

DIFFERENTIAL THERMAL ANALYSIS

By G. CHAPLENKO and A. J. MITTELDORF

ALL forms of spectroscopy—whether emission, absorption, excitation or fluorescence—rest squarely on one common denominator: their data are best presented as a display of energy *vs.* frequency. Neither parameter is a surprising choice. Energy is the keystone of the universe. Because of its close relationship with the periodicity of rotational and vibrational motions of atoms and molecules, frequency is almost as fundamental a yardstick. The bewildering maze of tools and methodology developed for the various forms of spectroscopy attest to the fact that it is currently the dominant tool for unearthing the secrets of physical and chemical phenomena.

On further reflection, however, one questions whether frequency (or mathematical variations thereof) is the only meaningful function against which energy can be referred. There are other continuous parameters which, analogous to frequency, can graphically serve to “dissect” a substance, to allow one to study not the overwhelmingly complex mass as a whole but its structural components, one by one. In this context, temperature fills the bill. Taken through a wide range of temperatures, a substance undergoes physical and chemical changes, reacts with the ambient atmosphere, jettisons water of crystallization and other fragments. All changes are accompanied by the absorption or release of energy in the form of heat. Like spectroscopy, therefore, thermal analysis—the study of these energy changes with temperature—emerges as a powerful tool capable of spotting small differences in substances ostensibly identical or similarities in ones ostensibly different. Like spectroscopy, too, it often acts as a cowbell to the researcher, telling him where in the vast pasture to look for further information.

Though recognized almost a century ago by Le Chatelier, thermal analysis lay essentially dormant until about twenty years ago. True, during that time, many thermal measurements had been carefully conducted and constants such as heat of vaporization, Curie point and phase transformation temperatures were dutifully added to the ever-thickening handbooks. Only in the past few years, however, have the broad industrial implications of thermal analysis become apparent.

Until now the principal types of thermal analysis have been largely chemically oriented. It might be well, however, to mention a few dawning mechanical, electrical, and optical applications. A mechanical example is dilatometric analysis in relation to temperature. As accessories for their measurement are devised, surface tension, hardness, elasticity, tensile and compressive strength may be monitored with respect to temperature changes. A significant electrical effect is the change of magnetic properties with temperature and at least one research group has already undertaken such measurements (1).

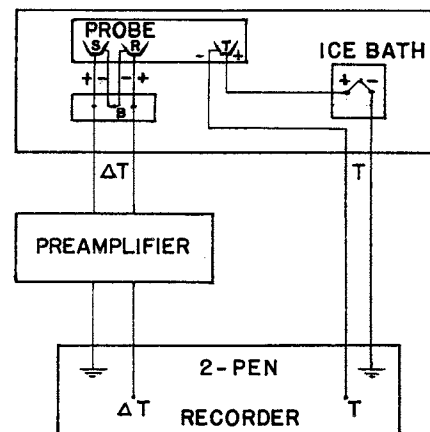
Resistivity, dielectric constant, frequency changes of piezoelectric crystals are other electrical properties whose variation with temperature is of interest particularly today where circuitry must be operable under outer-space conditions.

Of the several optical properties of materials, variations with temperature of refractive index, polarization, and transmittance may some day attain industrial significance and, if so, may spark the development of appropriate measuring devices.

WITH electrical, optical and mechanical applications still on the sidelines, present interest has been focused on the most basic variable in thermal analysis: energy itself. When a substance is heated, its temperature rises proportionately to the heating rate provided that no changes—physical or chemical—occur. Conversely, all such changes give rise to thermal peaks or valleys at the transition temperatures. The plot of differential temperature *vs.* temperature of an inert reference material is called a thermogram; the measuring technique, differential thermal analysis (DTA).

Fig. 1 is a schematic diagram showing how DTA measurements are commonly made. S, R, and T represent thermocouples fabricated as closely alike as possible and kept in a chamber carefully designed to minimize temperature gradients. The output of thermocouple T is connected to a high-sensitivity recorder, frequently through a reference cold junction, to make temperature readings more accurate. (Most modern recorders can be obtained with a room-temperature compensator obviating the need for an ice bath.) S and R are the sample and reference material thermocouples. From the circuitry, it is evident that, if the temperature of both is identical, the EMF generated by the thermocouples will buck each other out so no signal will be generated. A net EMF appears only when the two temperatures differ.

Fig. 1. Block diagram of a typical DTA instrument



One can choose between two ways of presenting the thermo-electric data. The first is to plot differential temperature *vs.* temperature of the chamber using an x-y recorder. The resulting thermogram, while extremely useful as a "fingerprint" of the material and therefore ideal for routine analysis, furnishes no information on the rate of heating, an essential parameter for more basic measurements. For this reason, those engaged in research rather than control prefer a two-pen strip-chart recorder such as that schematically shown in Fig. 1.

