THERMOMAGNETOMETRY

S.St.J. WARNE

Department of Geology, The University of Newcastle, Shortland, N.S.W. 2308 (Australia)

P.K. GALLAGHER

AT & T Bell Laboratories, Murray Hill, NJ 07974 (U.S.A.)

ABSTRACT

Thermomagnetometry: "A technique in which the magnetic susceptibility of a substance is measured as a function of temperature, whilst the substance is subjected to a controlled temperature program", is one of the less commonly known and used methods of thermal analysis. This technique is reviewed herein with reference to the instrumentation and methods used, the property measured, suitable standard reference materials and applications to mineralogy, metallurgy, other compounds and solid phase reaction kinetics. It is a technique of considerable, but not general, application which has not as yet reached its true potential in research.

INTRODUCTION

This is to be a brief survey of thermomagnetometry and some of its applications. It is not intended to be an exhaustive review of the entire subject. Thermomagnetometry (TM) by definition is: "A technique in which the magnetic susceptibility of a substance is measured as a function of temperature, whilst the substance is subjected to a controlled temperature program," Mackenzie [1]. The first use of the term "Thermobalance" and the equipment's earlier use in "Magnetochemistry," appears to have been made by Honda [2] and Honda and Takagi [3], respectively. The main elements which show ferromagnetism and are suitable for the application of this technique are Fe, Co * and Ni, although at very low temperature a number of rare-earth elements also show this property, i.e. gadolinium, terbium, dysprosium, holmium, erbium and thulium [4]. The equipment generally used to make such determinations consists of a balance suitable for thermogravimetry (TG), where a magnetic field gradient may be applied and removed at will to the sample while undergoing its preset heating or cooling program, see Fig. 1.

Thermal analysis Highlights, 8th ICTA, Bratislava, Czechoslovakia.
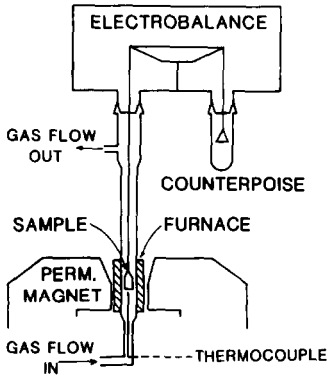* Cobalt occurs in two ferromagnetic allotropic modifications Haglund [4].

Fig. 1. Typical experimental apparatus for thermomagnetometry. (After Aylmer and Rowe [45].)
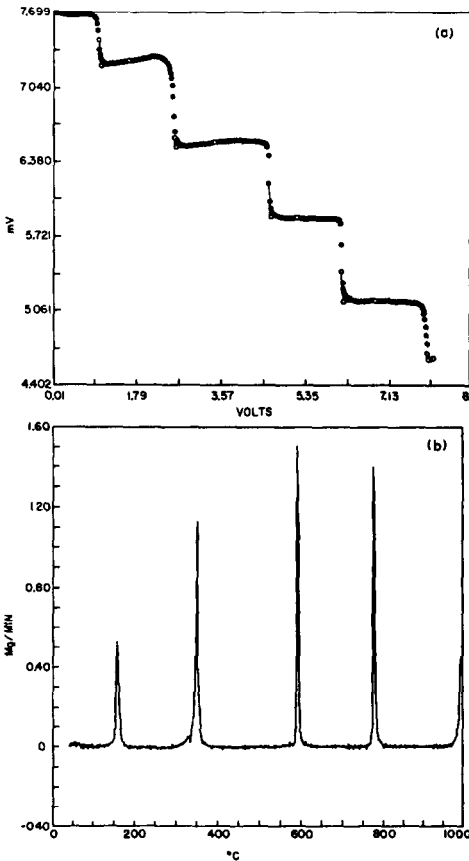

Fig. 2. Sample thermomagnetometric curve for TG temperature calibration purposes. Alumel, nickel, Perkalloy, iron and Hisat (Gallagher and Schrey [7]). (a) Raw TG signal data, (b) corrected DTG output.

