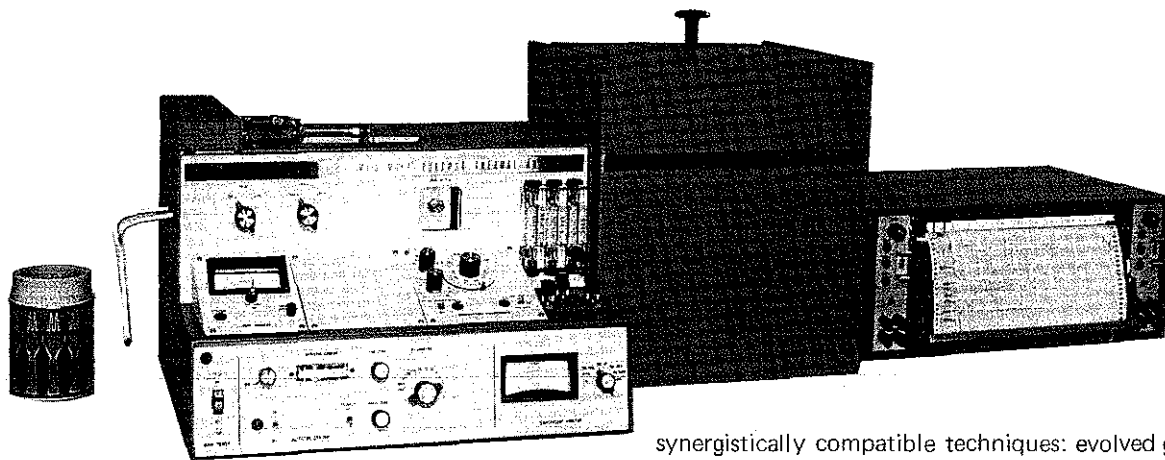


The**SPEX**

INDUSTRIES, INC. · 3880 PARK AVENUE · METUCHEN, N. J. 08840 · (201) 549-7144

Speaker**THERMAL CHROMATOGRAPHY**

THERMAL chromatography introduces a dramatically novel concept in chemical analysis. Embracing applications in quality control of a broad and growing list of chemical products, as well as in basic research, the technique is certain to find itself a secure spot in the already crowded analyst's toolbox.

Conceived by D.G. Paul, Chromalytics Division of Spex Industries, thermal chromatography (as we've dubbed the procedure) derives its impact by coupling two different but

*The Committee on Standardization of the International Confederation of Thermal Analysis would refer to what we call a thermogram as an EGA or EGD record. See Anal. Chem. 44: 640, 1972.

synergistically compatible techniques: evolved gas analysis and gas chromatography. A thermogram* of the substance under analysis is obtained by heating it as a solid, liquid or gas to as high as 800C. The evolving gases flow through the thermal conductivity detector, generating a record of thermal conductivity vs. time (or temperature). Trapped at room temperature or below, the gases can then be back-flushed and properly inserted into a GC column by heating the trap; the GC effluent is once again directed through the TC detector. To attain extremely high sensitivity both the thermogram and chromatogram can be monitored by a flame ionization detector. From either detector a "fingerprint" of the sample emerges; it is unique, readily duplicated and catalogable. Moreover, the information is quantitative in that peak intensities and areas can be converted into percent concentration.