Because Nature has been uncooperative and has not provided a single substance to depict the various phenomena amenable to DTA, we have contrived a hypothetical one whose thermoanalytical "personality" is depicted in Fig. 2. Unlike any real material, it exhibits every type of transformation beginning at the left side of the curve where a second-order transition occurs at T_1 . Here a broad endotherm, associated with polymers and glasses (and sometimes called a glass transition), points up a slow change in heat capacity. Given sufficient thermal energy, molecular segments begin to rotate and, in so doing, engender the flexibility and elastomer qualities which have made polymers so essential to our technocracy.

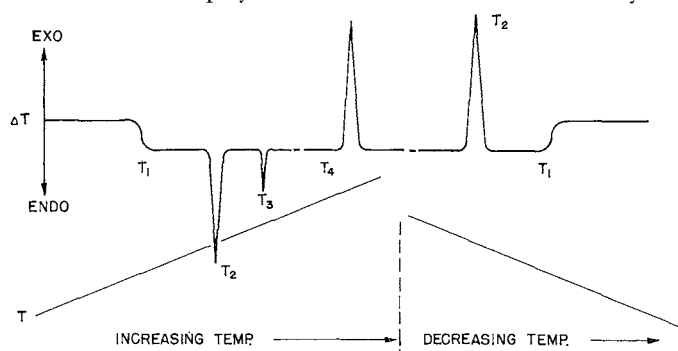


Fig. 2. DTA thermogram of a hypothetical substance contrived to illustrate the discussion.

Raised first to T_2 then to T_3 , the material undergoes two further endothermic changes, sharp dips as contrasted with the broad T_1 valley. Endotherms generally represent physical rather than chemical changes, sharp ones indicative of crystal-line rearrangements, i.e., structural changes. On further heating an exothermic peak is observed at T_4 . An exotherm at moderate temperatures generally represents a chemical reaction. Since T_4 was found not to recur on cooling, the reaction is obviously non-reversible, e.g., a pyrolytic decomposition.

Above T_4 , then, a new substance exists. Upon cooling, its thermogram would be distinct from that of the original material. So, instead of taking it up to T_4 , let us cool the original substance before that temperature and follow the descending curve. As it cools, the substance is seen to have lost T_3 , one of its transition peaks. Judging from the area under the T_2 peak, the transition energy of T_3 has been added to T_2 . This indicates a metastable condition at T_3 , the retained energy being released in one big step at a lower temperature. Of course, where an endothermic reaction occurred on heating, now an energy-compensating exotherm takes place. Further along the cooling curve, the glass transition at T_1 falls properly in place to complete the cycle.

In the example cited in Fig. 2, a metastable phase was apparent from DTA measurements alone. Often, however, a non-reversible change requires further data before it can be interpreted. Suppose water of crystallization is lost on heating, again a non-reversible reaction, but this time accompanied by a loss of weight. A thermobalance continuously weighing the substance as it is heated offers a convenient means of tracking such a change.

When chemical transitions involve the loss of a vapor less familiar than water, the effluent gas may be collected for subsequent analysis (EGA) by, for example, infrared spectroscopy.

FURNISHING "unknowns" to its students, Nature has been as tough as the severest Qualitative Analysis instructor. Mixing minerals in every conceivable blend—aging, heating and pressing them—dotting them with unsuspected elements and compounds—she continues to challenge the mineralogist to the limit of his analytical resourcefulness. Despite having a laboratory full of the latest equipment, he finds basic questions still unanswered, the simplest minerals incompletely understood.

This background in mind, one is not surprised that DTA has found so many loyal, enthusiastic disciples. Here is a tool capable of surveying samples over the range of temperatures to which they have been subjected during their geological evolution. Unlike x-ray diffraction techniques which are largely static and "see" a substance only at a single temperature, DTA is dynamic. It reveals temperatures at which transitions occur. It tells the mineralogist where to set his furnace for other specific studies, often by x-ray diffraction.

One of the leaders in DTA research is Prof. Charles Mazieres at the University of Paris. He gives an excellent example (yet unpublished) of the power of DTA in crystallographic studies. Alone, zirconium oxide is a poor refractory material because above 1100°C it converts from a monoclinic to a structurally weak tetragonal form. The addition of calcium carbonate blocks this transition, stabilizing the zirconium oxide. Although the modified material is widely applicable as a refractory, the blocking mechanism has not been known. Studying ZrO_2 with a DTA unit, Dr. Mazieres tried heating some of the white material in the absence of oxygen and found that it was transformed to a black hitherto-unknown substance which, upon analysis, proved to be a few per cent deficient in oxygen. Like the commercial material, it was stable over 1100° . Dr. Mazieres has theorized that production of oxygen voids—whether by the substitution of CaCO_3 in the matrix or through heating in an oxygen-free atmosphere—is the mechanism responsible for the stability imparted to ZrO_2 .

