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SIMULTANEOUS MEASUREMENT OF WEIGHT LOSS AND DELTA TEMPERATURE

P. S. Gill and C. L. Marcozzi

TA INSTRUMENTS, INC., 109 LUKENS DRIVE, NEW CASTLE, DELAWARE, USA

Simultaneous TG (thermogravimetric analysis)-DTA (differential thermal analysis) measures both differential temperatures and weight changes in a material as a function of temperature or time in a controlled atmosphere. Simultaneous measurement of these two material properties not only improves productivity but also simplifies interpretation of the results. The complementary information obtained allows differentiation between endothermic and exothermic events which have no associated weight loss (e.g. melting and crystallization) and those which involve a weight loss (e.g. degradation). The combined evaluation also assures identical experimental and sampling conditions for both measurements, thereby eliminating those sources of uncertainty. This paper briefly describes a new simultaneous TG-DTA instrument with emphasis on how the measurements are made and with several typical applications.

Keywords: simultaneous TG-DTA

Principles of operation

A schematic for a typical simultaneous TG-DTA (TA Instruments SDT 2960) is shown in Fig. 1. The system is based on a dual-beam horizontal design in which each ceramic beam (arm) functions as one half of a DTA thermocouple pair, as well as part of a horizontal null-type balance. One arm accommodates the sample and measures its property changes. The other arm accommodates the reference (typically an appropriate amount of inert material such as aluminum oxide) and is used to generate the DTA (ΔT) measurement, as well as to correct the TG measurement for temperature effects like beam expansion.The weight change is measured by a taut-band meter movement located at the rear of each ceramic arm. An optically activated servo loop maintains the balance arm in the horizontal reference (null) position by regulating the amount of current flowing through the transducer coil. An infrared LED light source and a pair of photosensitive diodes detect movement of the arm. A flag at the end of the balance arm controls the

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amount of light reaching each photosensor. As weight is lost or gained, the beam becomes unbalanced, causing unequal light to strike the photodiodes. A restoring current is generated to eliminate this imbalance and reattain the null position. The amount of restoring current is a direct measure of the weight change.

