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THE USE AND EXTENDED LIFETIMES OF MICROFURNACES FOR THERMOGRAVIMETRY. PART I. CONSTRUCTION, APPLICATION, AND CLEANING

C.M. EARNEST

Department of Chemistry, Berry College, Mt. Berry Station, Rome, Georgia 30149 (U.S.A.)

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ABSTRACT

The role and application of microfurnace technology in modern thermogravimetry are discussed. The construction and advantages and disadvantages of such microfurnaces are presented. All the microfurnaces considered are commercial platinum-wound ceramic mandrels which have been coated with an alumina-based ceramic material by a special flame spray mechanism. Methodology for extending the lifetime of such furnaces through proper cleaning procedures is also given.

INTRODUCTION

Modern thermogravimetric analyzers vary considerably with respect to the type and size of furnace used. Most of the thermogravimetric systems which are designed for high temperature use ($> 1000\,^{\circ}C$) employ large external furnaces. Common examples of these are the Cahn model 171 thermogravimetric analyzer, the Perkin–Elmer TGA 7 HT, and the Omnitherm model TGA–1500. External furnaces are also employed in many general-purpose thermogravimetric systems such as the Dupont model 951 (which is usable to $1200\,^{\circ}C$), the Cahn model 121 (usable to $1100\,^{\circ}C$), the Mettler model TG 50 (usable to $1000\,^{\circ}C$), and the Sieko TG/DTA 200 (usable to $1100\,^{\circ}C$).

There are commercial systems, however, in which a small microfurnace is placed internally (inside the furnace tube) in the system. In this case, the purge gas sweeps over the sample pan and microfurnace as the microfurnace supplies heat to the analysis specimen located in the sample pan. Figure 1 shows a cutaway view of a system employing a microfurnace, with vertical wire suspension of the sample pan from the microbalance, and furnace tube enclosure. In this arrangement, purge gas flows vertically along the direction of the wire. Provision for the admission of an active gas (e.g. oxygen or air) or a second gaseous component for the total purge system is provided for by means of the upper side arm as shown in Fig. 1.

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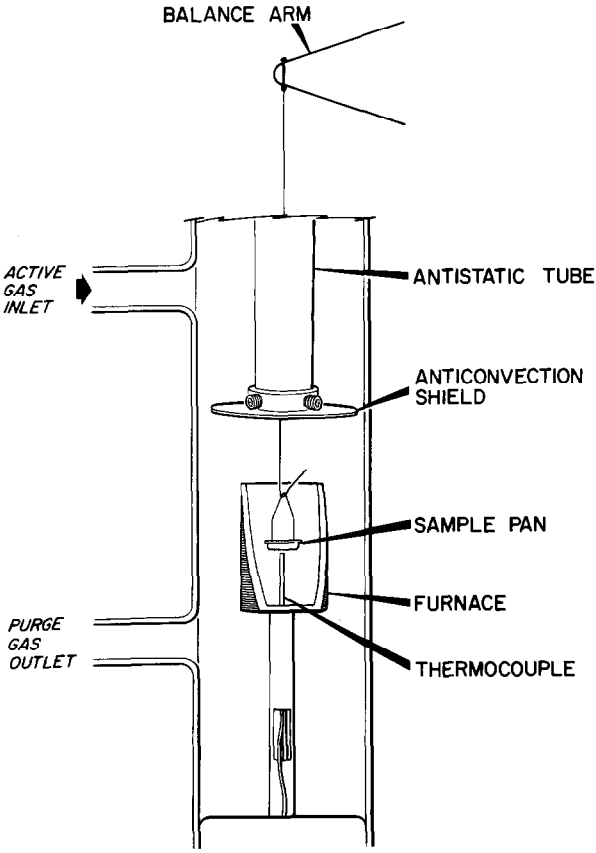

Fig. 1. Cutaway view of internal microfurnace with external Pyrex thermogravimetric furnace tube.

