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THE DEVELOPMENT OF THERMAL ANALYSIS INSTRUMENTATION 1955-1985

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ABSTRACT

The development of thermal analysis instruments in the author's laboratory from 1955 to 1985 is discussed. In the 1955-1965 period, instruments were developed to solve a specific chemical problem. From 1970 to the present, new instruments were developed to advance the state of the art of thermal analysis instrumentation. Instruments described include thermobalances, DTA, EGD-EGA, light emission, thermoelectrometry, and others.

INTRODUCTION

The publication of the 100th Volume of *Thermochimica Acta* permits me to discuss the events that shaped my work and philosophy of thermal analysis and calorimetry during the past 30 years. Since I have always been interested in thermal analysis instrumentation, it was thought appropriate to review many of the instruments that have been designed and built in my laboratory from 1955 to 1985.

In the time period, 1955-1965, the development of thermal analysis instrumentation was motivated by a particular chemical problem. For example, we wanted to know more about the thermal decomposition mechanism of cobalt(III) ammine coordination compounds. To do this, we developed instruments that would monitor changes in the: (a) structures of the intermediate species (high temperature reflectance spectroscopy); (b) magnetic properties due to structure changes and/or oxidation-reduction processes (thermomagnetic analysis); (c) composition of the evolved gaseous products (EGA-MS); and (d) phase composition of the intermediate products (thermoelectrometry). In more recent years, 1970-1985, the thermal analysis instruments were developed to advance the state of the art of this field of research. These new or improved techniques included automation of TG, DTA and EGD; thermovoltaic detection (TVD); emission thermophotometry (ETP); and others.

A general outline of this paper is shown in Fig. 1. The dates on each technique represent the year that the first publication in that area appeared,

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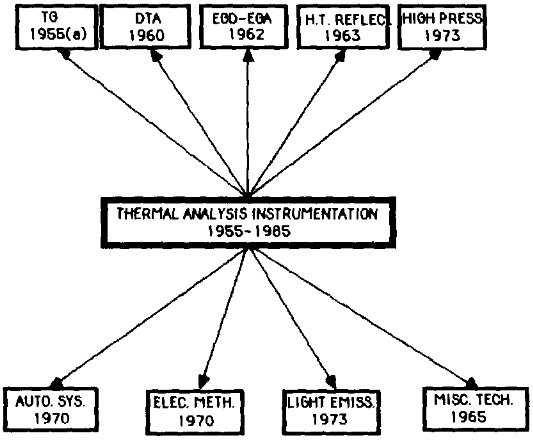

Fig. 1. General outline of thermal analysis instrumentation, 1955–1985.

not the year that our interest began. For each of the nine areas, a general discussion is presented with representative illustrations of the technique shown. Due to space limitations, the descriptions are not comprehensive. They do, however, present an outline of the development of the techniques, and their uses to solve a particular chemical problem and/or advance the state of the art of thermal analysis instrumentation.

A. TG and thermobalances

The first thermal analysis instrument to be constructed was a thermobalance [1]. As always, there was a very limited amount of funds available to purchase the components, but we wanted to study the thermal properties of the cupferron complexes of Sc, Y and the rare earth elements. These complexes were first synthesized during my Ph.D. thesis work so it was logical to use them for my first thermal analysis investigations. As will be discussed later on, the thermal analysis experiment was secondary to the chemical experiment being conducted.

Since I had read that a two-pan analytical balance could not be successfully converted to a thermobalance, due to the dulling of the knife edges, it was decided to use a 0–102 mg range torque balance (Fig. 2(a)), built by a Dutch firm. The smallest scale division was 0.2 mg, hence, weighings could be made to about ±0.1 mg. Conversion of the balance to a thermobalance was carried out by suspending a sample container from the right beam side, into a Vycor tube furnace. Operation of the balance was manual in that both sample and temperature readings were taken for each point on the TG curve. Needless to say, the plotting of the TG curve was a tedious and time consuming process. However, student labor was inexpensive so numerous TG curves were recorded of many different substances.

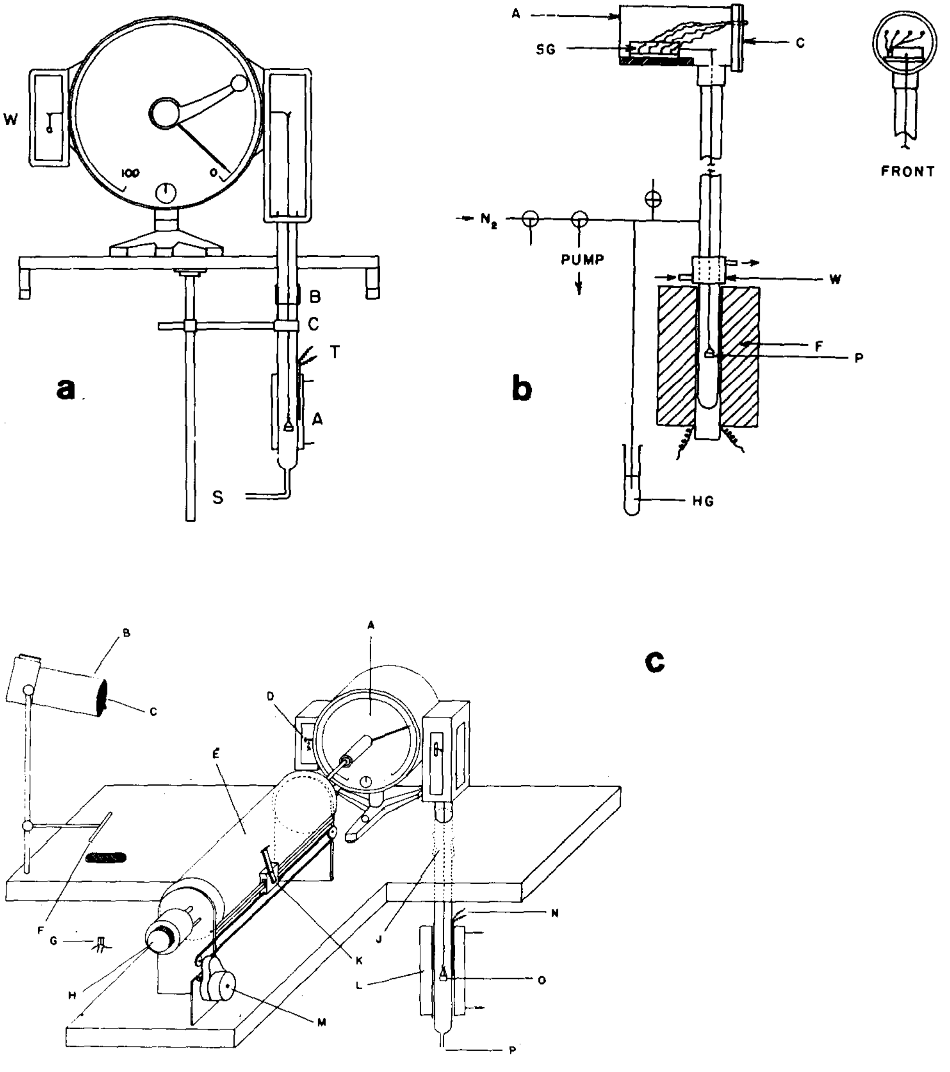

Fig. 2. Thermobalance constructed. (a) Manual torsion balance; (b) controlled atmosphere strain-gauge balance; and (c) automatic recording torsion balance.