The magnetic force on the magnetic sample acts as an equivalent "magnetic mass" on the balance beam to alter the apparent sample weight on the resultant TG curve [5,6]. The magnet may be situated above or below the sample to give effective "weight gains" or "weight losses", respectively, on the TG curve. These "weight" changes are due to the attraction of any magnetic phases which may be produced, permanently, temporarily or reversibly due to the formation of suitable products of decomposition, reaction or simple magnetic transitions (Curie points). Figure 2 (from Gallagher and Schrey [7]) shows TG and DTG curves for a collection of several metals and alloys used for the purpose of temperature calibration *.

INSTRUMENTATION AND TECHNIQUES

To date, descriptions of suitable equipment or modifications to existing thermobalances and techniques to enable TM determinations to be made have been published by a number of workers [8–20]. A different technique based upon the impedance change in a coil surrounding the sample was described by Karmazsin et al. [19] who coupled it with dilatometry [21]. If the magnetic field has an effect upon the reaction temperature or rate, then any thermoanalytical technique may be used, e.g., EGA [22]. A new very sensitive apparatus, described by Thomas and Ropital [23], now allows non-ferromagnetic reactants and products to be studied.

For convenience, permanent high intensity magnets appear to have been used almost exclusively to date due to their ease of removal and replacement in close proximity to the test sample. For many studies such as qualitative analysis or temperature calibration which involve highly magnetic materials, a strong magnet is not necessary and may even be detrimental. The use of permanent magnets has a number of difficulties and disadvantages in providing the required symmetrical and reproducible magnetic field gradient, i.e.:

(1) The rapid and reproducible positioning of the magnet with the magnet directly above or below the sample. Other magnets may be needed to counter the offset or physical displacement away from the central position occupied by the sample suspension.

(2) The effects of heat, if the magnet is situated within the furnace. This aspect may be countered by using special heat resistant magnets, but magnetic retention above temperatures at about 550°C seems unlikely.

(3) Desired selectable variations in the magnetic field gradient. These can only be conveniently achieved in a step wise manner by the substitution of

---

* A set of standard calibration materials, i.e., GM-761, is now available from the U.S. National Bureau of Standards.

different magnets which may well be difficult to position in an identical manner.

The effects of these factors may be acceptable for some types of determinations. However, it would appear that the reproducibility, control, and continuous field strength variations obtainable with electro-magnets would be most desirable. In addition their common circular nature would be ideal. The experimental problems associated with additional stray magnetic fields resulting from furnance windings have been discussed [16,24–26].

The loss of sample material by decrepitation, coupled with magnetic attraction from above may be solved by the use of silica capsules [10,17] or a quartz wool plug or fine platinum mesh cover [27,28].

A further contribution relevant to TM (and TG) has been made in the area of measuring the correct sample temperature. This involves duplicate geometrically identical crucibles as suggested by Wendlandt [29] and confirmed and extended by Šesták and Šatava [30].

Operation under vacuum is recommended for the most sensitive measurements since oxygen is paramagnetic and gas absorbed onto the holder or sample may interfere [31]. Further, provided self generated gases are not involved, sample oxidation may be prohibited completely by determinations in vacuum or evacuated sealed silica capsules of the type used by Nishiyama and Ishida [10]. The theory, instrumentation and techniques of thermomagnetometry as reviewed by Daniels [31], still represents a valuable contribution, while Haglund [4] in his review of methods of determining Curie points of alloys also includes thermomagnetometry.

APPLICATIONS AND STANDARDS

There are two clearly different applications of Thermomagnetometry for a wide range of substances of a mineralogical, metallurgical or process product nature.

(1) Temperature calibration and qualitative analysis based upon the determination of Curie temperatures.

(2) Quantitative analysis of magnetic materials based upon magnetic saturation measurements.

In the case of temperature calibration the "Committee on Standardization" of the Internal Confederation for Thermal Analysis has selected a set of reference materials of such merit that these have been certified by the United States Bureau of Standards (No. GM-761).