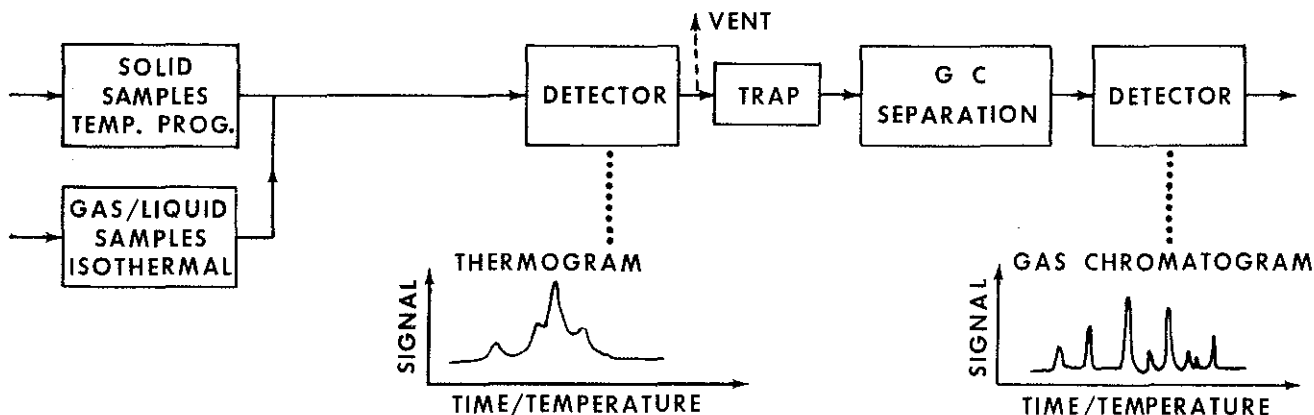


Fig. 1. Thermal chromatography is a triple-edged analytical tool. It separates a substance thermally, provides a thermogram of each of the resulting products and finally generates a gas chromatogram of each. When heated, the substance dissociates or degrades into gas fractions. Because these fractions exhibit differences in thermal conductivity with respect to a carrier gas, the detector can follow the changing composition with temperature and so generate a thermogram. Undestroyed, the gases are next collected on a trap. From here they are directed through a GC column and then through the same TC detector. Alongside the thermogram, a gas chromatogram is thus recorded. A flame ionization detector operating in both the thermal and GC modes is also available.

FLOW DIAGRAM

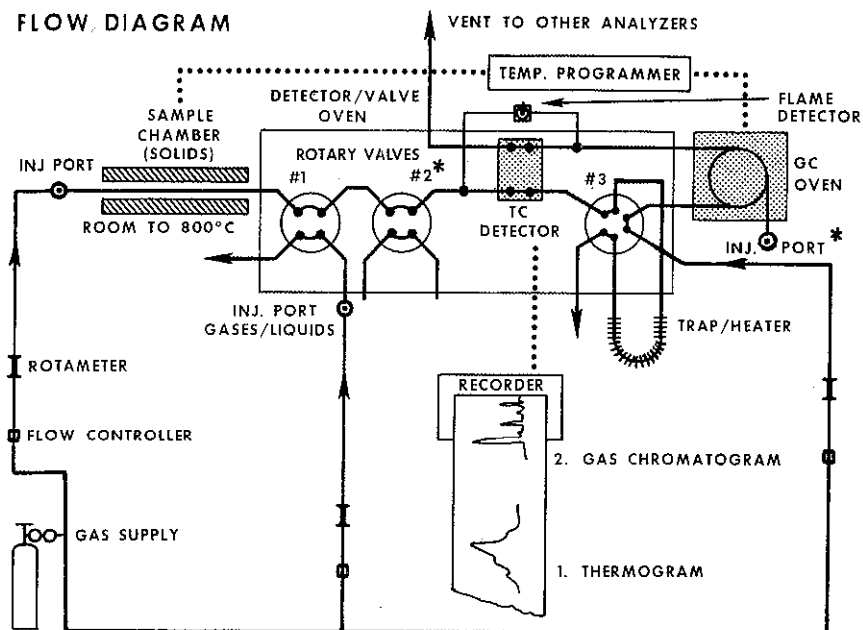


Fig. 2. One key to the versatility and low cost of the MP-3 is its ingenious system of valving. With it the same TC detector serves for both the thermogram and chromatogram. Instead of requiring another instrument, the trap and its associated plumbing permit the operator to save only those fractions wanted for further study. The optional #2 valve in the programmably heated compartment can introduce other gases or liquids to react with the substance trapped. With the optional injection port in the programmed or isothermally heated GC a conventional chromatogram can be run on the MP-3 without prior recording of a thermogram.

*OPTIONAL

Fig. 1 is a block diagram outlining the methodology while Fig. 2 depicts the flow diagram and particularly the valving and plumbing arrangement which, by encouraging so many procedural variations, enhances the versatility of the new MP-3 Thermal Chromatograph.

The thermal or EG section of the MP-3 combines aspects of thermogravimetry (TG) and pyrolysis. TG is a technique which continuously measures and records the weight loss of a material as its temperature is raised at a preset rate. Pyrolysis, a two-stage technique more appropriately called pyrolysis/GC, implies a rapid heating of a substance, the decomposition products of which are later chromatographed in the same instrument. In the MP-3, the sample temperature is normally programmed as in TG. Instead of recording the weight loss, however, thermal conductivity of the evolved gases is

measured. This is followed by gas chromatography, as in pyrolysis.