Another DTA application was reported by Mazieres a few months ago at the first International Conference on Thermal Analysis held at Aberdeen, Scotland. The substance studied by a research team headed by Prof. Guinier was tri-calcium silicate, an essential ingredient in Portland cement. Working with a micro-DTA instrument of his own design, Mazieres had already shown (2) a tiny yet reproducible, reversible endotherm around 990° , a peak which is undetectable with instruments requiring larger samples and in which thermal gradients seriously disrupt resolution. Yet he needed substantiation. Was the peak spurious, a product of some unsuspected malfunction in his apparatus? Only x-ray diffraction photographs could furnish conclusive proof of a phase transformation at this temperature. For months, Mazieres attempted to obtain such a photograph but repeatedly was disappointed with the appearance of diffraction patterns so broad they masked the transition. Persistence is, however, finally paying off. By switching to a special Guinier focusing camera employing a monochromatic copper k-alpha₁ beam and a thin layer of tricalcium silicate laid down on a platinum grid both to support and heat the sample, Dr. Mazieres has discovered a slight modification in the x-ray pattern at 990° just beyond peak D in Fig. 3.

To summarize the mineralogical applications of DTA is not possible in our limited space but a few additional examples will help show the extent of its domain. Much work has been done in identifying constituents in clays, investigators finding

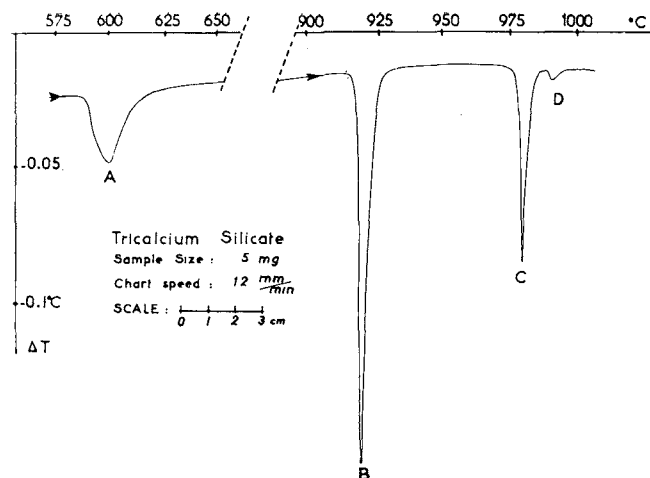


Fig. 3. DTA thermogram of Tricalcium Silicate

that it can even generate reliable quantitative data (3). More theoretical studies (4) have shown that the heat of decomposition of magnesite and of dehydroxylation of Kaolinite can be calculated from DTA data by at least two methods: simple direct calibration and one involving the Clausius-Clapeyron equation. DTA is routinely applied to the determination of decomposition, combination and dehydration temperatures. One intensive study (5) indicated six distinct, successive reactions on heating cerussite, including loss of CO_2 , oxidation, reduction and fusion.

WHILE not yet a full-fledged adjunct to gas chromatography and infrared spectroscopy, DTA is rapidly becoming popular with organic chemists, particularly those engaged in polymer studies. Again an analogy with emission spectroscopy comes to mind. When an alloy emerges from the furnace of a modern plant, its composition is checked largely through optical and x-ray spectroscopy. Differences large enough to influence the performance of the heat are easily measured. To these and most other analytical instruments, however, polymers appear singularly anonymous. Their inner structure, not the composite arrays of the building blocks, is what is seen. But it is the array—the polymer, not the monomer—that imparts significant properties to the final product. DTA can accurately measure melting point and glass-transition temperatures both of which are related to the degree of polymerization. It can measure pyrolysis temperature, composition of co-polymers, and oxidation stability by heating in a controlled atmosphere (6). It can reveal and show the degree of contamination.

Further, DTA can be relied on to measure phase transition temperatures and results in good agreement with x-ray diffraction have been obtained (7). Thermal history, molecular block formation, crystal perfection and orientation are still other areas amenable to DTA study (8). Finding that infrared spectroscopy did not give him sufficiently reproducible data and that x-ray patterns were ambiguously diffuse, one investigator (9) turned to DTA and found that isomerization and etherification polymerization could be assigned without reservation.

Listing the various areas of analysis is one thing; their significance is quite another. The important thing is that DTA measurements can be and are most often performed against a known reference standard. In quality control applications, a sample from a new batch is placed in one cup of the apparatus and run against a reference standard. In this instrumental

mode, two identical materials will generate no thermic peaks or valleys. The appearance of a voltage signals the operator that something has probably gone wrong in production.

Although principally composed of synthetic polymers, textiles, because of their importance, may be considered a class in themselves. The past decade has witnessed a fabric revolution with the advent of fibers that are, at once, resistant to wrinkling and retain creases; that stretch in one or two directions; that drip-dry in minutes; breathe yet are repellent to rain; resist stains yet take dyes; withstand sunlight without bleaching or deteriorating. No single accomplishment, the new miracle textiles actually contain blends of carefully chosen natural fibers as well as artificial polymers treated both chemically and physically to achieve desired properties. The examination of textiles, especially competitive ones, is an art in itself and DTA is proving highly successful in unravelling their secrets (10).