The accompanying certification document was prepared by Garn, Menis and Wiedemann (see also Blaine and Fair [32] and Charsley et al. [33,34]). The document states that three characteristics for such standard material are vital

(1) It must have an easily detected and reliable thermal effect, i.e. provide an easily measurable and reproducible signal.

(2) It must undergo its thermal change rapidly enough to be measured on commercially available dynamic instruments.

(3) It must be stable enough to permit its convenient use under the normal operating conditions of the instrument.

The materials selected in ascending temperature order of their magnetic transitions are: Permanorm 3 < nickel < Numetal < Permanorm 5 < Trafoperm.

Additional detailed work on these standard materials for thermomagnetometry, using a specially calibrated Stanton Redcroft STA-780 simultaneous TG-DTA unit has been described [33], and documented in detail [34]. Individual research workers have used other reference materials with success, e.g., Norem et al. [5], Gallagher and Schrey [7]. Elder [35] and Earnest [6] used alumel, nickel, perkalloy, iron and hisat (see Fig. 2). As the progressive Curie temperatures are reached the individual materials transform to the paramagnetic state (non-magnetic) and so apparently lose weight (due to loss of magnetic attraction). The actual temperature at which this happens may be accented by a DTG plot of the weight loss information.

It is also noteworthy that most alloying elements lower the Curie points of Fe, Co and Ni [4]. Furthermore, the temperature dependence of solubility for several metallic solutes in Fe, Co or Ni is generally approximated by an Arrhenius equation, where the solubility is a linear function of the reciprocal absolute temperature according to Borelius [36] and Borelius et al. [37].

It should be considered that the magnetic attraction in a ferro or ferri-magnetic material is constantly decreasing with temperature until it essentially vanishes at the Curie temperature. Consequently, the onset of the observed initial weight loss with temperature is dependent upon the strength of the magnetic field gradient, if at less than saturation. A weak field
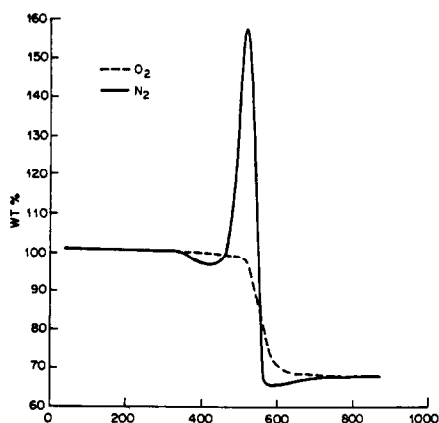

Fig. 3. Example of TM showing the formation of a magnetic phase during the decomposition of siderite in N_2 but not in O_2 (Gallagher and Warne [28]).

gradient, therefore, gives a sharper apparent weight change and, secondly, it is only the final loss that is associated with the actual Curie temperature. In this way accurate temperature reference points may be established by thermomagnetometry.

In the case of qualitative and quantitative analysis TM is used to detect the formation or loss of magnetic phases produced by decompositions, solid state reactions, phase transitions, or magnetic changes. As an example Fig. 3 from Gallagher and Warne [28] shows how Fe_3O_4 ($T_c = 585°C$) is formed during the decomposition of Siderite ($FeCO_3$) in N_2 but not in O_2.

Finally, the following is a list of numerous examples of the use of TM in various fields.

MINERALOGY

1. Sulphides

Pyrrohitite ($Fe_{n-1}S_n$): Bennett and Graham [38] and Schwartz [39].

2. Oxides

Maghemite (γ-Fe_2O_3): O'Reilly [40].
Magnetite (Fe_3O_4): Gallagher et al. [41] (A study of the effect of the internal magnetic field upon the rate of oxidation), Charles et al. [42] and also Smykatz-Kloss [91].
Titanomagnetites (Fe, Ti)$_3$O$_4$: Readman and O'Reilly [43].
Hematite (α-Fe_2O_3): Schwartz [39] and Karmazsin et al. [21].
Spinels: Moskalewicz [16].