The use of such internal microfurnaces in commercial thermogravimetric apparatus dates back to the introduction of the Perkin–Elmer TGS–1 system in the mid-1960s. The small platinum-wound furnace mandrel, which was subsequently coated with an aluminum oxide (Al_2O_3) based ceramic material, played an important role in this instrument and was radically different from those furnaces used in conventional thermogravimetric analyzers at the time. According to the manufacturer, this small furnace, shown in the center of Fig. 2, was designed specifically to increase the number of TG analyses performed in the laboratory on any given day. The low thermal mass allowed for both rapid heating and cooling of the furnace.

The platinum winding in this novel furnace played a dual role. Half of the time it served as the resistance heating element; on the other half cycle, it served as platinum-resistance thermometer, hence measuring its own temperature. This temperature measurement also served as the control feedback to the temperature programmer. The absence of a thermocouple in this TG instrument was puzzling to some. However, since the emphasis was on

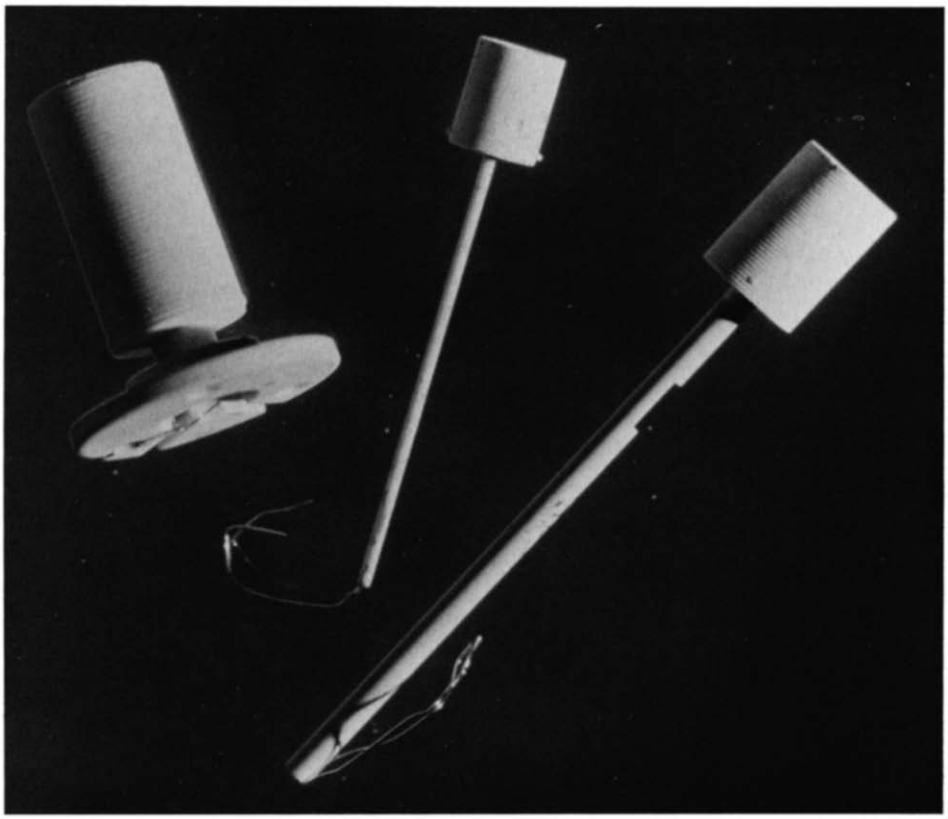

Fig. 2. Three commercial platinum-wound ceramic microfurnaces.

determining the actual temperature of the sample in the small platinum pan, Curie point standards were developed [1] to achieve this end. Thus, the advent of the use of microfurnaces led to another innovative development in thermogravimetry. The use of Curie point standards is now commonplace [2–4].

Microfurnaces have been employed by Stanton–Redcroft, Omnitherm, Perkin–Elmer, and recently by Netsch [5] in a dual symmetrical microfurnace design. Figure 2 shows three platinum-wound microfurnaces produced by the Perkin–Elmer Corporation for use in thermal analyzers. The largest furnace on the left was used as a high temperature option for the model TMS–2 thermomechemical analyzer. This furnace was designed for use in this system from ambient temperatures to 725 °C. A microfurnace of similar construction is employed in the new TMA 7 system. The TMA 7 allows operation from liquid nitrogen temperatures (−170 °C) to 1000 °C with the same platinum-wound microfurnace.