BECAUSE of the importance of phase transitions, their relationship to alloying constituents and heat treatment, metallurgy is another natural area for DTA. Some transitions are clear-cut first-order changes such as melting point and crystalline structure morphisms which give rise to abrupt peaks. These can be detected readily with almost any DTA apparatus. Others, however, are far more subtle although just as important from the standpoint of properties of the material. Theoretically, the degree of cold working or heat treatment—types of order-disorder transformation—can be determined by measuring the area under the endotherm at annealing temperature (11). Similarly, the Curie point at which temperature a metal or alloy loses its magnetism is measurable by DTA as is the newly-discovered Wigner effect in which neutron irradiation produces disorientation in the graphite lattice. In practice, however, only the most sensitive instruments are capable of detecting, let alone determining the degree of, such changes.

HAVING captured many imaginations and gained a foothold in research laboratories, DTA has predictably prompted the appearance of several commercial instruments. In general they can be divided into two categories: those requiring a fairly large sample and those utilizing a micro sample (under 1 mg). Both have proved satisfactory for many applications where large, sudden heats of transformation are involved. For the measurement of less energetic changes, however, the micro units are necessary. A DTA instrument essentially measures power as distinct from energy. Unlike a calorimeter which registers the *total* heat change in a sample, DTA apparatus plots the instantaneous intensity of the change. It indicates precisely how many watts are being used at any one time, not watt-hour consumption.

This conceptual difference is essential to the understanding of the DTA measuring technique and an appreciation of the problems entailed, as an example will readily clarify. Converted to electricity, the temperature changes are of such small magnitude (often 1 microvolt or less) that true signals are often buried in electronic drift. A second-order glass transition languishing along for 50° or so displaces the curve but slightly. Without duplicating the run, one could not be sure that such displacement is not spurious. Although the actual energy—the area under the curve—may be identical, the sharper the peak, the more easily can it be identified, the more closely can the transition temperature be assigned, the better it can be distinguished from other nearby peaks.

The simplest way to sharpen peaks is by increasing the heating rate; the best way, however, is to increase the effi-

ciency of the heat transfer by decreasing the sample to TC mass ratio. Thermal gradients increase with the sample quantity. Even with, say, a highly crystalline sample, its melting point is reached first at that portion of the sample thermally closest to the source of heat. (It is, of course, for this very reason that accurate melting point determinations are made microscopically with single crystals). The larger the sample, the longer the time interval over which its various portions undergo a transition and the higher the energy losses. The result is a broadening of peaks and smearing of the inflection in the curve. Table I summarizes the advantages of Micro DTA.

TABLE I

Comparison between features of Micro and Macro-DTA

Criterion	Micro-DTA	Macro-DTA
Heat transfer efficiency (sample to TC)	60-80%	1-5%
Temp. gradients across sample	Negligible	Substantial
Sample mass/TC mass	very small (0.01)	large
Heat transfer speed	very fast	slow
Resolution at a given heating rate	1	>2
Time required per determination	1	>2
Effect of heating rate on peak integrals	small	large
Effects of packing granularity	small	large

THE BDL M-1 MICRO-DTA INSTRUMENT

Considerations discussed in preceding sections were the basis for a novel DTA instrument designed by Prof. Mazieres (2). The design was converted to a commercial instrument by the Bureau de Liaison in France, where it is marketed as the M-1 Micro-DTA. It is available in the United States from Spex Industries, Inc., who provide a complete DTA system consisting of the M-1 unit, and an American-made sensitive detection and read-out unit; a TGA accessory is also available.

The BDL M-1 is unique in two respects. First, it employs an extremely minute sample: under 5 milligrams for operation with the standard (or semi-micro) probe, and only a few micrograms when the micro-probe is utilized (Fig. 5 shows the relative size of the two probes). Secondly, the sample is contained within the thermocouple proper, which is fashioned in a cup shape. This provides an intimate, continuous contact between sample and thermocouple, assuring rapid and complete heat transfer. Both features reduce thermal gradients across the sample-thermocouple system to such an extent that the sensitivity and resolution of the M-1 instrument are unsurpassed. Differential temperatures as small as 0.003°C can be detected; phenomena separated by as little as 1°C can be charted as discrete peaks. In both respects the M-1 Micro-DTA has a definite advantage over instruments based on more conventional design, where considerably larger samples are needed and the appending thermocouple touches the sample at only one point.

In order to optimize the resolution and to bring the sample rapidly into a temperature region where transitions of interest are known to exist, DTA apparatus must be equipped with means for providing a wide range of heating rates. Conventionally, these rates are controlled by relatively elaborate and expensive closed-loop servo systems. The Micro-DTA concept, however, again simplifies the situation; with micro-samples, precisely linear heating rates are rarely if ever necessary, because heat transfer efficiency from sample to TC is very high and is little affected by slight variations of heating rate. Therefore the M-1 instrument (shown in Fig. 6) was designed with a very inexpensive but flexible temperature programmer based on current-time relationship. The system employs a dc motor, the speed of which is adjustable through an autotransformer. The motor in turn drives a pair of ganged potentiometers determining the firing phase angle of an SCR and thus the heating current. With this arrangement, temperature changes may be controlled almost linearly at rates up to 25°C/min for heating and down to the natural cooling rate of the furnace for cooling. The electronic controls may be switched out at will to allow manual overriding at any time.