3. Carbonates

Siderite ($FeCO_3$): Gallagher and Warne [27,28].
Ankerite Ca(Mg, Fe)(CO$_3$)$_2$: Milodowski and Morgan [44] and Warne [48].

4. Pyrite and siderite in coals

Pyrite (FeS_2): Aylmer and Rowe [45,46], Hyman and Rowe [18] and Warne et al. [47].
Siderite ($FeCO_3$): Gallagher and Warne [28] and Warne [48].
Ankerite Ca(Mg,Fe)(CO$_3$)$_2$: Warne [48].

5. Iron compounds in coal char, solvent-refined coal filter cake and oils from coal and oil shale

Iron oxides and sulphides: Richardson [14].
Pyrrhotites; Petrakakis et al. [49], Maxwell et al. [50,51] and Jeong et al. [52].

6. *Silicates*

Garnets (Fe): Moskalewicz [16].

7. *Clays*

Nontronite: Mackenzie et al. [53].

METALLURGY

Lecoq and Michel [54,55], Bäckman et al. [56], Kopp [15], Wachtel and Kopp [57], Gallagher et al. [58], Tumanov and Korchakova [59], Charles [17,60], Haglund [4], Rahman et al. [61].

COMPOUNDS AND SOLID PHASE REACTION KINETICS

1. *Ferrite and garnet formation*

Mehandjiev and Nikolova-Zhecheva [62], Tzechoval and Steinberg [63], Roy et al. [64], Sztatisz et al. [65].

2. *Coordination compounds*

Simmons and Wendlandt [12], Miyokawa et al. [66], Kinoshita et al. [67].

3. *Catalytic Materials*

Gasparoux [68].

4. *Effects of external magnetic fields*

Gallagher et al. [22], Mackenzie et al. [53], Rowe et al. [69].

5. *Effects of mechanical treatments*

Boldyrev [70].

6. *Corrosion*

Charles [17].

CONCLUSIONS

The conversion of modern thermobalances for thermomagnetometry is usually relatively simple using detachable permanent high intensity magnets. It is a technique with considerable, but not general application, which has not as yet attracted the research interest it warrants. It offers considerable scope for the detection of "short lived" magnetic phases, produced during heating and in particular offers potential in mineralogy/earth science studies, where it may even prove useful, for example in detecting ferro-organic grain coatings in unconsolidated sediments [71].

EDITORIAL NOTE ON THERMOMAGNETOMETRY AND THERMOELECTROME-TRY BY JAROSLAV ŠESTÁK AND VLADIMÍR BALEK

By measuring the force acting on a sample, experimental physicists usually set up curves of the dependence of magnetization on the magnetic field and only consequently derive the dependence of magnetization on the temperature at constant field. The final goal is the determination of the type of magnetic ordering and the position of the Curie temperature (T_c). Such thermomagnetometry has also recently been used to monitor the structural relaxation of metallic glasses [72] and particularly to describe crystallization processes that take place below T_c [73]. The degree of crystallinity (α) is then determined by the measurement [74] of the saturation magnetization [$M_{(t)}^s$] in crystalline (M_{cr}^s) and glassy (M_{gl}^s) states at different temperatures. The results are analysed in terms of the ordinary nucleation growth (JMAKY) equation [74]. Constant heating rate experiments were also carried out [75] and the temperature dependence of magnetization [$M_{(t)}$] for a glassy alloy with a given crystalline phase content was discussed [76] [i.e., the validity of the equation $a = (M_{(t)}^s - M_{gl}^s)/(M_{cr}^s - M_{gl}^s)$].

