |
| 55 | 7.385 | 175 | 21.74 |
| 60 | 8.585 | 200 | 22.63 |
| 65 | 9.759 | 250 | 23.78 |
| 70 | 10.86 | 300 | 24.46 |

Furukawa, Saba, and Reilly [29] have critically evaluated the heat capacity data on copper in the literature up to February, 1967 and have given a table of selected values of the heat capacity and other thermodynamic functions from 1 to 300 K. Their values are recommended for the heat capacity of RM 5 above 25 K. Part of their tabulated values are given in Table 2. These values were selected such that four-point finite-difference interpolation will produce an error of not more than one in the last figure.

Measurements by Martin on ASARCO 99.999+% copper from 20 to 300 K [30], and from 16 to 90 K [31], as well as measurements by Robie, Hemingway, and Wilson on 1965 Calorimetry Conference Standard Copper from 16 to 380 K [32], agree with the table of Furukawa et al. [29] within less than 1% above 25 K.

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