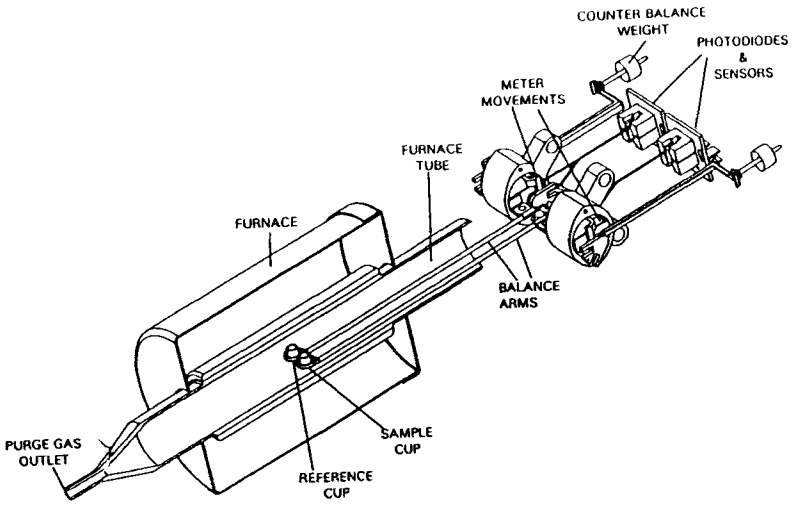

Fig. 1 Schematic of TA Instruments SDT 2960

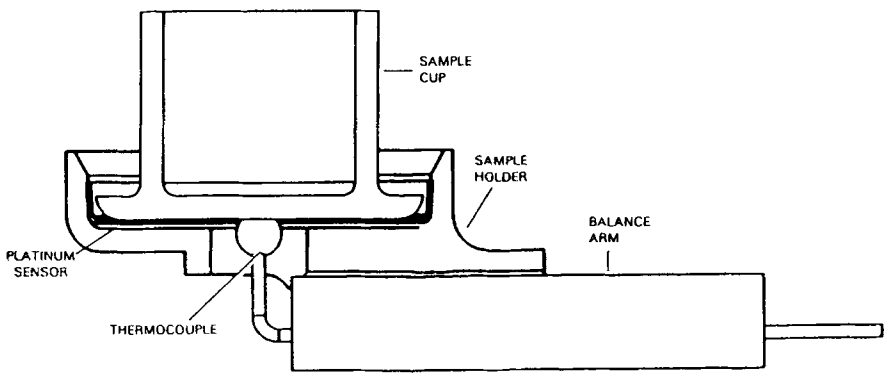

Fig. 2 Close-up of sample platform area

The DTA (ΔT) measurement is made by a pair of matched platinum/platinum-rhodium thermocouples which are contained inside the ceramic arms and welded to platinum sensors located in the bottom of the sample and reference holders

