Forschung Wissenschaft

The Automation of Thermal Analysis Instrumentation: Thermogravimetry and Differential Thermal Analysis*

By W. W. WENDLANDT

Thermochemistry Laboratory, Department of Chemistry, University of Houston, Houston (Texas) 77004 (U.S.A.)

Abstract

The automation of the thermal analysis instruments, differential thermal analysis (DTA) and the thermobalance, is described. The DTA instrument is capable of studying eight individual samples, each contained in a glass capillary tube, in a sequential manner. The samples are automatically introduced into the furnace, pyrolyzed to a preselected temperature limit, and then removed. After cooling the furnace back to room temperature, the cycle is repeated. Operation of the sample changing mechanism, furnace temperature programming, recording, and so on, is completely automatic.

The thermobalance is capable of recording the TG curves of eight samples in a sequential manner. The instrument consists of a recording top-loading balance, a furnace and temperature programmer, and an automatic sample changer. Each sample in the sample holder disk is positioned into the furnace automatically, heated to a preselected temperature, and then removed. After the furnace is cooled back to room temperature, the cycle is repeated with a new sample. Operation of the thermobalance is completely automatic and it requires no operator attention once the cycle is begun.

Introduction

Present day thermal analysis instruments are the culmination of a long period of development. The first crude instruments were manually controlled in that the data, *e.g.*, temperature, differential temperature, mass change, and so on, were recorded point by point by the operator. With the advent of various recording techniques, this tedious task was eliminated. Further sophistication of these instruments included automatic temperature programming and control, controlled furnace and sample environment, and data manipulation (differentiation, integration, and so on). The operator may now introduce a sample into the thermal analysis instrument, press a single button to start the heating cycle, and return in several hours to examine the conveniently recorded thermal curve.

One of the major disadvantages of the modern thermal analysis instrument is its inability to change samples automatically. The operator must still manually introduce and remove each sample from the sample holder and furnace (except for multi-sample systems). The inability to perform this simple task prevents the automation of these instruments and also the unattended operation of them for long periods of time.

I would like to present the results of our work on the automation of thermal analysis instruments, namely, that of the thermobalance and differential thermal analysis. In attaining this goal, I have had to discard some of the traditional approaches to these instruments and implement new ideas to replace them. For clarity and simplicity, the automation of each instrument will be discussed separately.

Differential Thermal Analysis (DTA)[1]

The modern differential thermal analysis (DTA) instrument is derived from the two thermocouple design suggested by ROBERTS-AUSTEN[2] in 1899. Many instruments have been designed and constructed since that time, each slightly different in the design of the furnace, furnace programmer, recording equipment, sample holder geometry, and so on. SMOTHERS and CHIANG[3] in 1958 described some 225 instruments located throughout the world. This list was deleted in the second edition[4], but the latter included a bibliography of some 4248 references to DTA literature, many of them describing the instrumentation employed by the investigators. Modern DTA equipment is adequately summarized in various textbooks[5–8] while specifications on commercially available instruments are described elsewhere[9].

Present day instruments are capable of automatic operation in that after manual introduction of the sample, the temperature rise is controlled by a furnace programmer which will turn off the instrument after a preselected temperature limit is attained. After cooling

* Lecture given at the Technical Congress on the occasion of the 5th International Exhibition of Laboratory, Chemical Engineering, Measurement and Automation Techniques in Chemistry on September 15, 1971, in Basle.

the furnace back to room temperature, the pyrolyzed sample is removed from the sample holder, a new sample is introduced, and the heating cycle repeated. The automated DTA instrument reported here is capable of studying eight samples in a sequential manner. The samples are automatically introduced into the furnace, pyrolyzed to a preselected temperature limit, and then removed. After cooling the furnace back to room temperature, the cycle is repeated. Operation of the sample changing mechanism, furnace temperature rise and cooling, recording, and so on, is completely automatic.