One day, one of my assistants suggested that the balance be converted to automatic recording, thus relieving him of the task of manual operation. It was decided to automate the weighing process of the torsion balance by using a light beam-mirror-twin photocell null system, as shown in Fig. 2(a) [2]. The recording drum containing the chart paper was a 3 in. diameter aluminum metal cylinder attached to the torsion balance shaft. Rotation of the drum and hence, the mass axis, was controlled by a 1 rpm servo-motor whose rotation was controlled by the null circuit. A second small motor was used to drive the recorder pen along the drum surface in synchronization with the temperature rise of the furnace. Thus, a recording of mass versus time (temperature) was made. Although relatively crude by today's thermobalances, the instrument worked very well and was used to record a number of TG curves.

The need for a controlled atmosphere thermobalance, which could operate at subambient pressures as well, resulted in the construction of a uniquely simple strain-gauge thermobalance, as shown in Fig. 2(b) [3]. The balance used a strain-gauge as the mass transducer and has a mass range of ±0.15 oz. and an EMF output of 21 mV per 9 V excitation. The strain-gauge was enclosed in an aluminum metal cylinder with provision for the sample container to be suspended from the gauge probe into a tube furnace. The entire thermobalance, including components and labor, cost US $350 to build. An accuracy of ±1% was claimed for the mass measurements while the temperature could be detected to ±2%. The advantage of the system over previous balances was that controlled and subambient pressure atmospheres could be employed.

In 1962, a completely digital thermobalance was constructed [4]. Mass and temperature signals were available in analog (X–Y recorder) or digital form. The latter was obtained from the analog signals by use of a voltage-to-frequency converter, which was switched between mass and temperature signals by a motor-driven switch. Signals from the V–f converter were counted by an electronic counter and then recorded on a digital printer. Thus, a printout, in digital form, of the mass–temperature curve was made as well as the analog X–Y recorder plot.

Many other thermobalances were constructed and/or purchased after these initial models. One such system, which was used for thermomagnetic measurements as well as TG, is shown in Fig. 3(a) [5]. The system consisted of an Ainsworth semi-micro automatic recording balance coupled to a 4 in. electromagnet. The sample was placed in a glass container, which was suspended from one of the balance pans by a platinum wire. To perform Faraday type magnetic measurements, the magnet was elevated and lowered around the sample container. Thus, at a constant temperature increase, the normal TG curve was recorded with perturbations on the curve caused by the changing magnetic field. From these mass pertubations, the magnetic properties of the samples were calculated as a function of furnace temperature. This system was used to observe the reduction reaction of $Co^{3+} \rightarrow Co^{2+}$ (by ammonia in the thermal decomposition of $[Co(NH_3)_6]Cl_3$). It also proved that $[Co(NH_3)_3]Cl_3$ was not an intermediate decomposition product, as has been previously proposed from TG experiments. One lesson taught to us by this experiment was that a TG curve was not conclusive enough to characterize the decomposition of coordination compounds; much more information than this was needed!

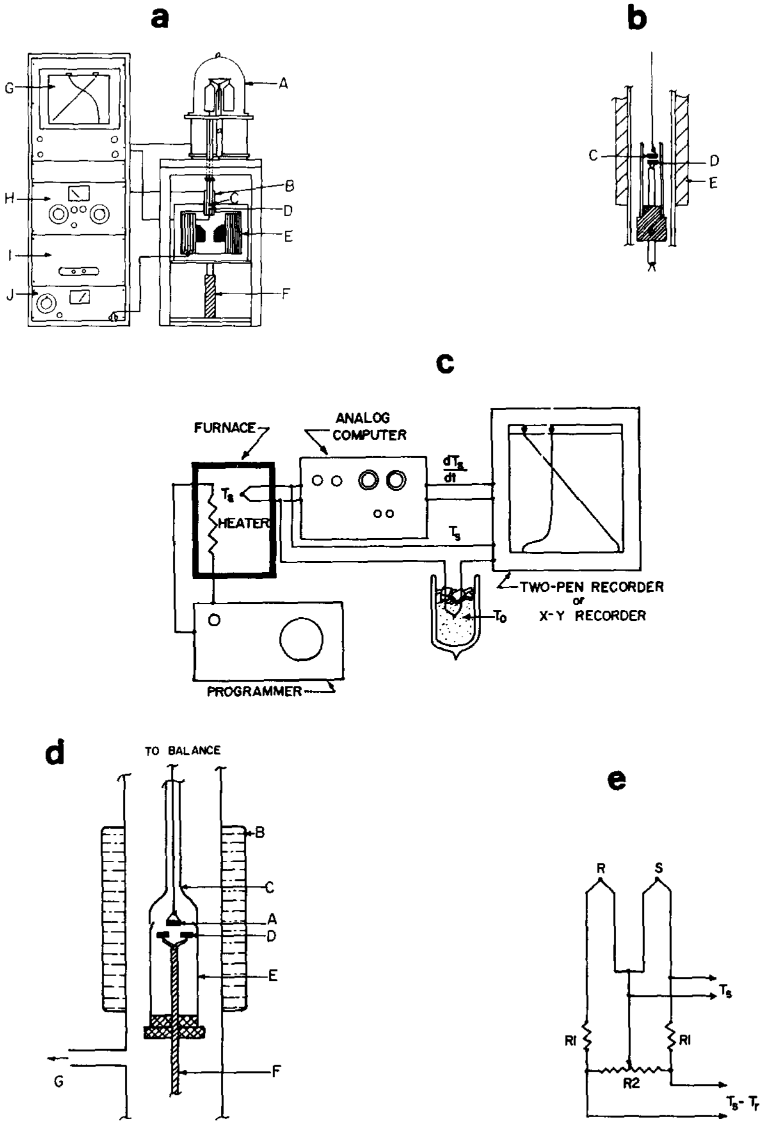

Fig. 3. Miscellaneous TG applications. (a) Magnetic susceptibility balance; (b) measuring TG furnace temperature; (c) detection of furnace heating rate; (d) concurrent TG–DTA; (e) ΔT equalization circuit.

Numerous useful aids for TG systems were published, such as the measurement of furnace temperature using an externally mounted thermocouple, as illustrated in Fig. 3(b) [6]. The determination of the linearity of the heating rate of a thermal analysis instrument (thermobalance) is shown in Fig. 3(c) [7]. The procedure was based on taking the first derivative of the sample, reference, or furnace temperature and recording it as a function of time. Small, short-term, random changes in the heating rates were detected from these curves which could not be observed visually by a temperature–time curve plot. A concurrent TG–DTA system is shown in Fig. 3(d) [8], which uses an externally mounted DTA sample and reference holder. Also, as shown in Fig. 3(e), a simple voltage divider circuit that could be used to adjust the slope of the DTA baseline, either in a positive or negative detection, was described. A similar "outboard" arrangement was also described for TG–DTA and TG–EC measurements, using a DuPont 950 thermobalance [9].

B. Differential thermal analysis

As might be expected, numerous DTA instruments were designed and constructed from 1955 to 1985. However, only a few of the instruments were novel enough to be published in various journals. One of the early DTA systems is shown in Fig. 4(b) [10]. For convenience in weighing the samples, small Inconel cups, 7 mm diameter ×10 mm length, were used to contain the sample. The two cups rested on the differential thermocouples, one containing the sample, the other the reference material. A quartz tube furnace permitted operation from ambient temperature to 1000°C, in a controlled atmosphere from ambient pressure to 1–2 Torr. A small vacuum system completed the apparatus.

A programmable calculator for on-line interaction with a DTA system was described by Carpenter and Wendlandt [11] in 1974. This system, illustrated schematically in Fig. 4(c), used a microcomputer to perform instrument control, data collection, data processing, and plotting. It was stated that "the introduction of a low-cost microcomputer and plotter to a DTA system can add a new dimension to this technique". How true this is today!

A novel calorimeter, the Deltatherm dynamic adiabatic calorimeter, was described in 1970 by Dosch and Wendlandt [12]. This instrument, as illustrated in Fig. 4(a), was used as a module in the standard Deltatherm instrument. Adiabatic conditions could be maintained to ±0.05°C from 50 to 800°C with a stated accuracy and precision for C_p and/or heat of reaction measurements of ±1%.