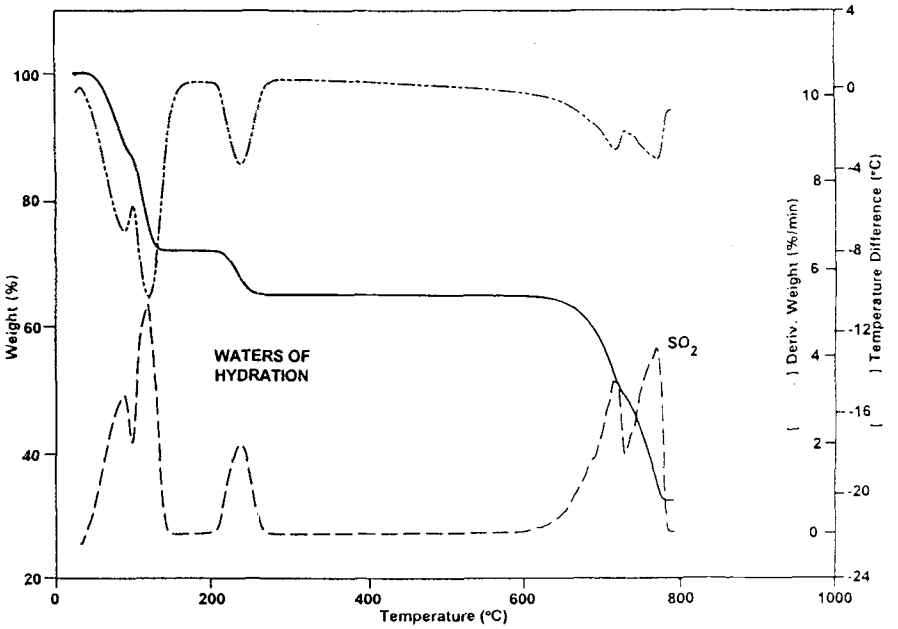

Fig. 3 TG-DTA results for copper sulphate

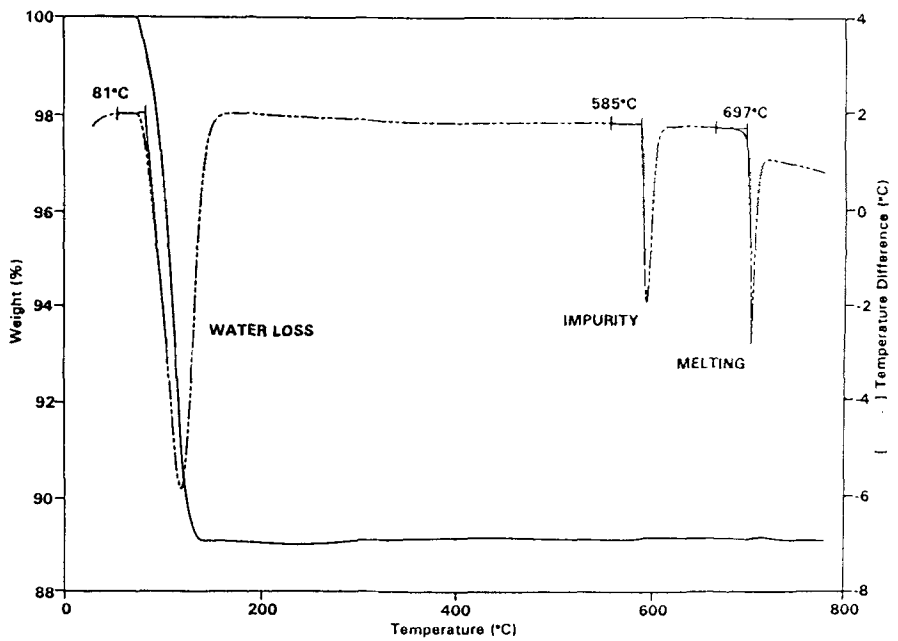

Fig. 4 TG-DTA results for sodium tungstate

(Fig. 2). The thermocouple in contact with the sample is also used to monitor sample temperature for display on the X-axis of the resultant thermograms. The furnace is bifilar wound with the furnace tube as an integral part of the furnace, and temperatures to 1500°C are attainable.

Applications

Simultaneous TG-DTA results are most often used to improve the interpretation of thermal events by providing information about whether a specific event is endothermic or exothermic and whether or not it has an associated weight change. Figures 3 and 4 illustrate these points. Copper sulphate pentahydrate in nitrogen exhibits a series of endothermic transitions which have corresponding weight losses. Hence, all the DTA events are decompositions representing the losses of water (in several stages) and sulphur dioxide. Sodium tungstate dihydrate, on the other hand, exhibits three DTA transitions when heated in nitrogen, but only one weight loss. The TG results confirm the assignment of the DTA transitions as decomposition (loss of waters of hydration), melting of an 'impurity' (probably a