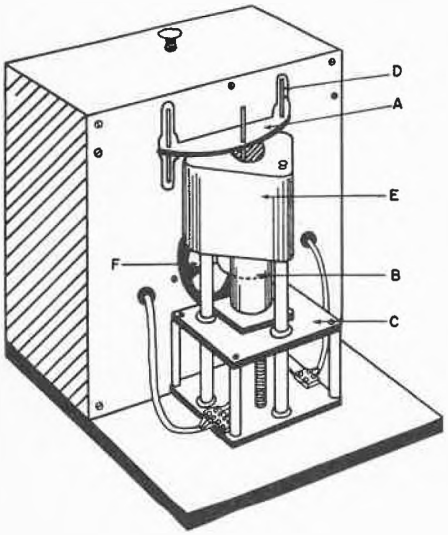

Figure 1. General view of instrument sample changer, furnace, and furnace platform. *A* Sample holder plate, *B* Furnace, *C* Furnace platform assembly, *D* Sample capillary tube, *E* Furnace insulation, *E* Cooling fan

General instrument features. A line drawing of the sample changing mechanism, furnace and furnace platform is shown in Figure 1.

The powdered samples are contained in glass capillary tubes, *D*, of 1.6 to 1.8 mm i.d., which are placed in the circular sample holder plate, *A*. The aluminum sample holder plate is 8.0 in diameter by 1/8 inch thick and has provision for retaining the eight glass capillary tubes. The glass tubes are held in their respective positions by means of small spring clips. The plate is rotated by a small synchronous electric motor equipped with an electromagnetic clutch. The rotation of the plate by the motor is controlled by a lamp-slit-photocell arrangement. Adjacent to each sample holder position is a 0.50 × 0.06 inch slit cut in the aluminum plate. Alignment of the plate slit between the lamp and photocell by the drive motor permits exact positioning of each capillary tube with furnace cavity.

After the capillary tube is in position, the furnace platform, *C*, is raised so that the tube is positioned into the aluminum heat transfer sleeve, located on the sample thermojunction. Movement of the furnace platform is controlled by a reversible electric motor connected to the platform by a screw-drive. Upper and lower limits of travel are controlled by two micro-switches. The furnace is insulated from the platform by a 0.25 inch layer of transite and while in the heating position, by a Marinite sleeve, *E*. Rotation interval for sample changing is 15 sec while it takes 50 sec to raise the furnace platform to the full upper limit.

After the sample has been heated to the upper temperature limit, the furnace is lowered, the sample holder plate rotates to a new position, and a cooling fan is activated to direct air on the hot furnace. Cooling time for the furnace, from 450 °C to room temperature, takes about 20 minutes. After the furnace has been cooled to room temperature, the above cycle is repeated with a new sample.

Furnace and sample chamber. A schematic diagram of the furnace and sample chamber is shown in Figure 2.

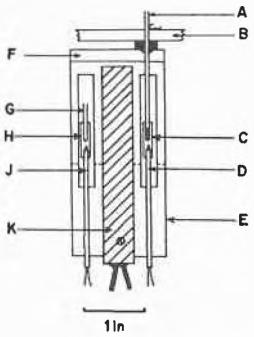

Figure 2. Furnace and sample chamber. *A* Glass capillary tube for sample, *B* Sample holder plate, *C* Sample heat transfer sleeve, *D* Sample thermocouple, *E* Furnace block, *G* Reference capillary tube, *H* Reference heat transfer sleeve, *J* Reference thermocouple, *K* Heater cartridge

The cylindrical furnace, *E*, is 1.5 inches in diameter by 3.3 inches in length, and is heated by a 210-watt stainless steel heater cartridge, *K*. The upper temperature limit of the furnace is about 500 °C. The sample and reference cavities are about 0.25 inches in diameter by 1.5 inches in length. Thermal contact between the sample and reference capillary tubes, *A* and *G*, is made by the aluminum heat transfer sleeves, *C* and *H*. The cylindrical sleeves are about 0.7 inches in length. The

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ends of the sleever are drilled out so that the sample tube and the 1/16 inch in diameter ceramic insulator tube, *D* or *J*, fit closely within the sleeve. To minimize heat-leakage from the furnace to the sample holder plate, *B*, a transite cover, *F*, is used to enclose the top of the furnace.

A schematic diagram of the instrument components and the furnace programmer is shown in Figure 3.