A sealed-tube DTA system was developed in 1970, which permitted the study of cation–water bond breaking and cation–water bond making reactions in metal salt dehydration reactions [13]. The sealed tubes prevented the vaporization of water from the system and the consequent masking of the above reactions by large heat evaporation effects. The technique led to some rather interesting results in the dehydration and anation reactions of $[Co(NH_3)_5 \cdot H_2O]X_3$ type complexes. Although the above technique was

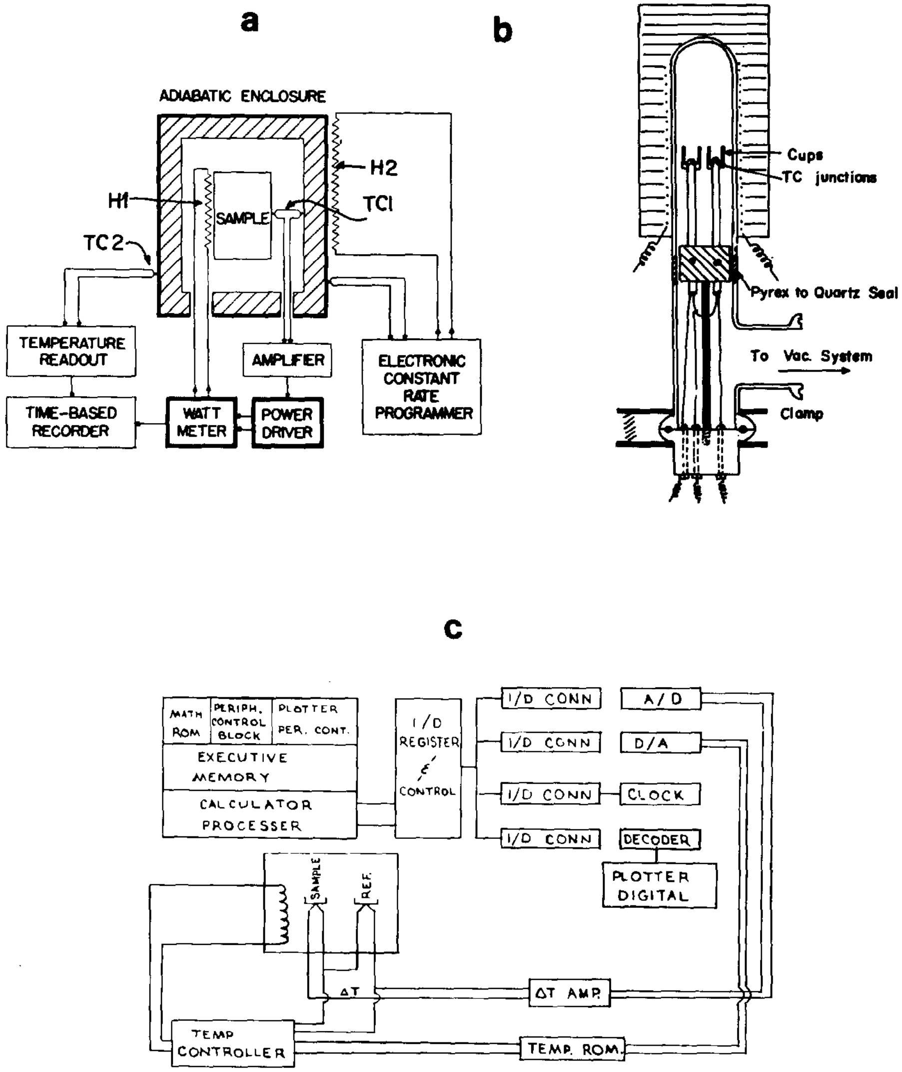

Fig. 4. Some DTA instrument systems. (a) Deltatherm adiabatic calorimeter; (b) controlled atmosphere DTA systems; (c) microcomputer controlled DTA.

used with the Deltatherm III DTA system, a sealed-tube sample holder was also developed for the Perkin-Elmer DSC-1 [14].

Williams and Wendlandt [15] introduced the concept of constant sensitivity DTA in 1972. In this technique, the ΔT parameter of the system is maintained invariant with temperature resulting in a constant-value calibration coefficient. Hence, the DTA calibrations only had to be determined at one temperature. The effect of sample mass on the curve peak : mass ratio was also determined [16].

C. Evolved gas detection (EDG) and evolved gas analysis (EGA)

In the early 1960s, many workers were interested in obtaining EGD data to supplement DTA curves. The EGD curve aided in the interpretation of the DTA curve in cases where volatile products were involved. Thus, decomposition or vaporization reactions could be distinguished from phase

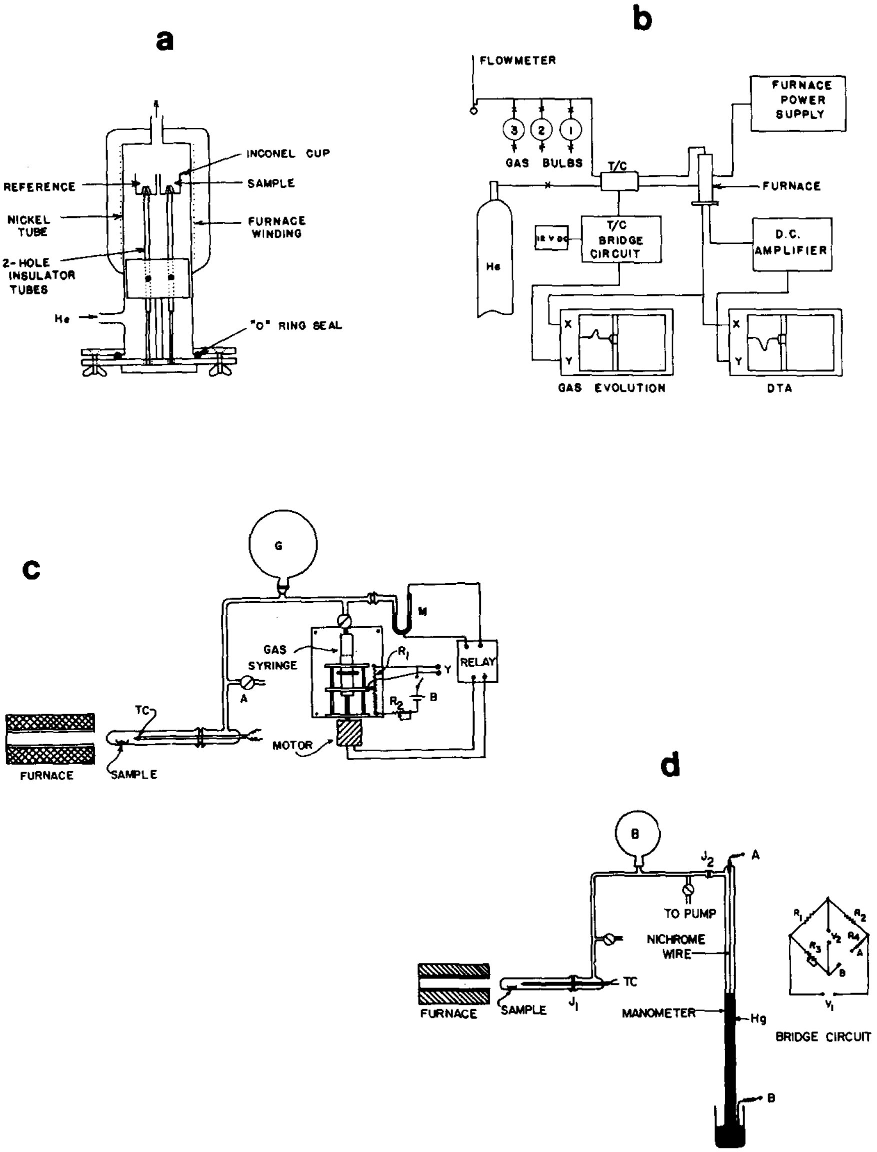

Fig. 5. EGD techniques. (a) Furnace and sample holder for EGD system; (b) schematic diagram of EGD system; (c) $V-T$ system; and (d) $V-P$ system.

changes such as solid → liquid, solid → gas, or liquid → gas. With the above objectives in mind, a DTA–EDG apparatus (then called DTA–GE where GE = gas evolution) was developed, as shown in Fig. 5(a) and (b) [17].