A TG weight loss record is compared with an MP-3 thermogram of nylon-66 in Fig. 3. Essentially, the latter represents the first derivative of the former. What is attained in place of the slow, amorphous change in weight characteristic of a typical TG tracing is a sharp, readily identifiable set of peaks. The sensitivity of TG is limited to that of a microbalance, in the order of tenths of a microgram. By comparison the sensitivity of the thermal stage of the MP-3 is at least ten times better with the thermal conductivity cell and is easily improved by another order of magnitude with the flame ionization detector. Nanogram quantities can be detected.

Advantages of the MP-3 over conventional pyrolysis accrue from several innovations for which a patent has been applied. Because the sample is heated "instantaneously" in pyrolysis, there is no practical way of removing the effluents selectively. By contrast, the programmed heating in the MP-3 permits analysis of each of the successive temperature fractions both through a thermogram and a chromatogram. Secondly, by isolating the thermal decomposition heating phase from the GC phase, another important aspect of flexibility is added to the MP-3. In the thermal phase, for example, the sample can be heated to react in an oxygen atmosphere. Then, after effluents are trapped, they can be flushed with an inert carrier gas such as helium to the GC column.

Table 1 compares the three techniques of pyrolysis/GC, TG and the new MP-3 thermal chromatography. Although we believe that the MP-3 is the most versatile, the others remain powerful and in some applications unique. The advantage of pyrolysis/GC is speed, for example, in studying catalytic cracking reactions. TG, on the other hand, offers the best means of determining water of hydration and is specific where weight loss is desired. It can quantitatively distinguish between and measure adsorbed and chemically bonded water.

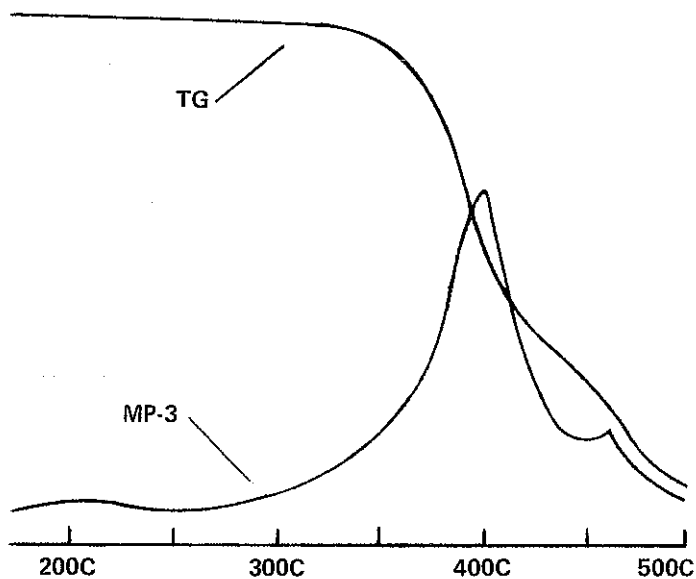


Fig. 3. Comparison of a TG and an MP-3 tracing of nylon-66 identically heated. Plotted in TG is a weight loss while the ordinate for the MP-3 is thermal conductivity. Subtle weight changes lost in the slope of a TG curve appear distinctly in an MP-3 plot.

TABLE 1

Capability	Pyrolysis/ GC	TG	Thermal Chroma- tography, MP-3
Thermal/GC combination	Yes	No	Yes
Sample Form (gas, liquid, solid)	S	S	SLG
Thermal profile	No	Yes	Yes
Temperature rise programmed	No	Yes	Yes
Selective trapping of evolved gases	No	No	Yes
Selective atmospheres	No	Yes	Yes
Dilution — Carrier gas: sample	High	Low	High
Quantitative thermal data	No	Yes	Yes
Qualitative GC data	Yes	No	Yes
Sensitivity	High	Low	High
Choice of detectors	Yes	No	Yes
Direct weight loss	No	Yes	No
Temperature rise to maximum	<1 sec.	100 sec.	10 sec.
Sample Size	Very small	Small	Very small to large
Price	\$5500	\$9,000	\$5000

L IQUIDS and gases are introduced quite conventionally into the MP-3 by hypodermic injection through a silicone rubber septum. Handling of solid samples departs from, and we believe, is quite advantageous over that in commercial TG and pyrolysis instrumentation. The solid is placed in a fused silica tube, sandwiched between wads of glass wool. The tube, in turn, is "Swagelocked" into the carrier gas line. Surrounding the silica tube is a resistance furnace which consists of two halves of a cylinder, the upper one hinged. Replacing a sample takes but a few moments and there is little concern with intersample contamination. Since it is removed between samples, the tube is readily cleaned and to speed up analytical turnaround time, samples can be preloaded.