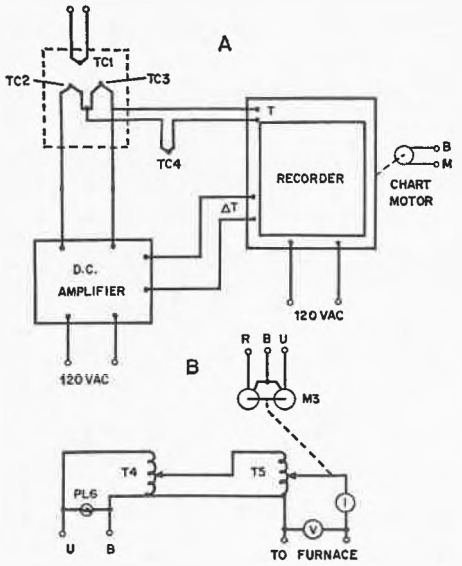

Figure 3. *A* Schematic diagram of DTA components, *B* Schematic diagram of furnace programmer. *TC2*, *TC3*, *TC4* Chromel-Alumel thermocouples; *M3* Motor, dual; *T4* and *T5* Transformer, variable voltage; *PL6* Pilot lamp; Voltmeter; Ammeter

The ΔT voltage from the differential thermocouples *TC2* and *TC3*, is amplified by a Leeds and Northrup microvolt d.c. amplifier, and is recorded on one channel of a Varian Model G-22 strip-chart potentiometric recorder. The sample temperature, as detected by thermocouple *TC3* and the 0 °C reference junction thermocouple *TC4*, is recorded on the other channel. A chart-speed of 6 inches per hour was employed on all of the heating runs.

The furnace temperature programmer is similar to that previously described[10]. Movement of the contact wiper arm of transformer *T5* is controlled by a dual-speed motor unit. The drive motor speed is ½ RPH while the reset motor is ½ RPM. Reset limit of the wiper arm is controlled by a micro-switch connected in series with the reset motor. Variable furnace heating rates can be obtained by varying the output voltage from transformer *T4*. A 120 V output gives a furnace heating rate of about 7 °C/min; 90 V gives a heating rate of 4 °C/min.

Procedure. The procedure for a run consists of weighing out the samples into the eight glass capillary tubes. Sample sizes usually ranged in weight from 1 to 8 mg. The glass capillary tubes are placed in the sample holder plate, a convenient ΔT range is selected on the amplifier, and the meter relay activated by movement of the lower temperature contact. Operation of the instrument is then completely automatic. All eight samples are heated in a sequential manner and after the eighth sample is run, the instrument shuts off all power to the various components *via* the latching relay.

Applications

Two sequential DTA runs of $CuSO_4 \cdot 5\,H_2O$ samples are shown in Figure 4.

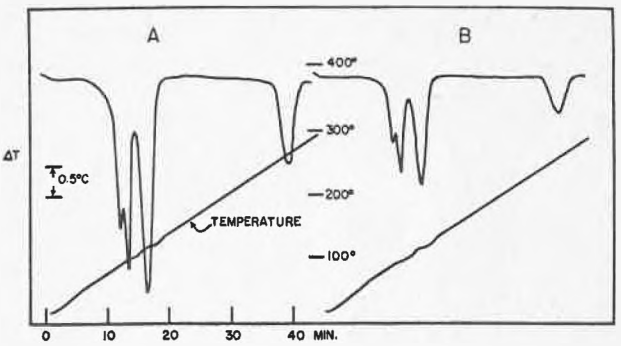

Figure 4. DTA curves of two samples of $CuSO_4 \cdot 5\,H_2O$. Sample A 5.72 mg; Sample B 3.32 mg

The DTA curve and the temperature of the sample are shown by the two curves for samples *A* and *B*. The only difference in the samples is their weight. The curves show the dehydration reactions of $CuSO_4 \cdot 5\,H_2O$ very clearly. The first shoulder peak indicates the evolution of liquid water by the reaction,

$$CuSO_4 \cdot 5\,H_2O\ (s) \rightarrow CuSO_4 \cdot 3\,H_2O\ (s) + 2\,H_2O\ (l) \quad (1)$$

while the second endothermic peak is due to the vaporization of the liquid water[11]. The formation of the *l*-hydrate is indicated by the third endothermic peak, as given by the reaction,

$$CuSO_4 \cdot 3\,H_2O\ (s) \rightarrow CuSO_4\,H_2O\ (s) + 2\,H_2O\ (g) \quad (2)$$