The sample was placed in an Inconel cup in a furnace arrangement similar to the DTA system previously described. The volatile products, flushed from the furnace with helium gas, were passed through a thermistor thermal conductivity detector. A set of three gas collection bulbs permitted collection and storage of the evolved gas, with subsequent analysis by mass spectrome-

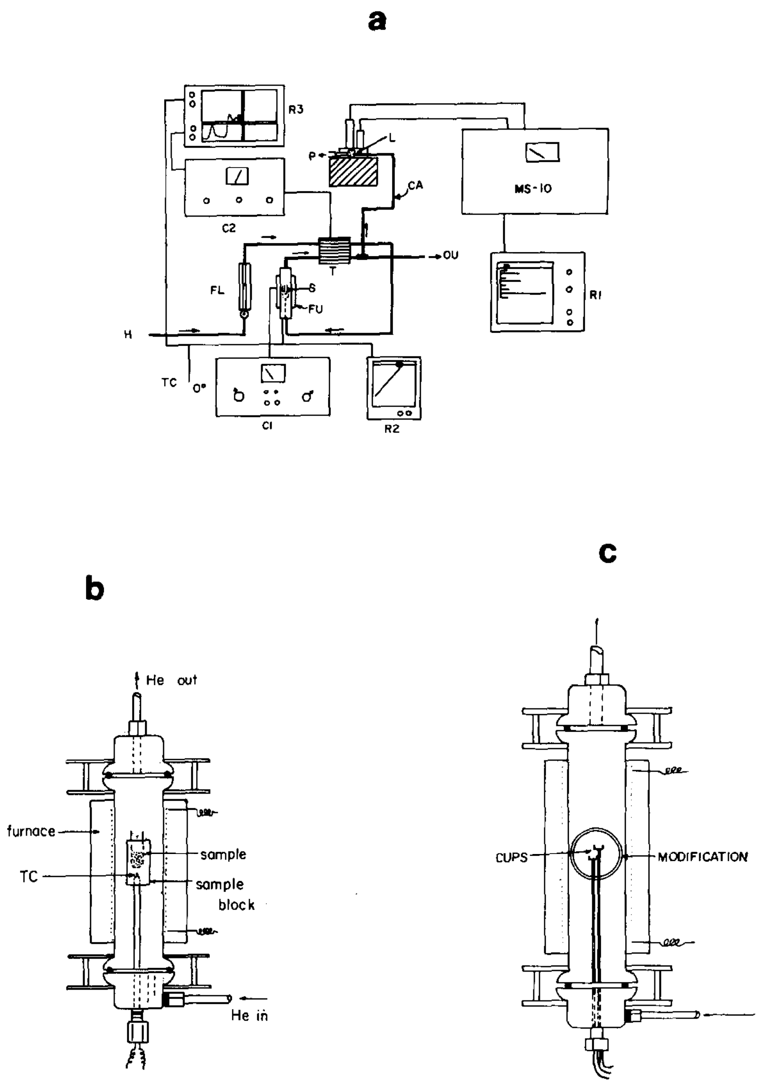

Fig. 6. EGA Systems. (a) EGA–EGD–MS system; (b) furnace and sample holder; (c) EGD–EGA–DTA–MS sample holder.

try, IR, gas chromatography, and so on. The system proved useful in detecting the presence of gaseous products in some decomposition reactions.

Because the gas composition could only be determined by "batch" analysis, it was only natural that a continuous analysis system using mass spectrometry be developed. Such a system, involving EGD–EGA–MS and DTA–EGD–EGA–MS, is shown in Fig. 6(a)–(c). Since the EGD–DTA system could not analyze the evolved gases, a small mass spectrometer, an AEI MS-10, was added to the EGD system [18]. Two different sample holders were developed, one was used only as a pyrolysis chamber, Fig. 6(b); and the other used DTA measurements as well, Fig. 6(c) [19]. One early application of the EGD–MS system was to study the thermal decomposition of $[Cu(NH_3)_4]SO_4 \cdot H_2O$. It was not known if water (MW ~ 18) or ammonia (MW ~ 17) came off first during the thermal decomposition reaction. Since TG could not detect the differences in molecular masses, the MS curve (m/e curve) could. It was observed that water came off first. Numerous other systems were also investigated by this very useful tool.

Two other EGD systems should be mentioned, the P–T and V–T systems, as shown in Fig. 5(c) and (d), respectively. In the P–T system, the evolved gases caused an increase in pressure which was recorded by a recording manometer [20]. The V–T system, on the other hand, was maintained at constant pressure, and the change in volume recorded [21]. Both systems were used to study the thermal decomposition of $KHCO_3$, $CaC_2O_4 \cdot H_2O$, Mg, Ni and Co(II) carbonates, BaO_2, and numerous other compounds.

D. High temperature reflectance measurements

Since we were interested in the structural changes that occurred in transition metal coordination compounds as they were heated, one interesting tool that we developed was high temperature reflection spectroscopy [22–24]. Usually, diffuse reflectance measurements are made at low temperatures; we wanted to use them at temperatures up to 500°C. Since transition metal complexes and their decomposition products usually exhibited a wide variety of colors, diffuse reflectance curves in the visible region were indicative of structural changes as a result of thermal decomposition reactions. As mentioned earlier, this was a problem that needed a new thermal analysis technique. Two new techniques were developed: (a) high temperature reflectance spectroscopy (HTRS) and (b) diffuse reflectance spectroscopy (DRS). In HTRS, the reflectance of a sample was measured versus wavelength at various temperatures; in DRS, the change in relectance of a sample was determined as a function of temperature, at a fixed wavelength. HTRS was used first to determine the wavelength ranges at which reflectance occurred. Then, DRS was used to determine the transition temperature more accurately.