A thermoelectrometric analogue of thermomagnetometry can be termed dielectric thermal analysis, in which the dependence of the dielectric polarization [like the magnetization, $M_{(t)}$] on the applied electric field is measured. In contrast to ordinary frequency characteristics and electric current dependences of dielectric constants, the temperature dependences were determined less frequently, having first been measured in a dynamic temperature regime by Bergstein [77]. Interest in this method, using constant heating, has been reviewed during the past 20 years, e.g., refs. 78–88. Despite the possible extent of the information that can be provided by this method, it has not been widely used for the study and identification of materials. The principles and theoretical basis have recently been considered in detail by Egerer [89] and Roque-Malherbe and co-workers [88,90].

REFERENCES

1 R.C. Mackenzie, J. Therm. Anal., 13 (1978) 387.
2 K. Honda, Rep. Tohôku Univ., 4 (1915) 97.
3 K. Honda and H. Takagi, Sci. Rep. Tohôku Univ., 1 (1911) 229.
4 O. Haglund, J. Therm. Anal., 25 (1982) 21.
5 S.D. Norem, M.J. O'Neill and A.P. Gray, Thermochim. Acta, 1 (1970) 29.
6 C.M. Earnest, Anal. Chem., 56 (1984) 1471A.
7 P.K. Gallagher and F. Schrey, Thermochim. Acta, 1 (1970) 465.
8 H.A. Brown and J.M. Luttinger, Phys. Rev., 100 (1955) 685.
9 P.W. Selwood, Magnetochemistry, Interscience, New York, 1956, 435 pp.
10 A. Nishiyama and R. Ishida, Trans. Jpn. Inst. Metals, 3 (1962) 185.
11 J.T. Richardson and J.W. Beauxis, Rev. Sci. Instrum., 34 (1963) 877.
12 E.L. Simmons and W.W. Wendlandt, Anal. Chim. Acta, 35 (1966) 461.
13 W.R. Ott and M.G. McLaren, Proc. 2nd Int. Conf. Therm. Anal., Worcester, U.S.A. Vol. 2, 1969, Academic Press, New York, pp. 1439–1451.
14 J.T. Richardson, Fuel, 51 (1972) 150.
15 W.W. Kopp, Messtechnik (Brunswick), 80 (1972) 81.
16 R. Moskalewicz, Thermochim. Acta, 28 (1979) 229.
17 R.G. Charles, Proc. 7th Int. Conf. Therm. Anal., Kingston, Canada, Vol. 1, 1982, Wiley, Chichester, pp. 264–271.
18 M. Hyman and M.W. Rowe, ACS Symp. Ser., American Chemical Society, Washington, DC, 1982, p. 389.
19 E. Karmazsin, P. Satre, M. Romand and B. Durand, Thermochim. Acta, 55 (1982) 287.
20 M.W. Rowe, J. Geol. Educ., 31 (1983) 5.
21 E. Karmazsin, P. Satre and P. Vergnon, J. Therm. Anal., 28 (1983) 279.
22 P.K. Gallagher, E.M. Gyorgy and W.R. Jones, J. Chem. Phys., 75 (1981) 3847.
23 G. Thomas and F. Ropital, J. Therm. Anal., 30 (1985) 121.
24 R. Moskalewicz, Proc. 4th Int. Conf. Therm. Anal., Budapest, Hungary, Vol. 3, 1975, Heyden, London, p. 873.
25 R. Moskalewicz, Proc. 1st. ESTA Conf., Salford, U.K., 1976, Heyden, London. p. 25.
26 P.K. Gallagher and E.M. Gyorgy, Thermochim. Acta, 31 (1979) 383.
27 P.K. Gallagher and S.St.J. Warne, Mater. Res. Bull., 16 (1981) 141.
28 P.K. Gallagher and S.St.J. Warne, Thermochim. Acta, 43 (1981) 253.
29 W.W. Wendlandt, Thermochim. Acta, 21 (1977) 295.
30 J. Šesták and V. Satava, Thermochim. Acta, 27 (1978) 383.
31 T.C. Daniels, Thermal Analysis, Kogan Page, London, 1973, 272 pp.
32 R.L. Blaine and P.G. Fair, Thermochim. Acta, 67 (1983) 233.
33 E.L. Charsley, S.St.J. Warne and S.B. Warrington, Proc. 14th NATAS Conf. San Francisco, U.S.A., 1985, p. 217.
34 E.L. Charsley, S.St.J. Warne and S.B. Warrington, in preparation.
35 J.P. Elder, Thermochim. Acta, 52 (1982) 235.
36 G. Borelius, Ann. Phys. (Leipzig), 5, 20 (1934) 57.
37 G. Borelius, J. Anderson and K. Gullberg, I.V.A. Handlingor Nr 169, Stockholm, 1943.
38 C.E.G. Bennett and J. Graham, Am. Mineral., 65 (1980) 800.
39 E.J. Schwartz, Geol. Surv. Canada, Dept. Energy, Mines and Resources, Paper 68-37 (1968), 11 pp.
40 W. O'Reilly, J. Geomagn. Geoelectr., 20 (1968) 381.
41 P.K. Gallagher, E.M. Gyorgy and H.E. Bair, J. Chem. Phys., 71 (1979) 830.
42 R.G. Charles, J.G. Cleary and M.J. Wootten, Nucl. Technol., 58 (1982) 184.
43 P.W. Readman and W. O'Reilly, J. Geomagn. Geoelectr., 24 (1972) 69.