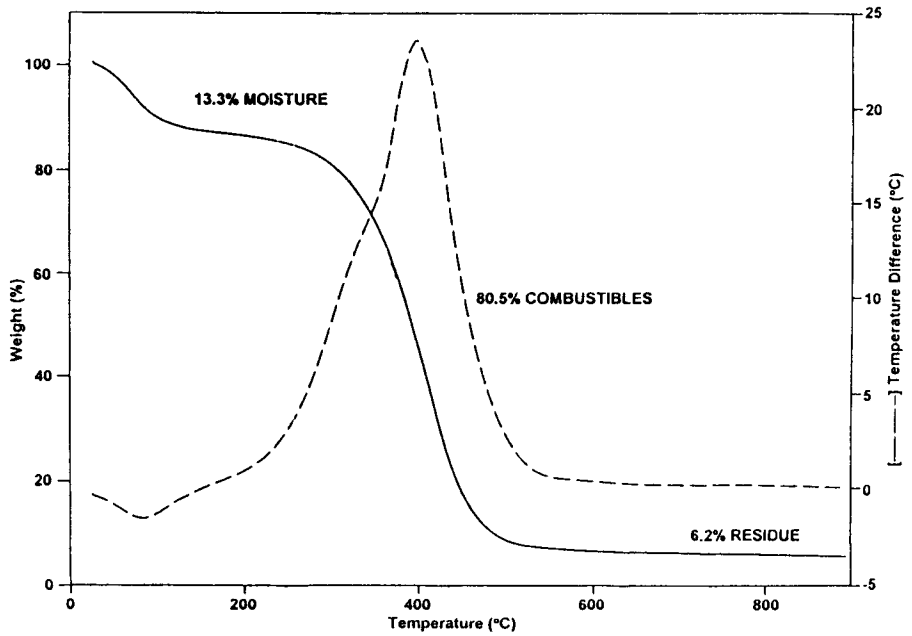

Fig. 5 TG-DTA results for coal

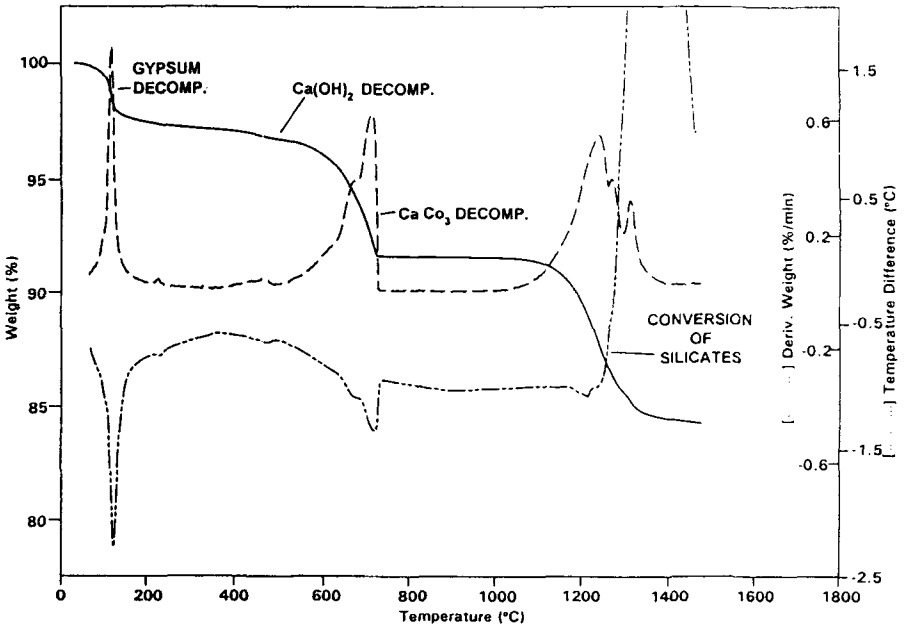

Fig. 6 TG-DTA results for portland cement

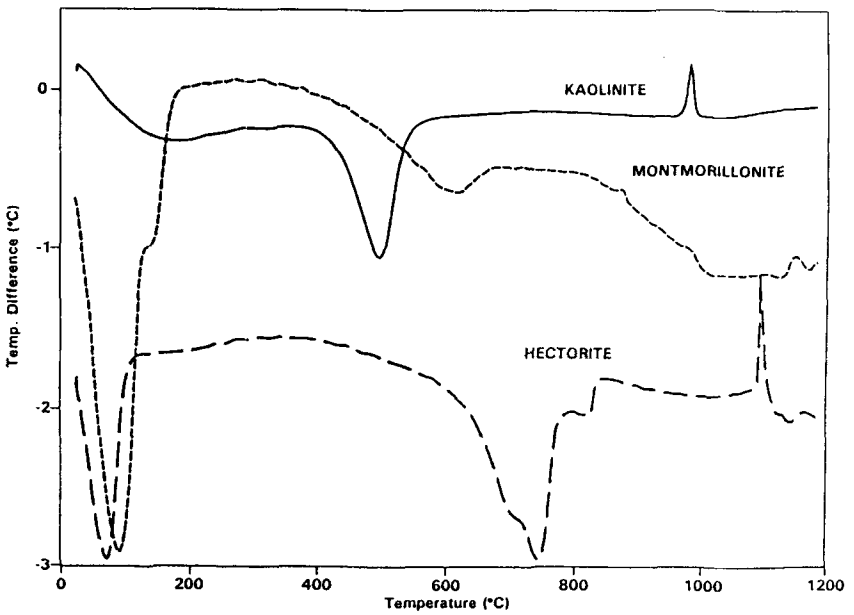

Fig. 7 DTA comparison of clay minerals

metastable crystalline form of anhydrous sodium tungstate), and melting of the base material respectively.

The ability to obtain two thermal measurements on a single material is valuable for rapidly comparing different batches of product or different sources of raw material in quality control situations where absolute quantitative information is not required. In coals, for example, TG-DTA curves such as those shown in Fig. 5 provide both proximate analysis (amounts of moisture, combustibles, and inert residue) and relative heat content information.

The ability to obtain measurements at temperatures up to 1500°C is useful for inorganic materials such as cements, clays, ceramics, superconductors, and metals. Figures 6 and 7 show typical examples.

Portland cements are complex mixtures of dicalcium and tricalcium silicates, as well as other calcium-based hydroxides, carbonates, ferrites, and aluminates. These materials are formed by firing a calcareous material such as limestone together with a siliceous material such as clay at elevated temperatures. The resulting clinker is then mixed with gypsum and ground to a fine powder to form the final cement. Figure 6 shows the TG-DTA results for a typical final cement. Four weight losses with associated DTA events are observed. In order, these represent decomposition of gypsum ($CaSO_4 \cdot 2H_2O$), decomposition of calcium hydroxide, decomposition of calcium carbonate, and conversion of dicalcium sili-

