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(54) METHOD AND APPARATUS FOR MODULATED DIFFERENTIAL ANALYSIS

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(56) **References Cited**

U.S. PATENT DOCUMENTS

5,080,495 A 1/1992 Hashimoto et al.

OTHER PUBLICATIONS

Physical Review Letters, First–Order Transition in Chromium at the Neel Temperature, P.R. Garnier and M.B. Salamon, Oct. 13, 1971, pp. 1523–1526.

Computerized Equipment for Measuring the Amplitude and Phase of ULF Harmonic Signals, Plenum Publishing Corporation, 1987, pp. 763–767.

"Complex Plane Analysis of Heat Capacity of Polymers in the Glass Transition Region," by H. Gobrecht et al., Journal of Physics E: Scientific Instruments, 1971, vol. 4, pp. 21–23.

S.C. Mraw and D.F. Naas, "The Measurement of Accurate Heat Capacities By Differential Scanning Calorimetry: Comparison of d.s.c. Results of Pyrite (100 to 800 K) with Literature Values from Precision Adiabatic Calorimetry," J. Chem. Thermodynamics, vol. 11, 1979, pp. 567–584.

P. Claudy, J.C. Commercon, and J.M. Letoffe, "Quasi–Study of the Glass Transition of Glycerol by DSC," Thermochimica Acta, vol. 128, Aug. 1988, pp. 251–260.

A. Maesono and R. Kato, translation into English of a Japanese article, "Recently Developed Instruments Relevant to ac Calorimetry." (no date).

H. Albert, "Pulsed–Current Control and Measurement System for Precision Microcalorimetry," The Review of Scientific Instruments, vol. 43, No. 5, 1972, pp. 766–774.

J. Zynger, "Automated, Stepping Differential Calorimeter for the Analysis of Purity," Analytical Chemistry, vol. 47, No. 8, Jul. 1975, pp. 1380–1384.

T. Sturgill, R. Johnson, and R. Biltonen, "Thermal Perturbation Techniques in Characterizing Ligand–Macromolecule Interactions: Theory and Application to the Proflavin–a–Chymotrypsin System," Biopolymers, vol. 17, 1978, pp. 1773–1792.

P. Privalov, "Scanning Microcalormeters for Studying Macromolecules," Pure & Appl. Chem., vol. 52, 1980, pp. 479–497.

C. Festa and N. Ceccanti, "A Differential Calorimeter for Measuring Heats of Solution With a Pulse Time Modulation System," Societa Chimica Intaliana, 1980, pp. 431–437.

(List continued on next page.)

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(57) **ABSTRACT**

The present invention relates to differential analytical techniques for determining the composition, phase, structure, identification or other properties of a material that undergoes a transition as function of a driving variable. As applied to differential scanning calorimetric analysis (DSC), the preferred embodiment comprises: (1) heating a sample of the material with a linear temperature ramp that is modulated with a sinusoidal heating rate oscillation; and (2) deconvoluting the resultant heat flow signal into rapidly reversible and non-rapidly reversible components.