Analytical time will, of course, depend on the heating program. Experience has indicated that most work can be done at a heating rate of 28C/min. The thermal cycle for a material completely decomposing at 400C thus takes about 15 minutes. Switchover to GC operation takes just a few seconds. The complimentary chromatogram up to 250C is normally run off in about 15 minutes.

The broad, latent power of the MP-3 results in large part from the flexibility of its controls, plumbing and measurement systems which can be tailored to the specific requirements of a particular analytical problem. The Fig. 4A thermogram and chromatogram taken of a red automotive paint chip distinguishes it unambiguously from another chip of identical appearance. Despite its size it would provide ample circumstantial evidence in the two complimentary traces to convince a jury that a paint chip found on a hit-and-run victim matches only a certain automotive paint. The further GC breakdown of the paint chip in Fig. 4B, however, represents the kind of work that would be done by an analytical chemist trying to learn what competition is adding to its paints.

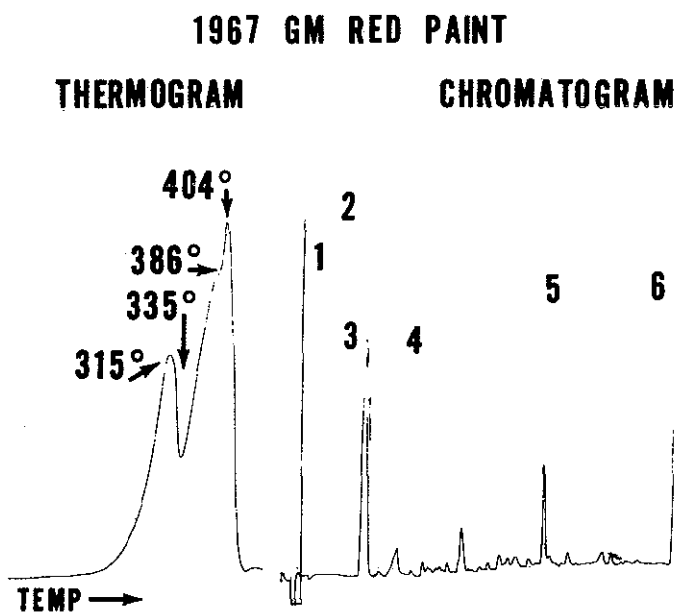


Fig. 4A. A pinhead size chip of paint from a 1967 GM auto yielded the MP-3 thermogram and gas chromatogram shown. Major GC peaks are marked 1 through 6 for further study.

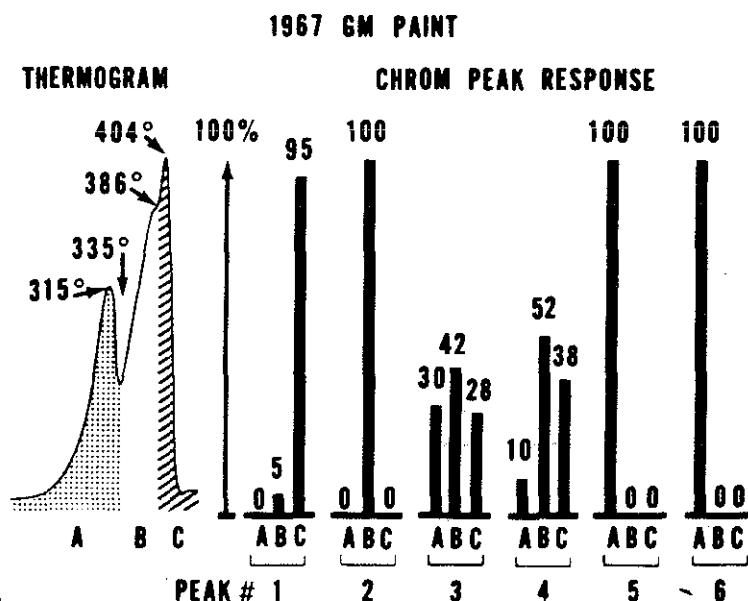


Fig. 4B. Another chip from the same paint sample was heated, its effluents trapped in three temperature stages. Effluents from each of the stages were then chromatographed. Note how the 6 major peaks shown in Fig. 4A are related to the temperatures of evolution. Peaks 5 and 6 arise entirely from the lowest-temperature fraction (A). Peak 2 arises from the middle-temperature fraction (B). The other GC peaks arise in various concentrations from all three thermal fractions.