The furnace on the right in Fig. 2 is a second generation microfurnace used for TG applications. This microfurnace was developed for the

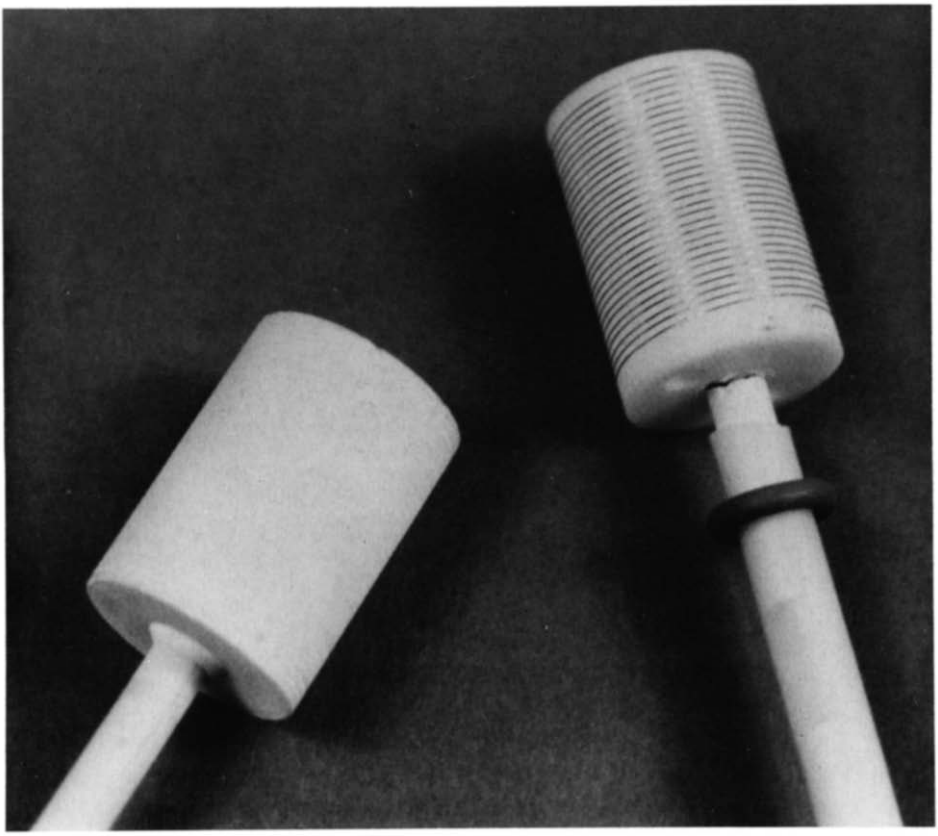

Fig. 3. Platinum-wound ceramic furnace mandrels before and after the addition of alumina coating.

Perkin–Elmer TGS–2 thermogravimetric analyzer. It is somewhat larger than its precursor TGS–1 furnace. The same furnace is employed in the new TGA 7 thermogravimetric analyzer with a different electrical connector and cable.

Figure 3 shows a platinum-wound TG furnace mandrel (on the right) before application of the ceramic alumina coating. The furnace on the left has already received its alumina coating which is applied by a 'plasma spraying' process. When coated, the alumina offers good electrical and mechanical protection to the platinum heater/sensor wire in the temperature range used (ambient temperature to 1000 °C).

After flame spraying the furnace at a high temperature, ceramic cement is applied to the alumina coating and cured into place at an elevated temperature. This gives further protection to the platinum heater/sensor winding from off gases, etc., encountered in thermogravimetric analyzers. The addition of a platinum sleeve to the furnace in the region of the Pt-wound mandrel serves to give uniform vertical heat distribution in the furnace.

One advantage is the improved linearity of the heating ramp when using such microfurnaces. The low thermal mass leads to reduced thermal lag, particularly in the early portion of the temperature programming. Typical power ramps for furnaces such as that used in the Perkin–Elmer systems is 8 mV $^{\circ}C^{-1}$. Modern microcomputer-based programmers have also led to improved furnace performance via built-in dynamic lag compensation factors. This dynamic lag compensation allows additional power to be supplied to the furnace during the early portion of the temperature ramp to prevent thermal lag of the furnace.