Other features of the M-1 instrument include a lightweight low thermal lag furnace, an easily accessible sample compartment (probe) and water cooling. The furnace is wound with Kanthal ribbon and, at the maximum current of 4.6 amp at 115 vac, will heat the sample compartment to 1200°C. Fully counterbalanced, the furnace rides on a tubular post grooved to constrain the movement of the furnace vertically; only when in its topmost position can the furnace be swung out of the way, allowing access to a ceramic sheath mechanically protecting and thermally insulating the delicate sample-holding probe. When in position, the sheath is hermetically tight, permitting the sample compartment to be evacuated to 10⁻³ torr or to be continuously flushed with an inert gas, either to preclude the effects of air, or for vapor collection in EGA. The sheath is secured by two thumb-screws and is thus easily removable for loading or unloading.

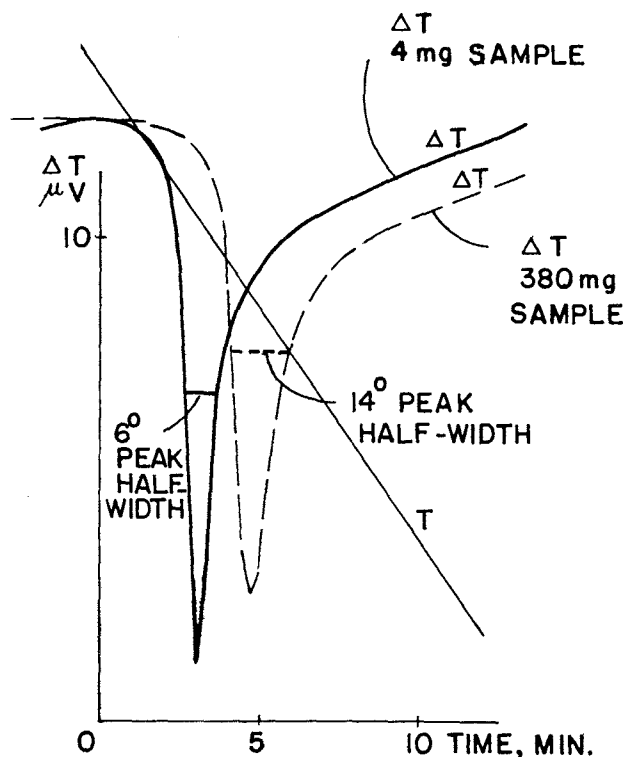


Fig. 4. Effect of sample size on resolution. A 4 mg sample of quartz in the M-1 apparatus yields a peak deflection of 10 μV at 573° with a half-width of 6° at a heating rate of 9.5°/min. Under the same conditions, a macro-DTA yields a half-width twice as great. Obviously, closely-separated transitions may remain undetected in any but micro-DTA instruments.

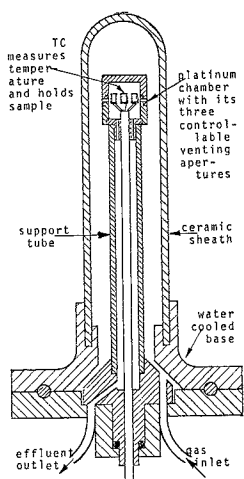


Fig. 5. On the left, a schematic of the S-1 Semi-Micro-probe; on the right, a comparison of the Micro (top) and Semi-Micro Probes.

The sample compartment proper consists of a cylindrical platinum chamber with a deep cover and is located atop a slender ceramic post. The base of the post is water cooled to prevent the furnace heat from spreading to other parts of the instrument. The platinum chamber contains three cup-shaped thermocouples supported on their lead wires and fitted with removable platinum liner-crucibles. One thermocouple senses the temperature of the sample compartment and is referenced against a cold junction kept optionally in an ice bath. The other two hold the sample and reference material. The delicate operation of loading the samples into minute crucibles is simplified with a special loading fixture. Held with tweezers, the crucible is transferred to the device and placed into an opening just large enough to hold it; the turn of a lever causes the crucible to drop down until its lip is flush with the loading surface. Powders, wires, lumps etc., can then be easily introduced into the crucible without danger of deforming it. A reverse rotation of the lever then brings the crucible up so that it can again be picked up with tweezers and placed into its appropriate thermocouple.

All thermocouples are made of Platinel, a material whose EMF output closely matches that of Chromel-Alumel and is so high that differential temperatures as small as 0.003°C can be measured. Widely used to measure the temperature of vital operating parts of jet engines, Platinel will stand up almost indefinitely in normal DTA use below 1250°C .

Two accessories are available for the M-1 Micro-DTA. One, the Micro-Probe, was already mentioned; its construction is essentially the same as that of the larger standard Semi-micro Probe, except that samples are loaded directly into the thermocouple cups instead of into removable liners. The Micro-Probe thus further improves heat transfer characteristics of the sample-thermocouple system and reduces thermal gradients within the sample. The second item is the Low Temperature Accessory, directly interchangeable with the standard probe protecting sheath and designed to cover the temperature range from -120 to 400°C . It has a glass-and-copper body with a built-in resistance heater connecting to a separate low-voltage outlet on the side panel of the instrument. A glass Dewar, fitting tightly over the heater, is filled with liquid nitrogen; when the sample reaches thermal equilibrium the heater is switched on, first to boil out the nitrogen and then to heat the sample at a desired rate.