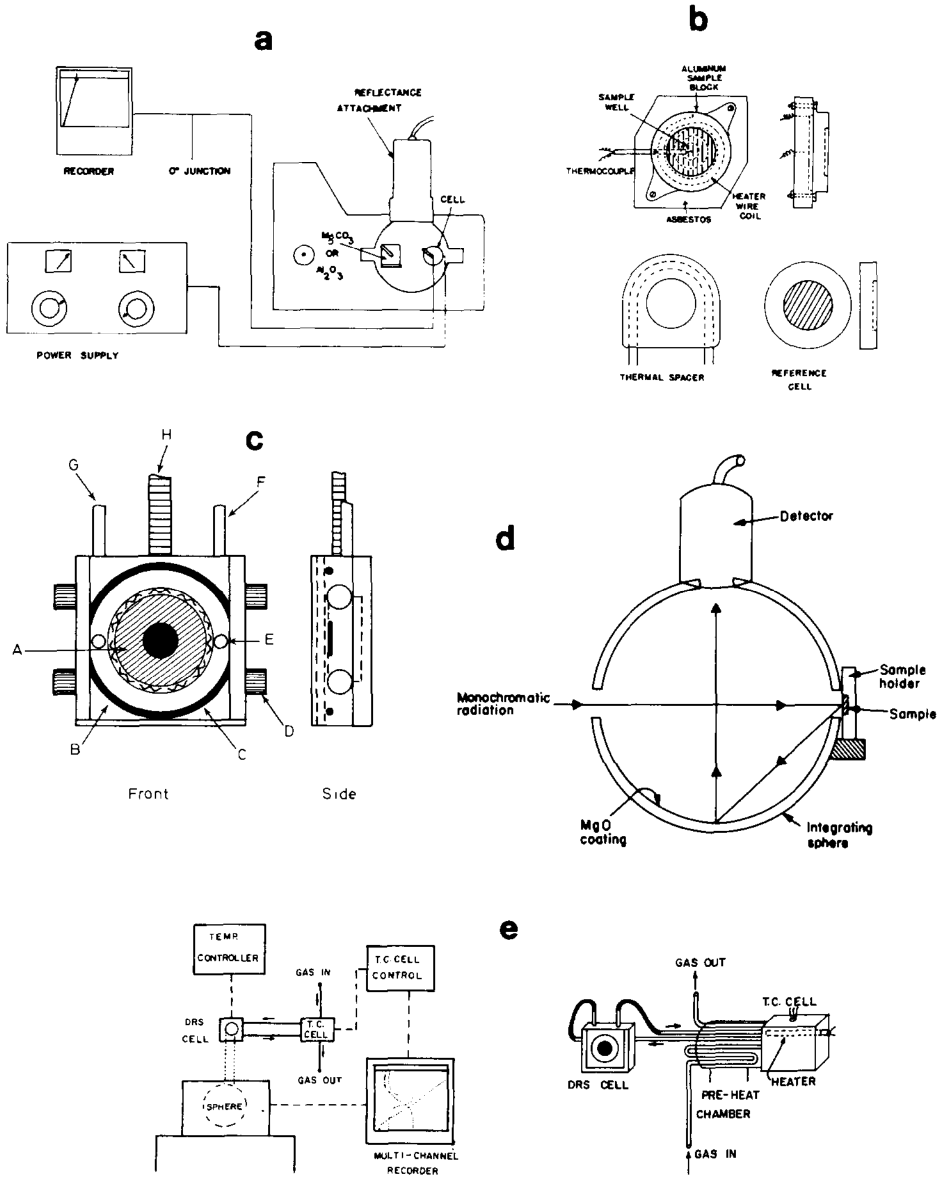

Fig. 7. High temperature reflectance spectroscopy. (a) Schematic of apparatus; (b) high temperature sample holder; (c) high temperature sample holder; (d) integrating sphere; (e) EDG–DRS system.

An overall view of the HTRS system is shown in Fig. 7(a), with a detailed enlargement of the integrating sphere shown in Fig. 7(d). A UV–VIS spectrophotometer equipped with an integrating sphere was required, of course, for reflectance measurements. We added the variable-temperature sample holder, as shown in Fig. 7(b) and (c). Numerous designs for the same holder were constructed, one even had the capability of EGD (Fig. 7(e)) [25,26]. Many transition metal compunds were investigated by this technique, including $CoBr_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $Co(py)_2Cl_2$, $CuSO_4 \cdot 5H_2O$, $[Co(NH_3)_6]Cl_3$, and others.

A microreflectance HTRS and DRS system was developed [24] which permitted the reflectance scanning of the surface of single crystals as they were heated under controlled heating rates. These techniques were called scanning microreflectance spectroscopy (SMS) and dynamic microreflectance spectroscopy (DMS).

Our interest in diffuse reflectance led to the publication of two books and the organization of a national symposium on reflectance spectroscopy [27,28].

E. High pressure systems

In 1970, we became interested in high pressure thermal analysis instrumentation. Consequently, we designed and built high pressure (to ~ 600 atm gas pressure) DTA, electrical conductivity, thermobalance, and magnetic susceptibility systems. The high pressure DTA cell is shown schematically in Fig. 8(a) [29]. It consisted of two 104 mm O.D. cylindrical segments of type 316 stainless steel secured together with six steel bolts, each 13 mm in diameter. The upper portion of the assembly contained the furnace, which had a temperature range of 25 to 500°C, while the DTA sample holders were fixed to the lower cylinder. A gas tight seal was provided by use of an "O" ring. Nitrogen gas from a gas cylinder was used to pressurize the system up to 600 atm.

The high pressure thermobalance is illustrated in Fig. 8(b) [30]. A commercial thermobalance assembly was enclosed within a large stainless-steel cylinder, which contained removable end plates. Access to the balance sample holder was through one of the end plates. The balance was capable of operation from 1 to 500 atm gas pressure in the temperature range from 25 to 500°C.

Two views of the electrical conductivity system (EC) are shown in Fig. 8(c) and (d) [31]. The EC cell, which contained removable sample holders and electrodes, is shown in (d), while the overall system is illustrated schematically in (c). As in the other two systems, the EC cell chamber consisted of a stainless-steel vessel, capable of operation in the pressure range from 1 to 170 atm, and in the temperature range from 25 to 500°C. The EC curves were dependent not only on the ambient pressure but also on the sample holder–electrode configuration.

A unique high pressure TG–magnetic susceptibility system is shown in Fig. 8(e) [32]. The balance mechanism was the same as previously described in the high pressure thermobalance. High temperature–high pressure magnetic susceptibility measurements were made on the thermal decomposition of $K_3[Co(C_2O_4)_3\} \cdot 3H_2O$ in the pressure range from 1 to 68 atm and