Another important advantage which microfurnaces have contributed to thermogravimetry is the ability to heat and cool the furnaces rapidly. The furnace shown on the right in Fig. 2 may be ramped at heating rates from 0.1 to 200 °C min^{-1}. The typical uncontrolled 'free fall' cool down time is 10 min from 1000 °C to 100 °C. Thus, a sample through-put of 12–20 samples per day (depending upon the temperature region) is not uncommon when using such furnaces.

The increased control of the temperature ramp along with the ability to achieve both rapid heating and cooling rates have made many rapid multistep TG analysis programs possible for the compositional analysis of materials. These programs may be executed with TG systems employing small microfurnaces and used in conjunction with modern microcomputer-based controllers. Figure 4 describes such a multistep TG program which is common used for the rapid proximate analysis of coals. The rapid proximate analysis of coals has been described by many researchers [6–12] using either the Perkin–Elmer or Stanton–Redcroft (Omnitherm) system. The program most often recommended by the author employs isothermal holds at 110 °C and 950 °C under flowing nitrogen with rapid heating rates to bring the sample specimen to these temperatures. After sufficient isothermal hold time under an inert atmosphere at 950 °C, the purge gas is then changed to either air or oxygen for ashing the char residue. The entire program and subsequent cool down requires about 30 min.

The low thermal mass of the furnace leads to minimum temperature overshoot when the system makes the transition from dynamic heating ramp to isothermal heating of the sample. Other common TG analyses which employ multistep heating programs include the compositional analysis of elastomer formulations [13,14] and lubricants [13]. A standard method based on these multistep procedures has recently been issued by ASTM [15] for the compositional analysis of materials.

The internal microfurnace itself helps to break the purge gas flow into the desired turbulent pattern. Another important fact is that the sample pan is located inside the small furnace during the actual thermal analysis and

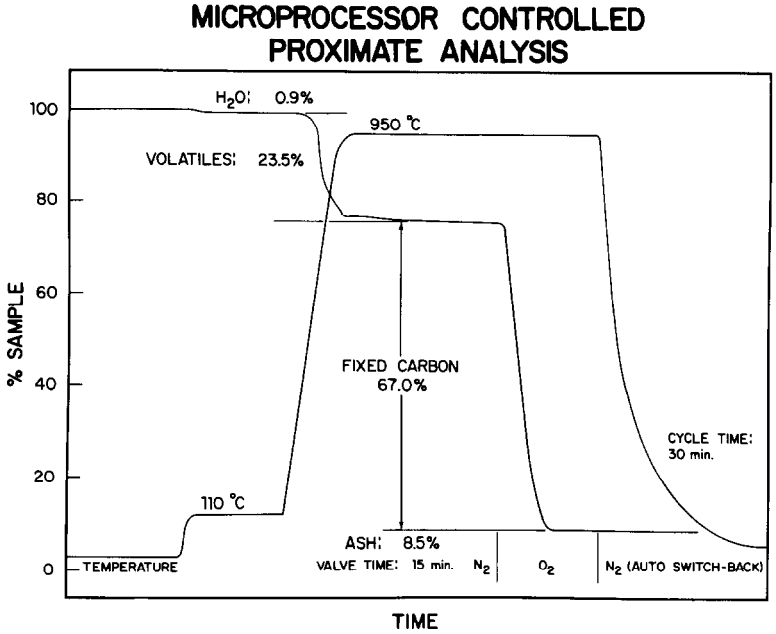

Fig. 4. Thermogravimetric thermal curve for the rapid proximate analysis of coals.

hence is shielded, to a large extent, from convection currents and the turbulent flow pattern which is generated inside the furnace tube.

Another advantage of the small internal microfurnace is the close proximity of the TG sample pan, and sample itself, to the furnace wall. This leads to good sample temperature and furnace temperature coupling. This means that there is much less thermal resistance between the furnace wall and sample than that incurred when the furnace is external to the surrounding furnace tube. The result of this good sample temperature to furnace temperature is that the sample temperature is increased almost instantaneously as the furnace temperature is increased by the power ramp. In all cases, the furnace temperature will be higher than that of the sample but the rate of temperature rise in each per unit voltage increase to the furnace will be almost the same.