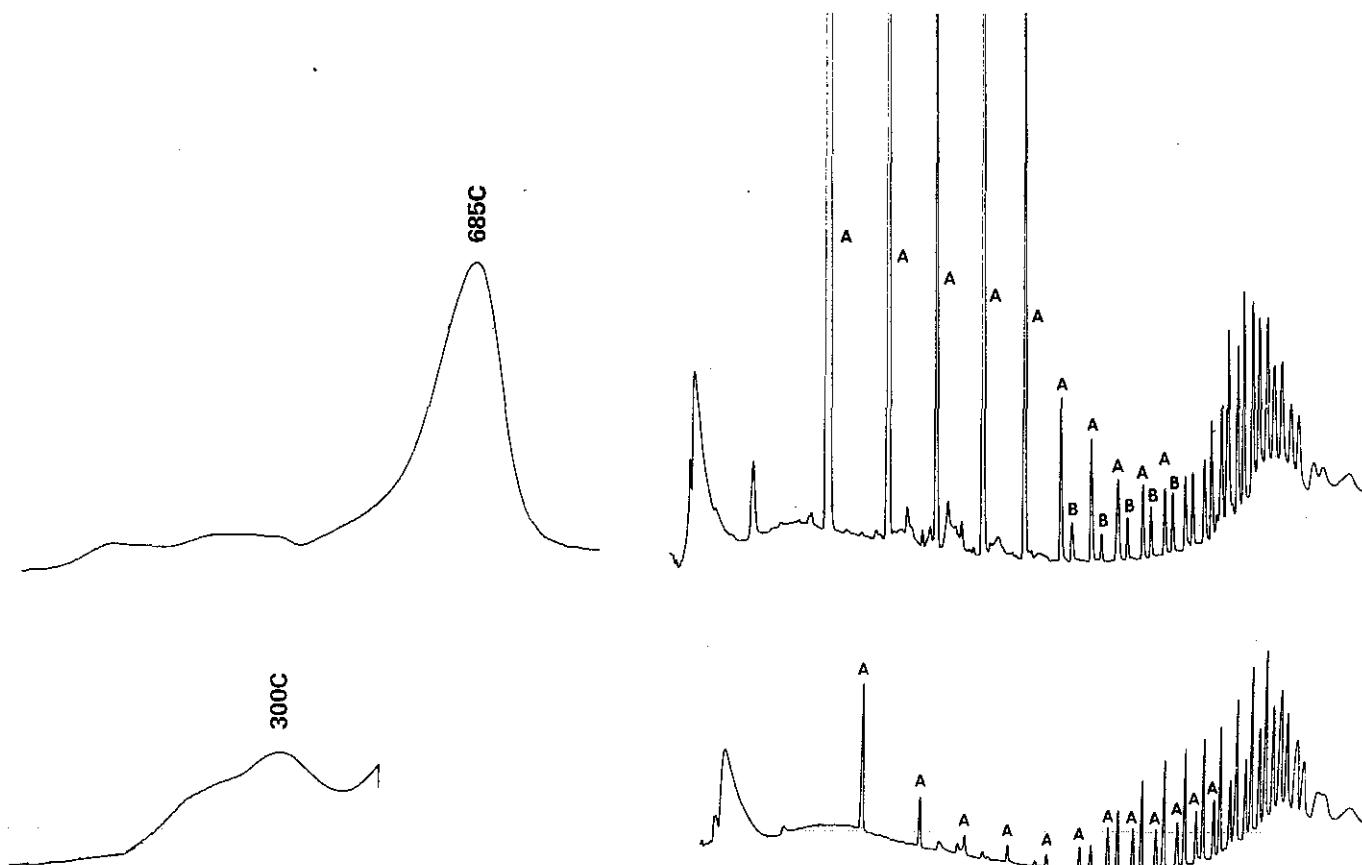


Fig. 5. The outstanding significance of selective heating can be gauged from this analysis of a viscous polymer. In the upper trace, the furnace was programmed to heat the sample at 28C/min from 50 to 740C. The entire effluent was trapped. Its thermogram reveals two components; below 425C, volatiles are evidently evolving while the peak at 685C marks the thermal decomposition of the polymer. Despite its clarity, the GC tracing fails to distinguish between the two components. In the lower figure, this has been remedied. By programming the sample temperature below 440C, only the volatile component was removed and analyzed. Intensities of the peaks marked A have dropped markedly while those of the peaks marked B have remained essentially unchanged. Obviously, the "B" peaks depict low-temperature components, the "A" peaks, high-temperature decomposition products.