In addition to the above, a TGA accessory is available as an option. It utilizes the Cahn RG Electrobalance, enclosed in an evacuable glass vessel, and a standard BDL furnace, controlled by the M-1 programmer. Both the balance and the furnace are mounted on a single supporting column, attached to a base large enough to accommodate the M-1 unit. The temperature of the sample is sensed by a Platinel thermocouple and the weight of sample appears as an electric signal at the output terminals of the balance control unit. These outputs are connected, respectively, to the temperature and the differential temperature channels of the Detection and Read-out Module.

The high-performance capabilities of the M-1 Micro-DTA can only be completely realized when the unit is coupled to a detection and read-out instrument of comparable caliber. This is available as a companion unit—the Spex Detection and Read-out Module—consisting of an amplifier and a two-channel strip chart recorder, both mounted in a single compact cabinet. The amplifier is the Keithley 150 AR microvolt-ammeter, an exceptionally stable instrument with thirteen voltage amplification ranges and up to 100 times full-scale zero suppression. The recorder is the Texas Instruments' two-channel Servo/riter II, modified to provide for front-panel switching of DTA and TGA and to operate as an indicating instrument only.

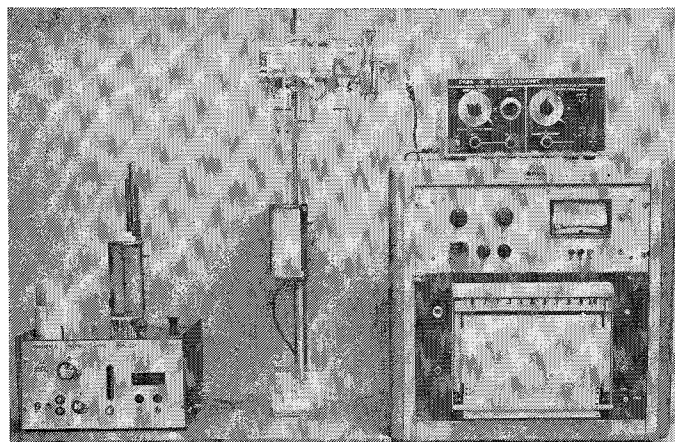


Fig. 6. The complete BDL-SPEX thermoanalysis system; M-1 Micro-DTA unit (left), Cahn RG Electrobalance with furnace (center and top right) and the Detection and Read-out Module.

References

1. Aharoni, A., Frei, E. H., Scheidlinger, Z., Scheiber, M. *J. App. Phys.*, **32**, 1851, 1961.
2. Mazieres, C., *Anal. Chem.*, **36**, 602, 1964.
3. Mackenzie, R. C., Robertson, R. N. S., *Acta Univ. N. Car. Geol. Supp.*, **1**, 335, 1961.
4. Ellis, B. G., Mortland, M. M., *Amer. Mineral.*, **47**, 371, 1962.
5. Warne, S. S., Baryliss, P., *Amer. Mineral.*, **47**, 1101, 1962.
6. Rudin, A., Schreiber, H. P., Waldman, M. H., *Ind. & Eng. Chem.*, **53**, 137, 1961.
7. Geacintov, C., Schotland, R. S., Miles, R. B., *J. Poly. Sci., C-6*, **197**, 1964.
8. Schulken, R. M., Boy, R. E., Cox, R. H., *J. Poly. Sci., C-6*, **17**, 1964.
9. Anderson, H. C., *Anal. Chem.*, **32**, 1592, 1960.
10. Schwenker, R. F., Zucarello, R. K., *J. Poly. Sci., C-6*, **1**, 1964.
11. White, J. I., Koyama, K., *R. S. I.*, **34**, 1104, 1963.

SPECIFICATIONS

Prices

I. BDL M-1 MICRO-DTA (incl. S-1 Probe)each \$2,160.00

- | | |
|-----------------------------|--|
| 1. Temperature range | |
| a. Standard furnace | ambient to 1200°C |
| b. Low temp. accessory | -120 to 400°C |
| 2. Sensitivity | 0.003°C |
| 3. Resolution | |
| a. Semi-micro probe | 1.0°C |
| b. Micro-probe | 0.1°C |
| 4. Sample volume (maximum) | |
| a. Semi-micro probe | 6 microliters |
| | S-1.....each \$ 688.00 |
| b. Micro-probe | 0.1 microliter |
| | SM-1.....each \$ 688.00 |
| 5. Programming | electro-mechanical, with manual override |
| 6. Heating rates | 0 to 25°C per minute |
| 7. Meters | Ammeter for heating current, flowmeter for flushing gas |
| 8. Sample containers | platinum crucibles |
| 9. Safety features | water-flow switch in series with main switch; fuse; temperature-actuated limit switch at the recorder. |
| 10. Power requirements | 500 watts max. at 115 vac |
| 11. Cooling | water cooled; about 4 gph at 7 to 10 psi required; pressure reducer supplied. |
| 12. Dimensions (basic unit) | 14"x12"x28" |
| 13. Weight (basic unit) | 40 lb |