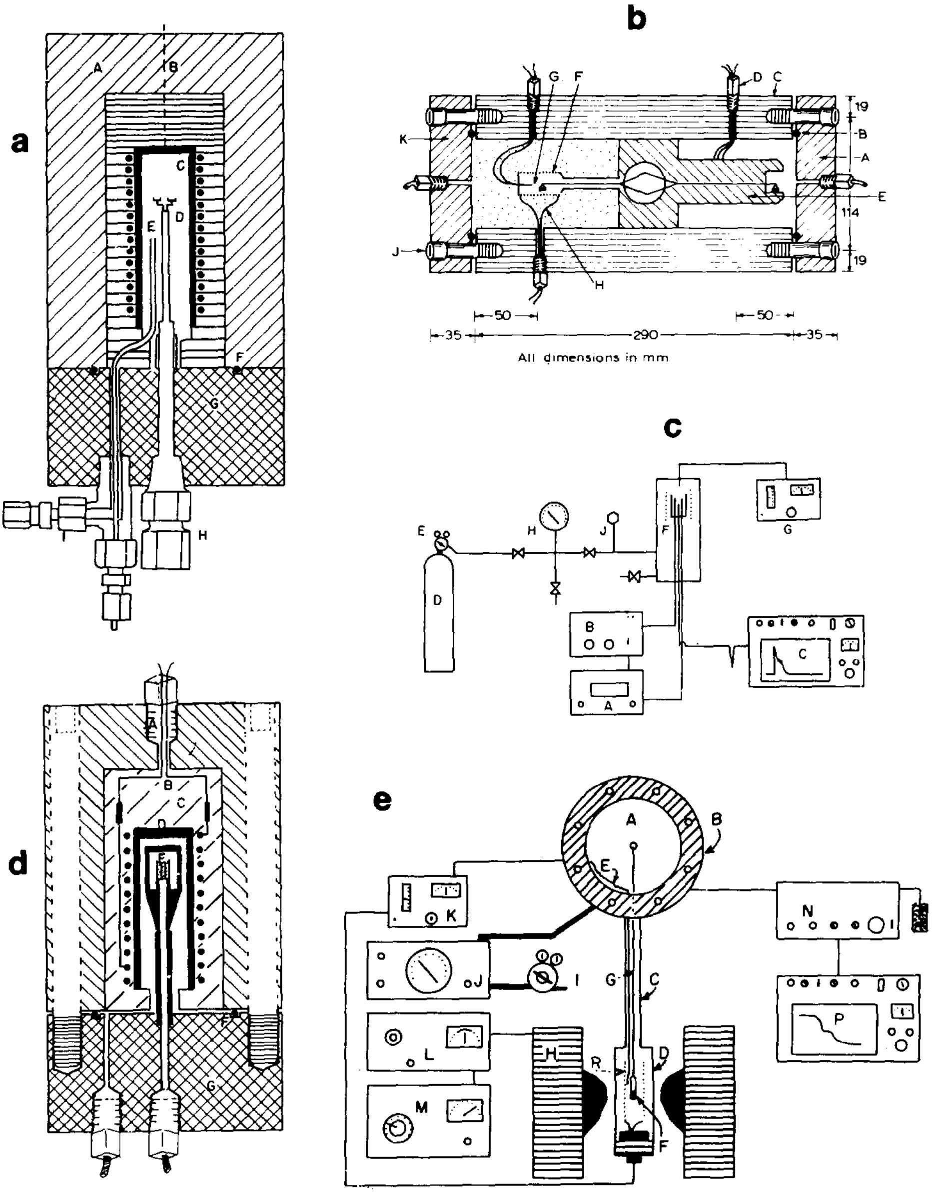

Fig. 8. High pressure thermal analysis systems. (a) DTA cell; (b) thermobalance; (c) EC system; (d) EC cell; (e) TC–magnetic susceptibility system.

temperature range from 25 to 450°C. This system was very useful for the study of many other solid-state thermal oxidation–reduction reactions.

F. Automated thermal analysis systems

Our work on the automation of thermal analysis techniques began in about 1968 with publication of the results in 1970–1974. It has always seemed unusual to us that while other analytical laboratory techniques were being automated, thermal analysis techniques were not. Although this pioneering work was done 12–17 years ago, the first commercial automated DSC system first appeared in 1985, and, to our knowledge, no automated thermobalance is presently commercially available.

Although there are many ways to define "automated", the term is used here to describe the completely automatic sample changing ability of the system, and of course, automatic temperature programming and data handling. The last two features are now easily carried out with microcomputers,

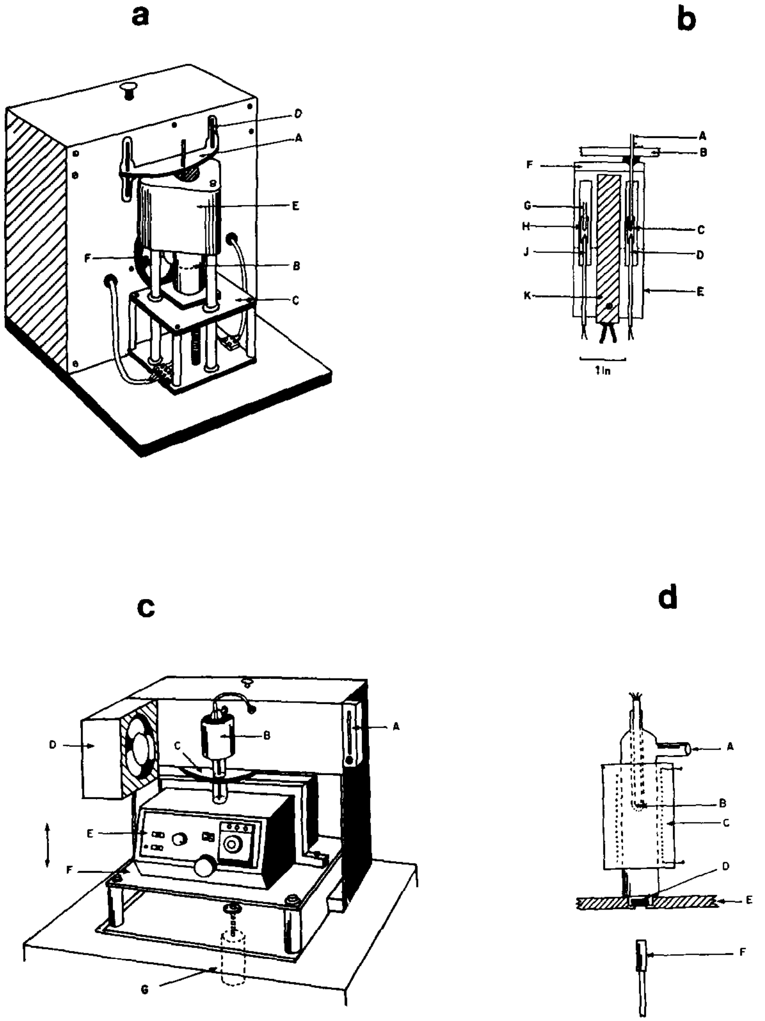

Fig. 9. Automated thermal analysis techniques. (a) DTA sample changer; (b) DTA sample holder and furnace; (c) thermobalance sample changer; (d) TG sample holder and furnace.

but in 1968 this type of computer did not exist. Three thermal analysis techniques were automated: DTA; the thermobalance; and EGD.

The various components of the automated thermobalance and DTA systems are illustrated schematically in Fig. 9. In Fig. 9(a) and (b), the DTA sample changer and furnace are shown [33,34]. Up to eight samples, loaded into 2 mm diameter glass capillary tubes, were placed on the circular sample changer disk, which could be rotated and locked into fixed position over the furnace assembly. The furnace was then elevated to engage the sample tube into a metallic heat transfer sleeve, placed over the sample thermocouple. At the end of the DTA run, or to a predetermined temperature, the furnace assembly was lowered, leaving the spent sample and capillary tube attached to the sample changer disk. After the furnace had cooled, the process was repeated with a new sample. In this manner, the DTA curves of up to eight samples could be determined, each without the attention of a human operator.

In a similar manner, the automated thermobalance was used to determine the TG curves of up to eight samples, also unattended by a human operator. An overall view of the system is shown in Fig. 9(c) and (d) [34,35]. The instrument consisted of a top-loading automatic balance, a furnace and temperature programmer, and a sample changer. Each sample on the sample holder disk is positioned into the furnace automatically, heated to a preselected temperature, and then removed. After the furnace has cooled back to room temperature, the cycle is repeated with a new sample. Up to eight samples can be studied by TG using this system. The maximum furnace temperature limit was 1000°C; a controlled gaseous atmosphere of air, N_2, O_2, or other non-corrosive gas could be employed.

In 1974, the technique of EGD was also automated [36]. This was more difficult to do since it involved an enclosed, gas-tight system. However, an eight-sample sample-chamber was developed, which operated without human intervention, once the cycle was begun.

G. Electrothermal analysis techniques

The thermal analysis technique of thermoelectrometry has been used in this laboratory since about 1968 [37]. In practically all of the instruments employed, the current, *I*, passing through the sample was recorded as a function of sample temperature, *T*. The *I*–*T* curves permitted detection of the quadruple points of a metal salt hydrate system as well as detection of conducting phase formation during the thermal decomposition of transition metal coordination compounds. More recently, the measurement of *V*–*T* curves resulted in the development of a new thermal analysis technique called "thermovoltaic detection" (TVD). In this technique, the EMF of a reacting system in contact with two dissimilar metal electrodes was recorded as a function of sample temperature.