In Fig. 5, another application of selective trapping is given, this time in conjunction with a viscous polymer. By heating and trapping the original sample in two temperature ranges, the source of GC peaks can readily be determined. Valving is so arranged that any temperature fraction in the trap can be retained for further study by the self-contained GC component of the MP-3; or the fraction may be vented so it does not interfere; or directed through an optional heated transfer line to another instrument.

Copolymers may be purchased in so many types and concentration ratios that quality control departments must remain ever alert lest mixups occur which could seriously disrupt production of thousands of end products. Fig. 6 illustrates the quantitative analysis of a copolymer of polyvinyl acetate/polyvinyl chloride. Although chromatograms were taken on duplicate samples of the same material, only the thermogram is needed for the assay.

Fig. 7 is an example of "fingerprinting," this time of cigarettes. At the recent Pittsburgh Analytical Conference, an MP-3 analyzed as many brands of cigarettes as could be obtained from visitors. Each yielded a distinct thermogram and chromatogram pattern; yet the class resemblance of all patterns was enough to reveal them as tobaccos. Even to a novice, the pattern of hashish in Fig. 7D could not be mistaken for that of a tobacco. Incidentally, samples consisted of a single unweighed flake of tobacco.

ANTICIPATING potential applications of the MP-3 is no strain to the imagination. The instrument has already proved so versatile and invaluable in so many diverse fields that new and unusual applications come as no surprise. A few examples, still in the evaluation stage, may provide a thinking start.

Thin Layer Chromatography

TLC techniques are widespread in forensic labs for proving that a suspect has taken a drug and pinpointing the exact drug ingested. After appropriate chemical treatment, a drop of urine is placed on a TLC plate. The migration smears of the drop on the TLC plate are actually — they do not merely represent — the separated components of the sample. And one of these small smears may be the drug or a derivative of it. Identification of the smear can be made unequivocally in the MP-3 by simply scraping it into the silica tube, taking and comparing its GC pattern with those of known drugs.

Complex Mixtures

A time-consuming, fractional distillation is often needed for the GC analysis of a complex mixture such as gasoline or petroleum intermediates. A technician must remain on hand to remove each of the temperature fractions as they distill off and then inject them individually into the chromatograph. Such distillations, it appears from preliminary work, may be carried out successfully in the furnace of the MP-3. Liquid or solid samples can be fractionated by heating them through adjoining temperature intervals, the fractions then individually analyzed in the GC section of the instrument.