A similar argument may be made for the close agreement between the sample temperature and the thermocouple temperature which is measured just beneath the sample pan in such an internal microfurnace. As one can observe in Fig. 1, the thermocouple is positioned very close to the sample pan and, once it is adjusted into place, its position relative to both the sample pan and furnace is fixed. The relationship between the thermocouple temperature and the actual sample temperature in the pan may be experimentally established. This is generally achieved by the use of a small magnet and selected Curie point standards.

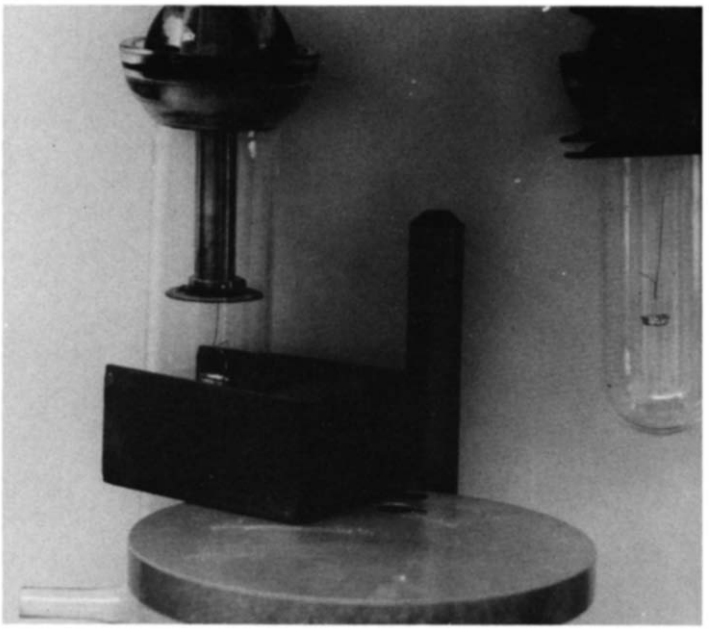

Fig. 5. Horse-shoe magnet positioned around thermogravimetric furnace for the purpose of temperature calibration with Curie point standards.

The ability to place a small horseshoe magnet around the small diameter TG furnace tube and hence perform the technique of thermomagnetometry using the Curie point standards is one of the major advantages of TG systems which use internal microfurnaces. Figure 5 shows the placement of such a small magnet around the furnace tube, and furnace chamber, of a Perkin–Elmer TGS–2 system located in our laboratory at Berry College. In practice, it is the magnetic force (not the sample mass) on the ferromagnetic Curie point standards which is displayed as the apparent weight of the standards in the TG sample pan. On heating the metal Curie point standard through its transition temperature, the loss of magnetism is observed as an apparent weight loss event.

Figure 6 shows a thermal curve which was obtained by the author using four different Curie point standards with the TG system at Berry College. Two of these standards were the pure metals nickel and iron (T_c values of 354 °C and 780 °C respectively) which are commercially available in high purities. The other two, Alumel and Perkalloy, are metal alloys. The Perkalloy standard (T_c of 596 °C) is available only from the Perkin–Elmer Corporation (Norwalk, CT) who developed this special nickel–iron alloy specifically for use in the temperature calibration of thermogravimetric systems. The Curie point temperature for Alumel is given as 163 °C in the original paper by Norem et al. [1].