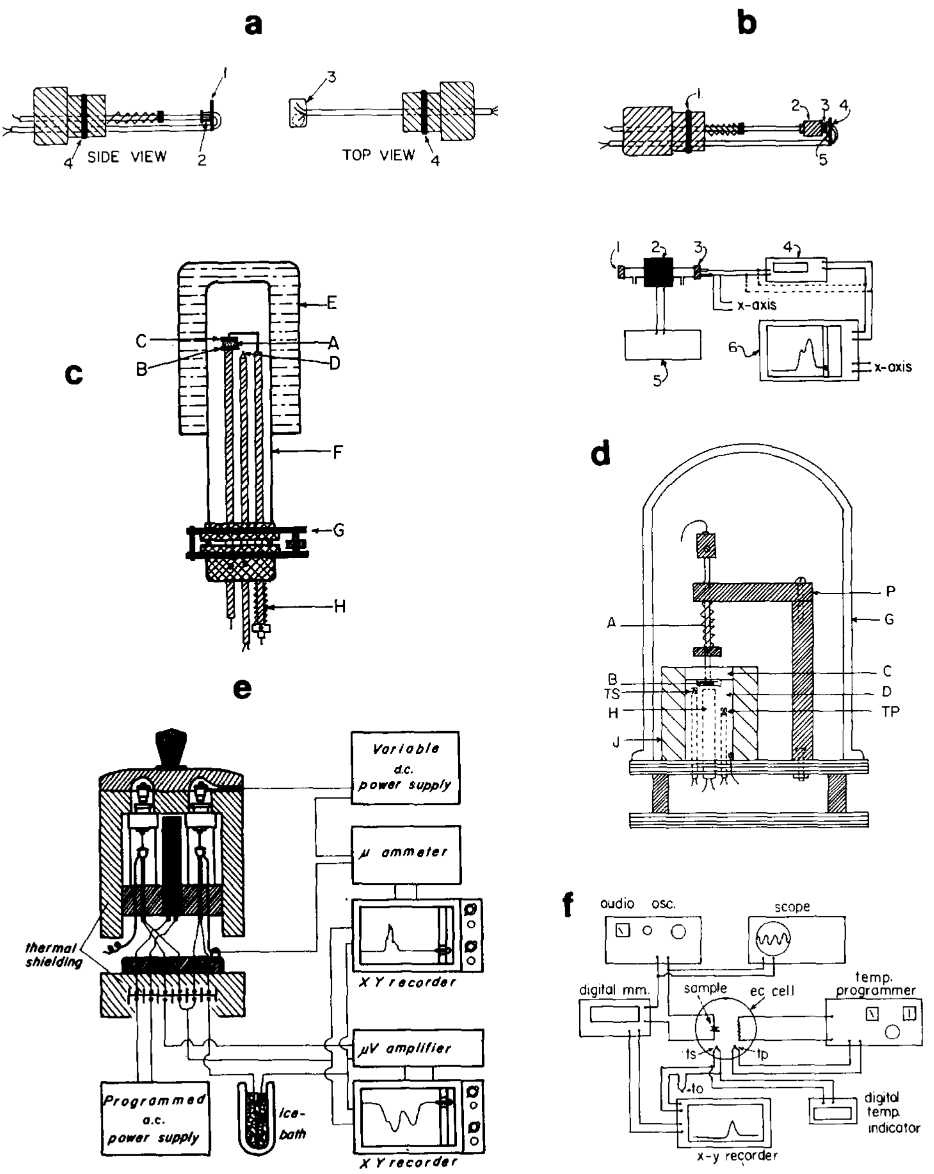

Fig. 10. Electrothermal systems. (a) Concurrent EC–DTA probes; (b) TVD apparatus; (c) high temperature EC apparatus; (d) medium temperature a.c. EC sample holder; (e) simultaneous EC–DTA system; (f) medium temperature a.c. EC system.

Since this area of research in the author's laboratory was recently reviewed [38], the techniques will only be briefly described here. Only a few of the many systems that were built are shown in Fig. 10(a)–(f). In (a), a concurrent EC–DTA system is illustrated [9]. The left figure is the EC probe while that on the right is the DTA part of the system. Both probes were

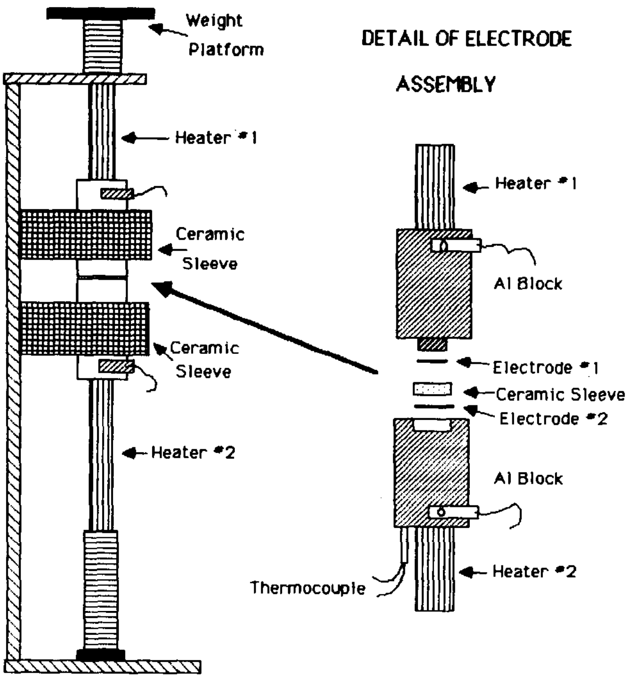

Fig. 11. New TVD sample holder and furnace assemblies [41].

inserted into opposite ends of a tube furnace, thus permitting concurrent EC and DTA measurements.

In (b), the probe for TVD is shown, as well as a schematic view of the system. As in (a), the TVD probe was inserted into one end of a tube furnace. Several other designs of this system have been published [40,41].

Apparatus (c) was used for EC measurements at temperatures up to 1000°C [42]. In (d) and (f) are illustrated a lower temperature version of (c) [43], which was noted for its convenience to use. The sample was in the form of a pressed disk, 1 mm thick by 5 mm in diameter. The most elaborate EC–DTA apparatus of all is shown in (e) [44]. Samples were contained in platinum cups that rested on the differential thermocouples of the DTA system. The cups also served as one of the two EC electrodes, the other being inserted through a hole in the cover.

The latest version of the TVD apparatus is shown in Fig. 11 [41]. It featured disposable electrodes and convenient sample changing as well as adjustable sample loading.

H. Light emission techniques

The technique of light emission (LE), which is also known as oxyluminescence, chemiluminescence, and other terms, detects the light emitted from a sample as the sample is heated to moderate temperatures in various dynamic

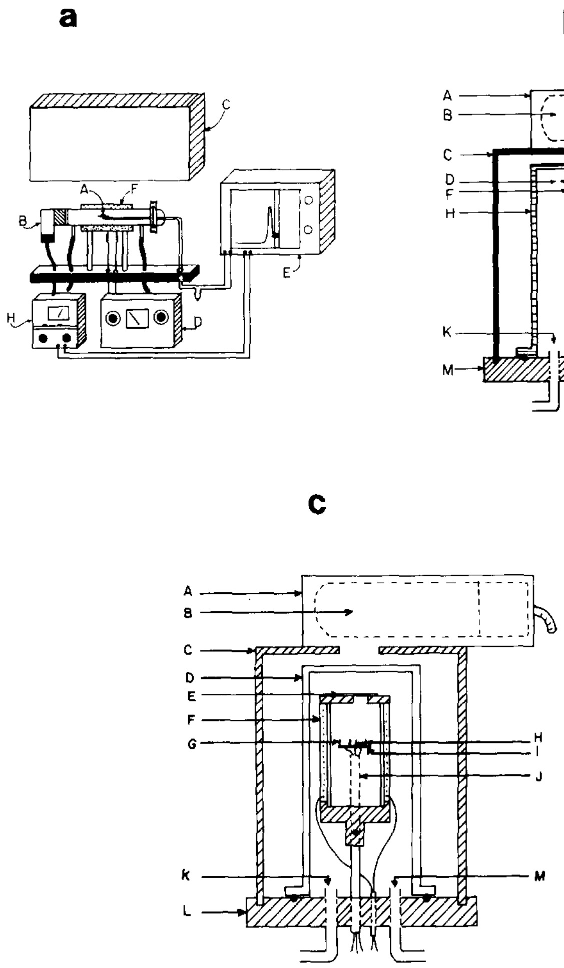

Fig. 12. Light emission systems. (a) Ignition or combustion apparatus; (b) LE apparatus; (c) LE–DTA apparatus.

gas atmospheres. It was first used by us to determine ignition temperatures of organic materials such as paper, wood, etc. [45]. This apparatus, as illustrated in Fig. 12(a), used a photomultiplier tube to detect the onset of ignition (combustion) of the organic material in air or oxygen atmospheres.