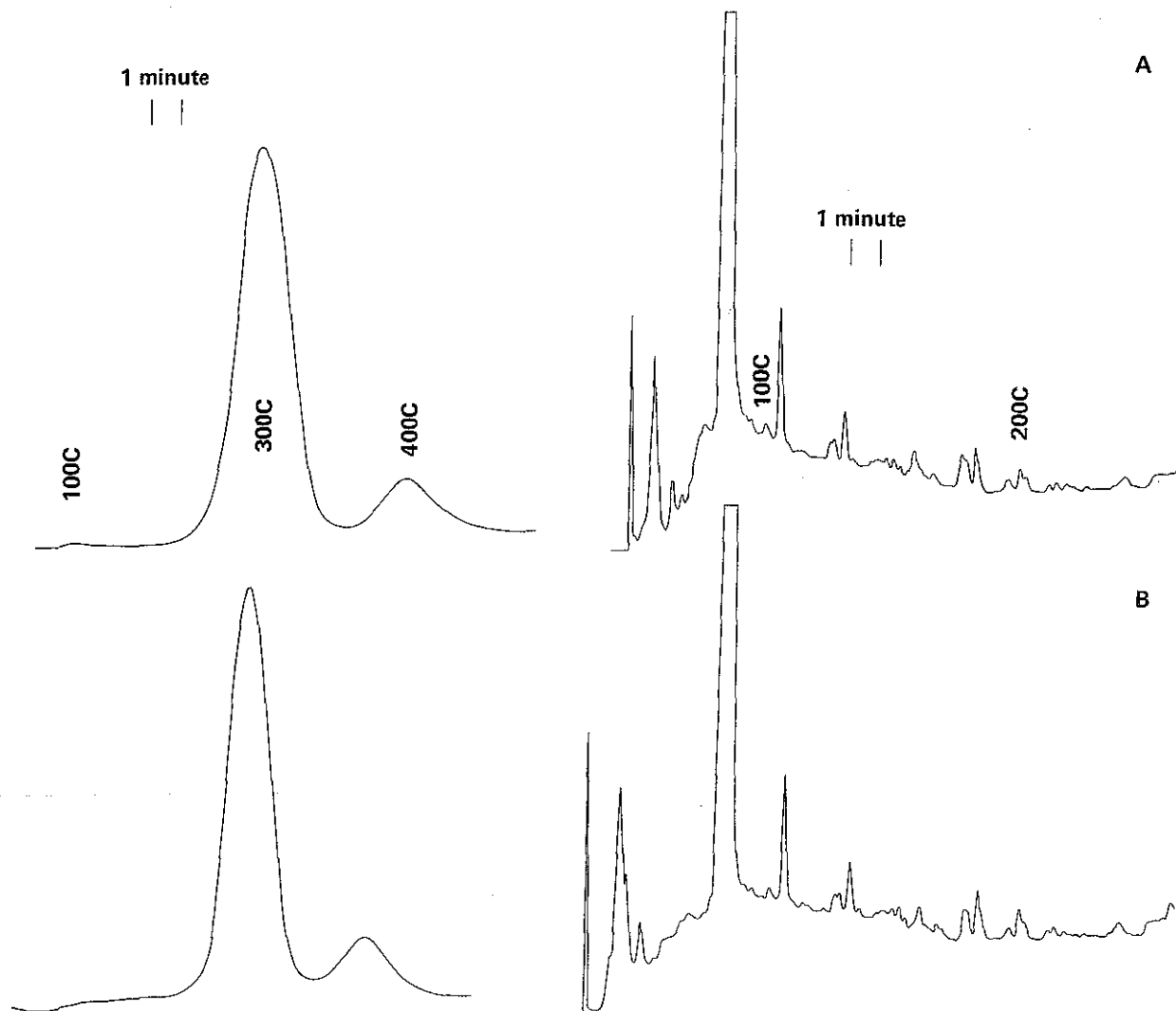


Fig. 6. Copolymer assay. Less than 1 mg of a copolymer of vinyl chloride/vinyl acetate was run in the thermal and GC modes. Although neither sample was weighed, that taken for the duplicate run in Fig. 6B was obviously slightly heavier than the other. Areas under the two peaks were ratioed to give an average of 85.2% of PVC, the lower boiling polymer. Actual value furnished by the supplier was 85.8%. The assay required only the thermogram which took 20 minutes to generate at the temperature-rise rate of 28C/min. The chromatograms are shown solely to indicate reproducibility of both sections of the MP-3.

Multiviscosity Oils

One of the most significant recent advances in engine oils has been the multiviscosity oil, a lubricant that does not become gummy at low temperatures to frustrate winter starting of an auto. The addition of certain polymers to oils has accomplished this. Identification of the polymers and measuring their concentration have in the past required their prior removal. In the MP-3 this is unnecessary. The sample is heated to a point where the oil is driven off but below the temperature of degradation of the polymer.

Surface Contaminants

Whether the end-product is an electronic device, a decorative finish or a protective coating, surface composition and uniformity are exceedingly important. Residual grease will, of course, prevent the adhesion of paint. A non-conductive surface inclusion will become a "holiday" in an electroplated surface. Diagnosis is the key to prevention. Because the MP-3 is so sensitive, because it is a true micro analytical tool, it can analyze a pinhead-size sample and readily permit the analyst to correlate the information it generates with that from a suspected source of the contaminant.

Gases and Airborne Pollutants

Recently a sample of volcanic fumes was analyzed on the MP-3. Drawn through a PVC filter, residuals deposited as a smudge. With a paper punch as the sampling tool, a small disc was inserted into the silica furnace tube. Despite its small quantity, the sample produced peaks so high that we are convinced that the MP-3 will soon find applications in the study of less polluted air than that spewing out of a volcano. Confirming this supposition, one instrument is presently being purchased for the study of factory air.