II. DRM-1 DETECTION & READOUT MODULE complete \$2,765.00

A. DRM AMPLIFIER (Keithley 150AR microvolt-ammeter)

- | | |
|-----------------------------|---|
| 1. Range | 1.0 microvolt to 1.0 volt full-scale in thirteen overlapping ranges |
| 2. Accuracy | ± 2.0% of full scale, exclusive of noise and drift |
| 3. Zero drift | less than 0.1 microvolt per 24 hrs, after one-hour warm up period |
| 4. Zero suppression | up to 100 times full scale |
| 5. Input noise (shorted) | less than 6 nanovolts rms |
| 6. Input resistance | 1.0 to 90 megohms |
| 7. Line frequency rejection | better than 50:1 |
| 8. Speed of response | less than one second to 90% of full scale |
| 9. Output voltage | 10 volts full scale, all ranges |

B. DRM RECORDER (Texas Instruments' Servo/riter II)

- | | |
|---------|--------------------------|
| 1. Type | strip chart, two-channel |
|---------|--------------------------|

- | | |
|---------------------------|---|
| 2. Span | |
| a. Temperature channel | 50 millivolts |
| b. Differ. temp. channel | one millivolt |
| 3. Zero position | |
| a. Temp. channel | left edge, 3% screwdriver adjust |
| b. Diff. temp. channel | fully adjustable, edge to edge |
| 4. Chart speed control | change gears |
| 5. Accuracy | 0.25% full scale or 5 microvolts, whichever is greater |
| 6. Linearity | 0.1% full scale |
| 7. Dead band | 0.1% full scale |
| 8. Input circuit | floating and guarded transf. type |
| 9. Interference rejection | AC transverse, 60 db at line freq.; AC longitudinal, 100 db at line freq.; DC common mode, 100 db |
| 10. Reference supply | Zener regulated, with long-term stability of 0.1% |
| 11. Pen response | |
| a. Temp. channel | 1.0 second |
| b. Diff. temp. channel | 0.4 second |

III. TGA-1 Thermogravimetric Unit, (includes Cahn RG Electrobalance)complete \$3,280.00

- | | |
|-----------------------|----------------------------|
| 1. Capacity | 2.5 grams |
| 2. Sensitivity | 0.1 microgram |
| 3. Recording ranges | 20 micrograms to 1.0 gram, |
| 4. Suppression ranges | 1.0 milligram to 1.0 gram, |
| 5. Power requirements | 30 watts at 100 - 130 vac |
| 6. Weight | 38 lb |

Winners of the Spex Sponsored S A S Journal Award, 1964

Our congratulations are extended to Dr. R. W. Johnson, Michigan Technological University and Dr. W. C. Schrenk, Kansas State University. Their joint article, "Mechanism of Interactions of Alkali and Alkaline Earths in Flame Photometry," was cited by the SAS Publication Award Committee as the most outstanding scientific research work published in APPLIED SPECTROSCOPY during 1964.



W. C. Schrenk



R. W. Johnson

ISN'T IMITATION THE SINCEREST FORM OF FLATTERY?

Newcomers may find it hard to believe but ten years ago most emission spectrographers went through ten minutes of non-automated day-dreaming while preparing a powder sample for arc analysis. The trusty Mullite mortar and pestle set was first acid cleaned, then, for critical work, "dry washed" with some of the material to be analyzed. This discarded, a new portion was ground together with graphite powder and often a buffer containing an internal standard.

Introduction of an assortment of vials and balls to be shaken in mechanical impact mixers clipped away 90% of this preparation time. Spex Industries pioneered in this area by adapting the Wig-L-Bug—a dental amalgamator manufactured in Chicago—for the purpose. Our first step was to supply and properly adapt various plastic, steel and agate vials. Later we began manufacture of two Mixer/Mills for handling more numerous or larger samples, particularly those needed in x-ray spectroscopy. By 1962 these were widely accepted and we responded to the many logical complaints that the commercially available, flat-bottomed, plastic vials frequently shattered from the pounding of the ball. The current vials of our own manufacture, bolstered with thickened bottoms and rounded on the inside, resist breakage and eliminate corners in which powders might lodge.

As each item was introduced it was assigned a catalog number which has been retained to date, despite continual design changes, in order to avoid confusion among our customers and staff. Across our desk the other day came a leaflet from one prominent manufacturer of spectrographs who, for reasons best known to himself, chose to identify his newly adopted corresponding items by our numbers. While we have asked that this practice be stopped, the burden will, at least temporarily rest on you, the customer, to remember that a 3111, 3116 or 6133

vial can mean two different things. Purchased from us, or our appointed representatives, the vials will be of the improved, heavy, round-bottom type. From other suppliers you may discover a disheartening reversion to the old-style, thin, flat-bottomed variety of plastic vial.