44 A.E. Milodowski and D.J. Morgan, Proc. 2nd ESTA Conf., Aberdeen, 1981, Heyden, London, pp. 468–471.

45 D.M. Aylmer and M.W. Rowe, Proc. 7th Int. Conf. Therm. Anal., Kingston, Canada, Vol. 2, 1982, Wiley, Chichester, pp. 1270–1275.

46 D.M. Aylmer and M.W. Rowe, Thermochim. Acta, 78 (1984) 81.

47 S.St.J. Warne, A.S. Bloodworth and D.J. Morgan, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 93 (1985) 745.

48 S.St.J. Warne, Thermochim. Acta, 87 (1985) 353.

49 L. Petrakis, P.F. Ahner and D.W. Grandy, Fuel, 59 (1980) 587.

50 E. Maxwell, D.R. Kelland, I.S. Jacobs and L.M. Levinson, in B.R. Cooper and L. Petrakis (Eds.), Chemistry and Physics of Coal Utilization, American Institute of Physics, 1980, pp. 452–453.

51 E. Maxwell, D.R. Kelland, I.S. Jacobs and L.M. Levinson, Fuel, 61 (1982) 369.

52 K.-M. Jeong, L. Petrakis, M. Takayasu and F.J. Friedlaender, Fuel, 63 (1984) 1459.

53 J.K.D. Mackenzie, B.M. Fry, I.W.M. Brown and M.E. Bowden, Thermochim. Acta, 60 (1983) 93.

54 P. Lecoq and A. Michel, Bull. Soc. Chim. Fr., (1962) 1412.

55 P. Lecoq and A. Michel, Bull. Soc. Chim. Fr., (1964) 1473.

56 U. Bäckman, B.O. Haglund and B. Bolin, Proc. 3rd Int. Conf. Therm. Anal., Davos, Switzerland, Vol. 2, 1972, pp. 759–765.

57 E. Wachtel and W.W. Kopp, Metallurgia, 27 (1973) 1174.

58 P.K. Gallagher, E. Coleman, S. Jin and R.C. Sherwood, Thermochim. Acta, 37 (1980) 291.

59 V.I. Tumanov and E.A. Korchakova, Poroshk. Metall., 6 (1981) 98.

60 R.G. Charles, Proc. 10th NATAS Conf., Boston, U.S.A., 1980, Howard University Press, Washington, pp. 27–32.

61 I.Z. Rahman, D. Melville and W.I. Khan, Phys. Status Solidi A, 70 (1982) K175.

62 D. Mehandjiev and E. Nikolova-Zhecheva, Thermochim. Acta, 51 (1981) 343.

63 H. Tzechoval and M. Steinberg, Isr. J. Chem., 22 (1982) 227.

64 D. Roy, D. Kumur and D. Bahadur, Phys. Status Solid A, 82 (1984) K. 11.

65 J. Sztatisz, Cs. Novak, M. Balla and A. Sztaniszlav, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 93 (1985) 445.