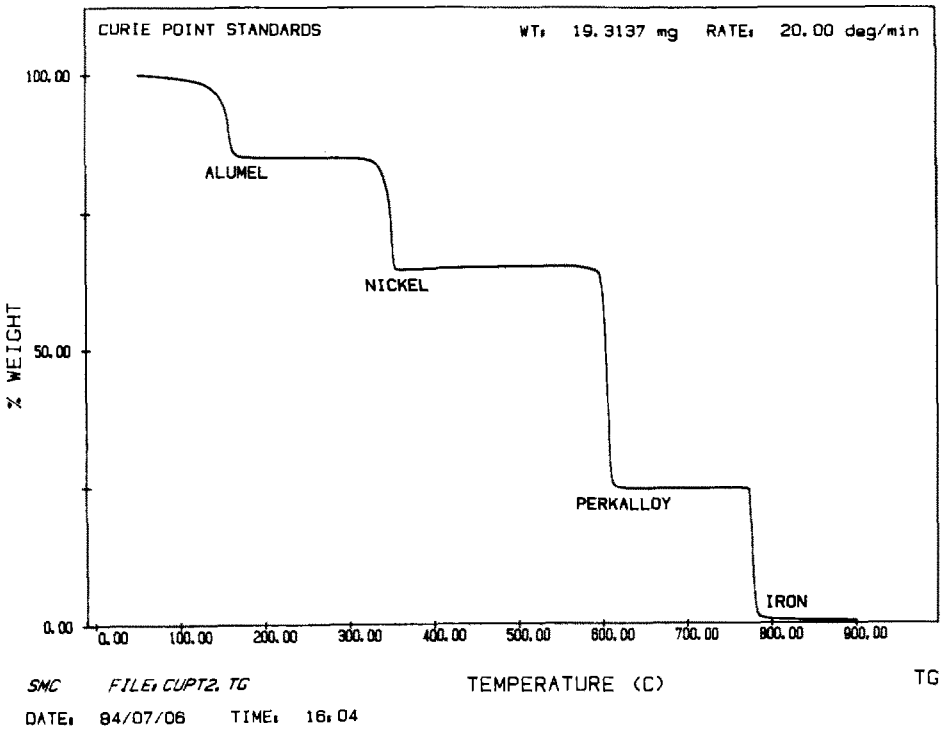

Fig. 6. Thermal curve obtained by using horse-shoe magnet and Curie point standards.

One of the more recent computerized commercial thermogravimetric systems includes a two-point temperature calibration program in which the thermocouple temperature is adjusted to read the actual TG sample temperature. This calibration program is based on the operator's choice of two Curie point standards and a linear regression algorithm in the calibration routine software. The two standards are chosen based on the temperature range of interest. The known Curie point temperatures for the two standards are compared with the experimentally obtained values using the TG system. From these data, the linear relationship is mathematically established by calculating a value for the slope (a) and the intercept (b) for the relationship

$$T_s = aT_m + b$$

Once this is done, the measured thermocouple temperature T_m is adjusted by the above expression so that the actual sample temperature T_s is displayed on the computer screen as the temperature.

Disadvantages of small microfurnaces include a lower maximum temperature limit of use. The larger external TG furnaces generally go to temperatures above 1000 °C. Another disadvantage is that the sample and sample pan must be of an appropriate diameter and geometry to fit inside the

internal furnace itself. Since this is not the case with external furnaces, a larger sample size can generally be accommodated in those systems having larger external furnaces.

Any microfurnace used internally (i.e., inside the furnace tube) must also endure the changing atmosphere during thermal decomposition of the analysis specimen. This places special requirements on furnace composition and temperature control. The lifetime of such furnaces can be shortened if proper attention is not given to furnace cleaning. The Al_2O_3 coating is, by nature, white in color. If absorbed decomposition products of rubber or coal are allowed to build up or absorb into the alumina, the lifetime of the furnace can be shortened. On the other hand, if the furnace is properly cleaned by burning off the accumulation of absorbed decomposition products, it can last for years in some of the toughest volatile decomposition product atmospheres. For example, an analyst who is performing rapid proximate analysis of coals should lower the TG furnace at the end of each day of operation and oxidize any sorbed decomposition product. The same could be said for those performing routine compositional analysis of rubber and elastomer formulations, lubricants, etc. This cleaning may be done in a static air environment at 700 °C. The contaminated furnace in this case will change color from gray to white (the correct color of the alumina coated furnace) as the organic contaminant is oxidized away.

CONCLUSION

Low mass furnaces which are used internally with respect to the furnace tube in TG systems play a large role in conventional thermogravimetry. Twenty-five years of performance have established this type of furnace system as an advance in the technology of thermogravimetry. The increase in sample throughput alone has been a major gain for those laboratories involved in quality control by thermogravimetric means. The ease and degree of temperature calibration of the TG sample pan temperature has also led to improved temperature axes in TG thermal curves. Finally, many rapid analytical heating programs have been developed for specific TG applications using these small microfurnaces.

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