Time has proved the little amalgamator had its endurance exceeded by the 3115 adapter which held two 3116 plastic or 3118 agate vials. The Wig-L-Bug rebelled, prematurely collapsing under the strain of such usage. We therefore unceremoniously retired the 3115 adapter, no longer recommend the Wig-L-Bug for shaking heavier loads than those for which it was originally designed. To fill the gap we manufacture the 5000 Mixer/Mill. Sturdier and larger (yes, twice the price, too) the 5000 is constructed to handle two vials simultaneously. Its continuously adjustable jaws accommodate any size vials up to 3/4" dia. x 2" long (6133).

The larger (8000) Mixer/Mill has undergone evolution too. Steadfastly clinging to the old catalog number, we extensively redesigned the 8000 four years ago. Vibration, severe enough to affect analytical balances in the next room, was tranquilized to the point where the current model can now amicably share a table with most other laboratory equipment. The leak-prone oil crankcase was discarded in favor of a pair of hefty, lifetime sealed ball bearings. The holding jaws of the 8000 were strengthened, the case coated with chemically resistant vinyl, the motor beefed up to take the pounding that does the grinding work. Result: a mixer so popular that we no longer are amazed when almost weekly an order arrives from such out-of-the-way places as Greece, Saudi Arabia, Spain, Turkey or Zambia in addition to the steady flow of orders from this country's busiest government, industrial and university laboratories.

NEW STAINLESS STEEL STANDARDS

Long sought, a set of austenitic stainless steel standards has been prepared by the British Bureau of Analysed Samples, Ltd. and is stocked by us in two forms, discs and chips. The principal alloying elements, nickel and chromium, are varied over a range encompassing the 300-series of stainlesses. Nickel is covered from 6.3 to 20.6%, chromium from 12.8 to 25.6%. The widely used AISI Types 316, 321 and 347 are represented by standards containing certified amounts of molybdenum, titanium and niobium, respectively. Individual certificates ac-

companying the standards give the values obtained by each of the 16 cooperating analysts, a summary of their methods and approximate values for copper and vanadium which are not standardized.

BCS 331-338	Austenitic Stainless Steel Standards,	
	Chips	set of 8, 100g each \$136.00
BSS 61-68	Austenitic Stainless Steel Standards,	
	Discs 1-3/4" dia. x 1/2" thick	set of 8 \$145.00

B.C.S. No.	S.S. No.	Description	C %	Si %	S %	P %	Mn %	Ni %	Cr %	Mo %	Ti %	Nb %	Ta %	Co %
331	61		0.062	0.42	0.016	0.016	0.77	6.27	15.2	—	—	—	—	0.040
332	62		0.063	0.43	0.020	0.015	0.80	12.5-	12.8	—	—	—	—	0.037
333	63	Austenitic	0.066	0.45	0.020	0.016	0.79	9.49	18.7	—	—	—	—	0.038
334	64	Stainless	0.079	0.45	0.021	0.012	0.86	20.6-	25.6	—	—	—	—	0.050
335	65	Steels	0.093	0.67	0.023	0.018	0.94	9.47	18.5	—	0.46	—	—	0.034
336	66		0.083	0.51	0.023	0.020	0.80	9.49	17.6	2.42	—	—	—	0.061
337	67		0.081	0.50	0.018	0.016	0.86	9.52	17.8	—	—	1.02	0.05	0.034
338	68		0.164	1.42	0.028	0.026	1.58	9.33	18.5	—	—	—	—	0.040

Return Requested

Metuchen, New Jersey

3880 Park Avenue

INDUSTRIES INC.



Production is under way on a new high-speed spectrograph with features uniquely amenable to several types of research studies. Of the side-by-side Czerny-Turner type, it is modified in accordance with the principle first theorized by W. Leo, (*Z. Angew. Phys.*, 8, 196, 1956) that coma can be dramatically reduced by arranging two mirrors of slightly different focal length in place of the ordinary symmetrical system. This done, the coma is effectively halved; instead of 50 mm of essentially coma-free spectra, 100 mm are attained. In the remaining 50 mm, the quality of the spectra is adequate for qualitative photographic work and for most photoelectric studies.

Following are some of the features that have already attracted enough purchasers to put crimps in our instrument delivery schedule:

Spectrometer—A kinematically-mounted and readily removable mirror deflects the exit beam to the side, converting the instrument into an accurate scanning spectrometer.

Polychromator—As many as six exit slits may be individually positioned accurately from outside the light-tight housing.

Beam Monitor—A quartz refractor plate after the entrance slit is turned on its vertical axis to correct for wavelength displacements in the polychromator caused principally by barometric pressure changes. The small amount of light reflected from this plate is directed to a photomultiplier for intensity ratio measurements.

Rapid Scanning—Specially mounted, the grating may be rotated to sweep the spectrum past the exit slit extremely rapidly.

Accessories—Most of the convenient accessories and attachments designed for our other spectrometers fit the 1800.

#1800 3/4-METER f/6.3

SPECTROGRAPH-SPECTROMETER