The fourth endothermic peak is caused by the dehydration of the *l*-hydrate, according to,

$$CuSO_4 \cdot H_2O\ (s) \rightarrow CuSO_4\ (s) + H_2O\ (g) \quad (3)$$

A large number of inorganic salt hydrates have been studied by the automated instrument. The convenient size of the recorded curve permits the chart paper to be cut to fit a *E-Z* sort punched card and hence filed for easy reference at some future date. The instrument should find a wide use for the routine DTA examination of a large number of samples, both inorganic and organic. The automated features of the instrument should permit convenient computer interfacing so that reaction temperatures, peak areas, and so on, can be easily calculated or tabulated.

The Thermobalance[12]

HONDA[13] was perhaps the first investigator to use the term "thermobalance" to describe an apparatus which was used to determine the continuous weight-change of a sample as the sample was heated to elevated temperatures in a furnace. Although the instrument was rather crude, it enabled him to obtain weight-change curves of a number of inorganic compounds and also to establish a Japanese school of thermogravimetry, the results of which have been summarized by SAITO[14]. In 1923, a similarly crude thermobalance was described by GUICHARD[15] which was to be the first of a large number of instruments used by French workers in this field.

The historical development of the modern thermobalance has been adequately described by GORDON and CAMPBELL[16], DUVAL[17], WENDLANDT[5], KEATTCH[18], SAITO[19], and others[6, 20]. The modern instruments have been described in well-known textbooks in the field[17, 5, 6] and other sources[18, 21]. By far the most sophisticated multifunction instrument is the Mettler thermobalance, as described by WIEDEMANN[22]. Besides recording the weight-change curves of a sample at two different sensitivities, it also records the derivative of the weight-change and the DTA curve. Another multi-function instrument, the Derivatograph, has previously been described by PAULIK *et al.*[23]

The modern thermobalance is an automatic instrument in that the weight-change of a sample can be recorded over a wide temperature range. Little attention has been given to the introduction of a new sample automatically into the furnace chamber or of stuying multiple samples in a sequential manner. The automated instrument reported here is capable of automatic sample changing and temperature programming. Eight samples, contained in the rotatable sample holder disk, can be studied in an individual manner. A schematic diagram of the balance, furnace, and sample changer mechanism is shown in Figure 5, while a diagram of the furnace and sample holder configuration is given in Figure 6.

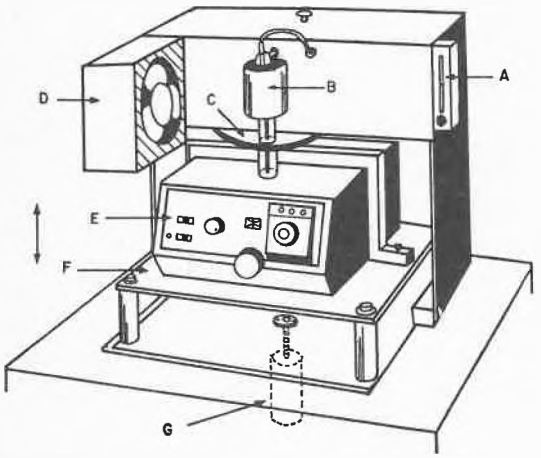

Figure 5. Schematic diagram of the balance, furnace, and sample changer mechanism. *A* Gas flow-meter, *B* Furnace, *C* Sample holder disk, *D* Cooling fan, *E* Cahm Model RTL recording balance, *F* Balance platform