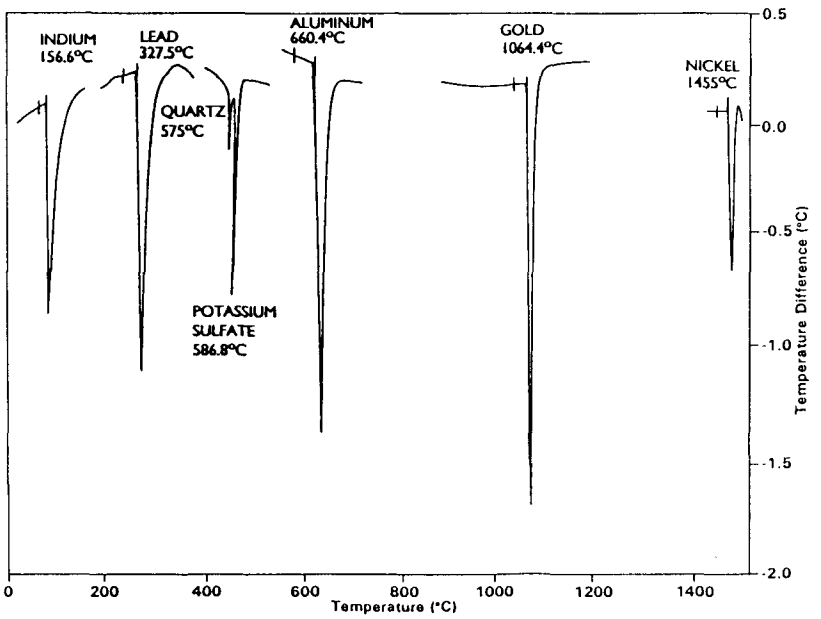

Fig. 8 Temperature calibration standards

cate to higher forms (e.g. tricalcium silicate). Thermal curves such as this can be used as 'fingerprints' for distinguishing between different formulations. More importantly, with suitable standards, important formulation information such as the amount of gypsum present can be determined.

TG-DTA results can also be used to identify the materials used to make the clinker. For example, Fig. 7 shows the DTA curves for several clays commonly used in cement manufacture. Kaolinite which contains mainly alumina and silica is the most desirable clay for the production of white cement. It is easily distinguished from montmorillonite and hectorite by its endothermic dehydration between 450°–530°C and exothermic crystalline transition at 980°C.

Simultaneous TG-DTA provides valuable information even in materials where no weight changes occur over the temperature range studied. For example, the technique provides melting point information (Fig. 8) for five different metals whose melting points cover the range 150° to 1500°C. Results such as these in combination with the SDT 2960 calibration software provide multipoint (up to five points) temperature calibration which subsequently assures accurate transition temperatures. In addition, the melting points of pure metals can be combined with those obtained for different alloy formulations to determine phase diagrams.

Transitions in other well-characterized inorganic materials such as quartz or potassium sulphate can also be used for temperature calibration of TG-DTA equipment. A mixture of these two standard materials (two peaks between 550° and 600°C in Fig. 8) has additional value as an indicator of DTA resolution in the simultaneous TG-DTA equipment being used. The SDT 2960 provides separation between these two closely spaced transitions comparable to that obtained from most dedicated DTA units, indicating that performance has not been compromised in designing this simultaneous unit.

Zusammenfassung — Simultane TG und DTA messen in einer kontrollierten Atmosphäre sowohl Differenztemperaturen als auch Gewichtsveränderungen als eine Funktion von Temperatur oder Zeit. Die simultane Messung dieser beiden Stoffeigenschaften steigert nicht nur die Produktivität sondern vereinfacht auch die Interpretation der Resultate. Die erhaltenen, sich einander ergänzenden Informationen erlauben es, zwischen endothermen und exothermen Geschehnissen ohne Massenverlust (z.B. Schmelzen und Kristallisieren) und mit Massenverlust (z.B. Abbau) zu unterscheiden. Außerdem werden durch die kombinierte Anwendung identische Versuchs- und Probenbedingungen für beide Messungen geschaffen, wodurch die sich aus solchen ergebenden Ungewißheiten ausschließen lassen. Es wird kurz eine neue simultane TG-DTA-Apparatur, deren Anwendungsart und typische Anwendungen beschrieben.