For more specific applications, the apparatus was used to measure the light emitted from the surface of a polymer, as it was heated in an air or oxygen atmosphere. Wynne and Wendlandt [46] used this technique (then called oxyluminescence) to study the light emission of a large number of polymers [47]. LE could also be coupled with DSC using a commercial DSC instrument.

Several LE instruments were designed and built, such as those shown in Fig. 10(b) and (c). In (b), only LE is measured [48] while in (c), simultaneous LE–DTA measurements can be made [49].

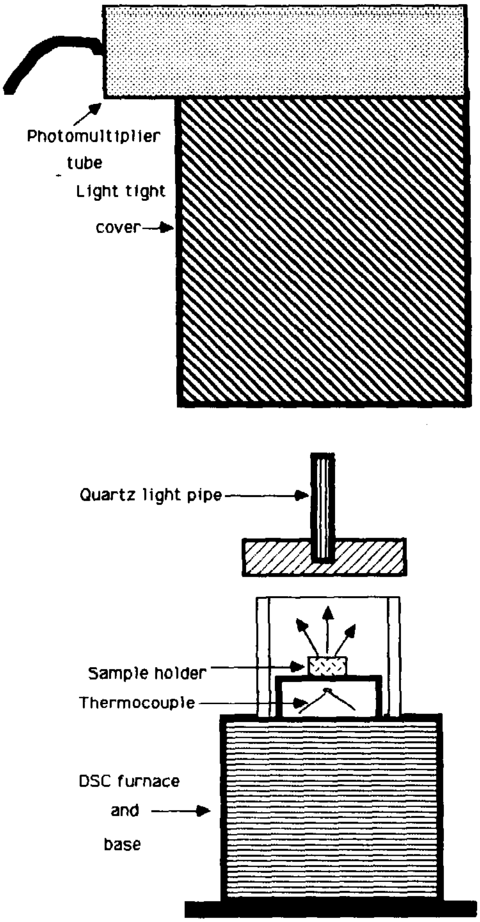

Fig. 13. Latest version of an emission thermophotometry apparatus [50].

The latest version of the technique, now called "emission thermophotometry", is shown in Fig. 13 [50]. The light emitted from polymers, organic compounds, coordination compounds containing vigorous oxidizing and reducing ligands, natural products, and others, can be determined. Needless to say, the light emission from polymers is of a very low intensity and requires sensitive photometric techniques to detect. For ignition determinations and for coordination compounds, less sensitive techniques are required. The emission thermophotometry technique was found to be useful to characterize various polymers since each polymer LE curve appears to be unique.

I. Miscellaneous techniques

In 1965, a technique was needed to study solid → solid transitions of some inorganic compounds such as Ka_5F_6, KCH_3SO_4, $KC_2H_5SO_4$,

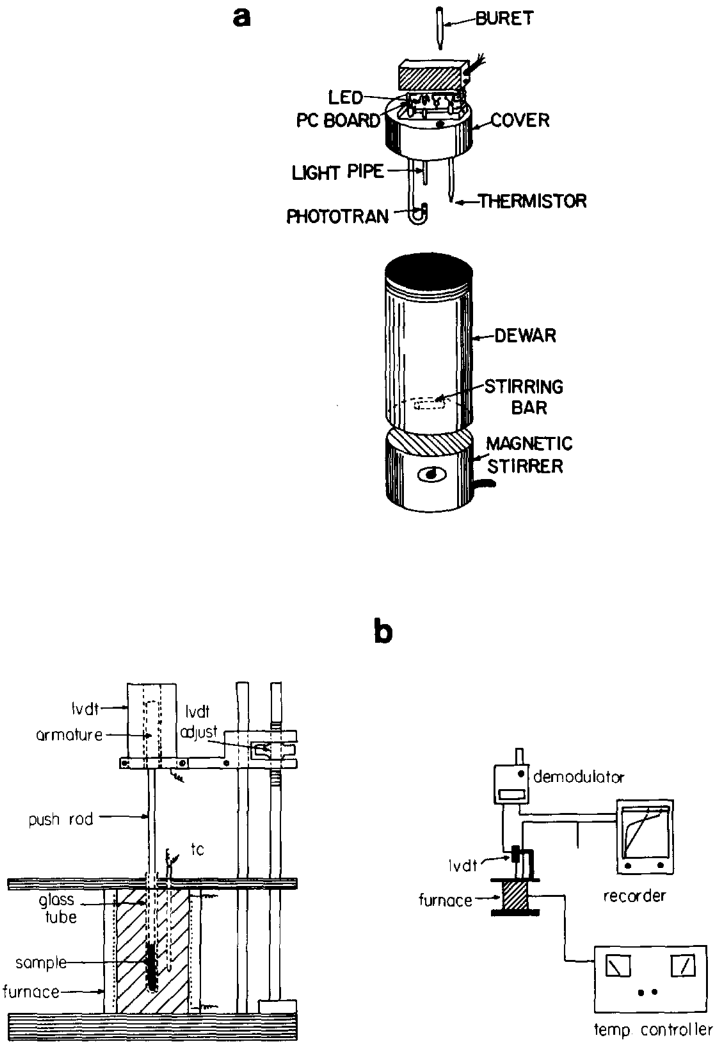

Fig. 14. Miscellaneous techniques. (a) Titration calorimeter–fixed wavelength colorimeter; (b) thermodilatometry apparatus.

$Co(py)_2Cl_2$, and others. One method of investigating this type of reaction is thermodilatometry, or the term that is widely used today, thermomechanical analysis. With this apparatus, the volume changes of the sample, due to the phase transition, were determined.

The dilatometer is shown in Fig. 14(b) [51]. A small furnace was used to heat the sample up to the transition temperature. Volume changes of the sample were detected by an LVDT (linear voltage differential transformer) via a push-rod assembly. Various linear displacement sensitivities could be employed, depending upon the size of the sample.

One of the few solution calorimeters constructed in this laboratory is shown in Fig. 14(a). This titration calorimeter was conventional in design but the apparatus also incorporated a fixed wavelength colorimeter [52]. Thus, calorimetric data as well as spectral information could be determined simultaneously. The apparatus was used to study acid–base (with colored indicator), iodine–formaldehyde clock reactions, and an oscillating iodine clock reaction.

To investigate further the photolytic decomposition of certain types of coordination compounds, an IR disk technique was developed [53]. The sample was pressed, along with KCl, into a thin disk, which was transparent to infrared radiation. After photolysis, the decomposition products were identified by their IR spectra. This technique was found to be a simple, sensitive, and rapid method for studying photolysis reactions.

The development of thermal analysis techniques, as history has shown, is intimately connected with data recording methods. One of the newer recording techniques is that of data center recorders. In this technique, the analog data are converted to digital form and stored on a floppy disk for subsequent data manipulation at a later time. Such a recorder was investigated by us in 1980 [54] and the thermal analysis (TG, DTA, etc.) applications described in detail. The data center recorder is a cross between an on-line microcomputer and an X–Y recorder. It thus has numerous applications to many analytical chemistry problems.

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