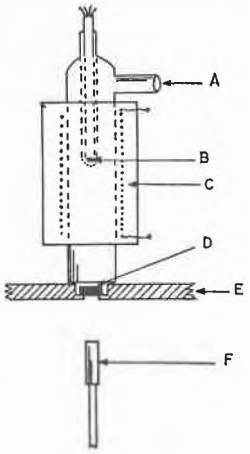

Figure 6. Schematic illustration of the furnace and sample holder. *A* Gas inlet tube, *B* Thermocouples, *C* Furnace heater windings and insulation, *D* Sample container, *E* Sample holder disk, *F* Ceramic sample probe

The thermobalance is conventional in design in that it consists of a top-loading recording balance (Cahn Model RTL balance), a Leeds and Northrup four-channel multi-point potentiometric recorder (0 to 5 mV full-scale), a small tube furnace, a sample changer mechanism, and an automatic furnace temperature programmer. Perhaps the most novel feature of the instrument is the automatic sample changing mechanism which operates in the following manner: The samples to be investigated are placed into small cylindrical platinum containers, Fig. 6 (*D*), (5.0 mm in diameter by 2.0 mm in height). Eight such containers are placed in the circular indentations cut in the periphery of the 0.25 in. thick by 8.0 in. in diameter aluminum sample holder disk, Fig. 6 (*E*). The sample containers are positioned directly below the opening of the tube furnace, Fig. 6 (*C*), by the rotation of a small electric motor connected to a micro-switch which is tripped by an indentation in the circumference of the disk. The positioned sample is picked up by the ceramic sample probe, Fig. 6 (*F*), which is attached to the beam of the balance. Movement of the entire balance

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[23] F. PAULIK, J. PAULIK, and L. ERDEY, *Z. Anal. Chem. 160* (1958) 241.

and the balance platform, Fig. 5 (*E* and *F*), is controlled by a motor-driven screw in the base of the platform. The motor is reversible so that the platform can be raised or lowered with limits of movement in both directions controlled by micro-switches. After the sample is positioned in the central part of the furnace, the furnace is flooded with nitrogen or some other gas, and the furnace temperature programmer activated. On attaining a preselected furnace maximum temperature limit, the balance is lowered and the sample container retained by the sample holder disk. The disk then rotates to position a new sample at the base of the furnace. A cooling fan, Fig. 5 (*D*), is activated, which cools the furnace to a preselected lower temperature limit at which point the entire cycle is repeated, using a new sample. The heating and cooling cycles are performed on eight successive samples. Each sample is preweighed into the sample containers using a Mettler semi-micro printing balance. The individual sample containers are tared to within ± mg (empty weight is about 130 mg); each sample is kept under 10.0 mg so that the recorder pen deflection remains on the recorder scale. The recorder mass range is 0 to 10 mg at 1.00 mg per in. on a 10 in. wide chart; a chart speed of $^1/_{15}$ or $^1/_6$ inch per min was normally used.

Procedure. The eight samples were weighed out into the previously tared platinum containers, using a semi-micro balance. Sample weights usually ranged from 5 to 9 mg although larger samples could be employed if the tare control on the balance was used to keep the recorder pen on scale. The sample containers were then loaded into the sample holder disk, the positioning of the latter being controlled by the manual override switch. The number 1 sample was then positioned under the furnace and the lower-limit set point of the meter-relay activated. This caused the balance platform to rise, activated the recorder chart-drive and recording mechanism, and turned on the furnace temperature programmer. Elevation of the balance platform was limited by a micro-switch which also deactivated the platform motor circuits. After the furnace reached a preselected upper furnace temperature limit, as set by the meter-relay, the balance platform was automatically lowered. The spent sample and container were retained by the sample holder disk, and the cooling fan was activated. A new sample was then positioned beneath the furnace. This entire cycle was then repeated for all of the samples retained in the sample holder disk. Operation of the instrument was completely automatic and it required no operator attention after it was started. All samples were studied under dynamic nitrogen atmosphere whose gas flow-rate was 50 ml per min.

The precision and accuracy of the weight recording were estimated at about ± 1% while the temperature recording was estimated at about ± 5%. Full scale recorder deflection for the temperature measurement was about 1000 °C, which was roughly the upper temperature limit of the Vycor tube furnace employed.