66 K. Miyokawa, H. Hirashima and I. Masuda, Bull. Chim. Soc. Jpn., 54 (1981) 3361.

67 S. Kinoshita, K. Miyokawa, H. Wokita and I. Masuda, Fukuoka Diagaku Rigaku, 14 (1984) 121.

68 H. Gasparoux, C.R. Acad. Sci., Ser. B, 272 (1971) 724.

69 M.W. Rowe, P.K. Gallagher and E.M. Gyorgy, J. Chem. Phys., 79 (1983) 3534.

70 V.V. Boldyrev, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 110 (1987) 303.

71 M.St.J. Warne, React. Solids, 1 (1986) 291.

72 E. Illeková, P. Ambrovič and K. Czomorová, in Supplement to the Proceedings of the 8th ICTA, SVŠT Bratislava, 1985, p. 85; J. Therm. Anal., in press.

73 T. Kémény, I. Vincze and B. Fogarassy, Phys. Res. B, 20 (1983) 279.

74 F. Stobiecki, in Methfessel (Ed.), Proc. 6th Int. Conf. on Soft Magnetic Materials, EPS, Eger, 1983, Pap. 4.12.

75 J. Wolny and W. Zajac, in ref. 74, Pap. 4.11; Sci. Bull. Academy of Mining and Metallurgy, Krakow, 1983, No. 952, p. 55.

76 F. Stobiecki and T. Stobiecki, J. Magn. Mag. Mater., 40 (1983) 111.

77 A. Bergstein, Collect. Czech. Chem. Commun., 20 (1955) 1058; 21 (1956) 542.

78 B.F. Howel and P.H. Licastro, Am. Mineral., 46 (1961) 269.

79 S.D. Krilyan and V.H. Krilyan, Zh. Nauchn. Prikl. Fotogr. Kinematogr., (1961) 397.

80 A. Kovach, B. Schlenk and V. Széky-Fux, Bul. Hung. Geol. Soc., 4 (1975) 495.

81 I.R. Bonilla, P.R. Andarade and A. Bristiti, J. Therm. Anal., 8 (1975) 387.

82 K. Adachi, M. Hattori and Y. Ishida, J. Polym. Sci. Phys. Ed., 15 (1977) 693.

83 P.N. Nandi, D.A. Desphande and V.G. Kher, Proc. Indian Acad. Sci., A98 (1979) 113; Thermochim. Acta, 34 (1979) 1.

84 Y.A. Badr, F. El-Kabbany and M. Tossen, Phys. Status Solidi A, 53 (1979) K161.

85 R. Nottenburg, J. Solid State Chem., 27 (1979) 1149; Anal. Chem., 51 (1979) 11.

86 K. Rajeshwar, R.N. Nottenburg and J.B. Dupon, Thermochim. Acta, 26 (1978) 1; 33 (1979) 157.

87 S. Yagihara and S. Mashimo, J. Polym. Sci., Polym. Phys. Ed., 9 (1981) 1333.

88 A. Montes, R. Roque-Malherbe and E.D. Shchukin, J. Therm. Anal., 31 (1986) 41.

89 F. Egerer, Bull. Mineral., 104 (1981) 763; Gerlads Beitr. Geophys., 81 (1982) 269.

90 R. Roque-Malherbe and F. Morales, Rev. Cienc. Quim., 12 (1981) 235.

91 W. Smykatz-Kloss, in R.L. Blaine and C.K. Schoff (Eds.), Purity Determinations by Thermal Methods, ASTM STP 838, American Society for Testing Materials, Washington, DC, 1984, pp. 121–137.