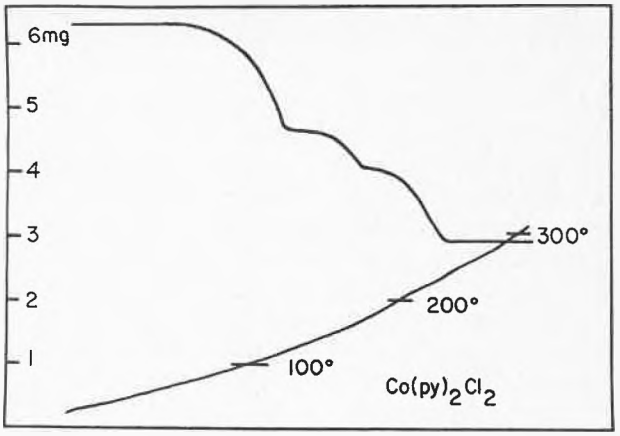

Figure 7. TG curve of $Co(py)_2Cl_2$ in N_2 atmosphere. Sample size 6.26 mg. Furnace temperature curve illustrated

Applications

The TG curve of $Co(py)_2Cl_2$ is illustrated in Figure 7. The TG curve of this compound has previously been described by ALLAN *et al.*[24] and OCONE *et al.*[25]. The curve obtained here agrees well with the thermal dissociation reaction, as given by the equations:

$$Co(py)_2Cl_2\ (s) \rightarrow Co(py)Cl_2\ (s) + py\ (g) \quad (4)$$

$$Co(py)Cl_2\ (s) \rightarrow Co(py)_{2/3}\ (s) + \tfrac{1}{3}\ py\ (g) \quad (5)$$

$$Co(py)_{2/3}Cl_2\ (s) \rightarrow CoCl_2\ (s) + \tfrac{2}{3}\ py\ (g) \quad (6)$$

Three successive TG curves of various nickel(II) salt hydrates are illustrated in Figure 8. In the case of $Ni(CHO_2)_2 \cdot 4H_2O$ and $Ni(C_2H_3O_2)_2 \cdot 4H_2O$, the first weight-losses in each curve were due to the hydrate water evolution. The resulting anhydrous nickel(II) salts then dissociated to yield a residue of NiO. In the case of $NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, the first weight-loss was due to the evolution of water followed closely by the sublimation of $(NH_4)_2SO_4$. The residue obtained was $NiSO_4$.

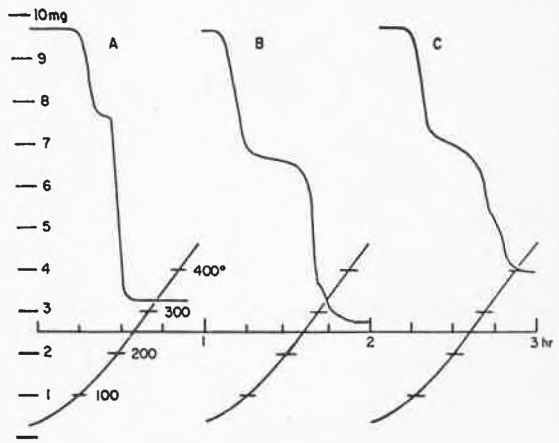

Figure 8. Successive TG curves of some hydrated nickel(II) salts. *A* $Ni(CHO_2)_2 \cdot 4H_2O$, 9.87 mg; *B* $Ni(C_2H_3O_2)_2 \cdot 4H_2O$, 9.24 mg; *C* $NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, 9.60 mg; furnace temperature indicated; nitrogen atmosphere

The obvious advantage of the automated thermobalance system over existing instruments is the ability to determine the weight-loss curves of eight successive samples. Operation of the instrument is completely automatic and once the cycle is begun, the instrument does not require the attention of the operator until the eighth sample curve is completed. The instrument should find use for the routine TG examination of a large number of samples, each to be studied under identical thermal conditions. Being completely automated, data reduction or control by a small digital computer could easily be accomplished.

Acknowledgments

The author would like to acknowledge the assistance of Mr. W. SHERMAN BRADLEY who so ably constructed these instruments and made other contributions to their development, and to the ROBERT A. WELCH Foundation of Houston (Texas) for their financial support.

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