Thread

Like most other modern household items, sewing thread ain't what it used to be. Once made simply by twisting together dyed fibers of wool or cotton, thread has undergone vast changes both to improve its properties, for specialized applications particularly, and to render it compatible with high-speed sewing. Today's thread bundle typically consists of mixtures of polymers and natural fibers. In fact, individual fibers within the bundle may themselves comprise complex polymers. To boost heat resistance, polymers may be cross-linked. To add stretchability, especially for sewing the

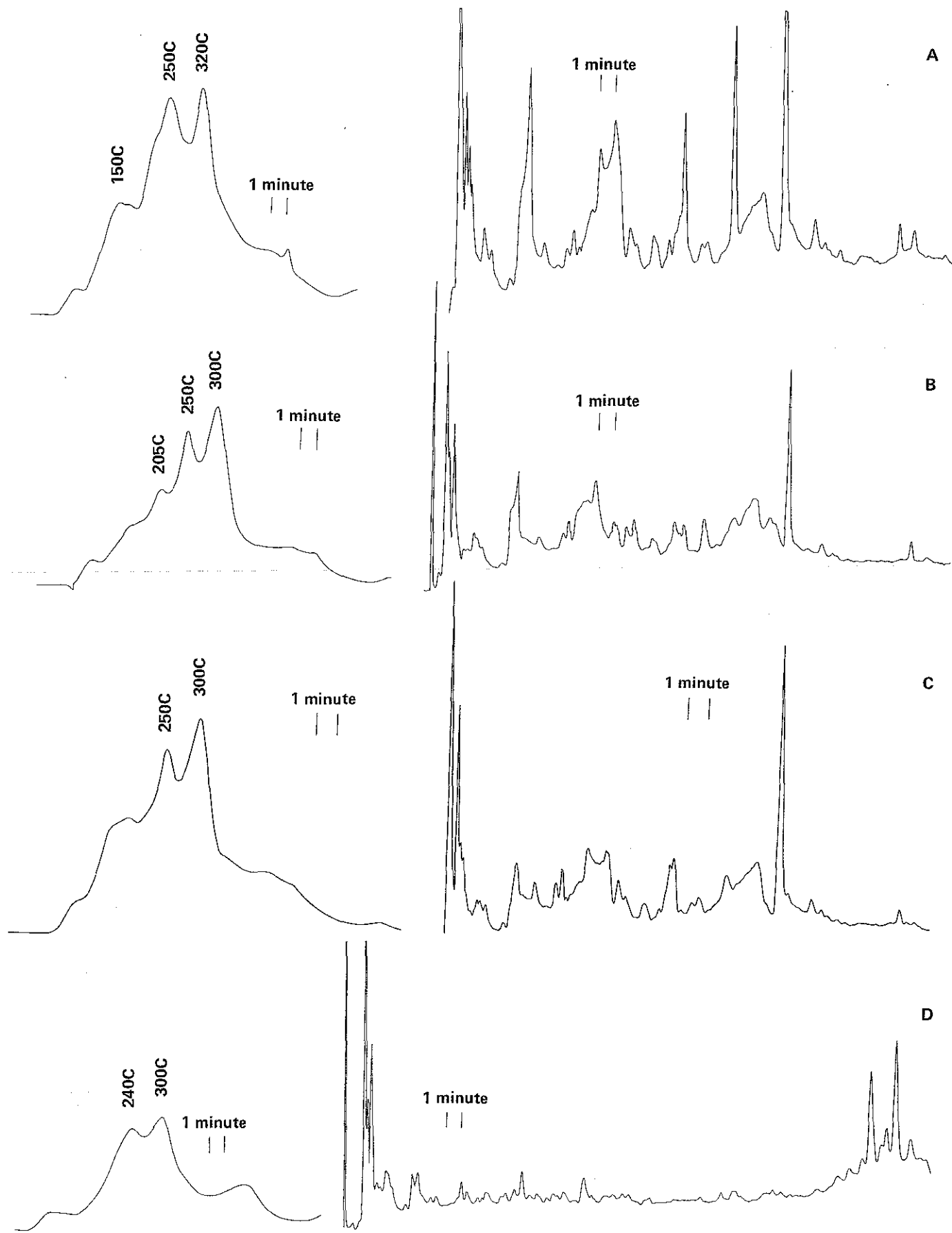


Fig. 7. TC traces of tobacco from three brands of cigarettes (A, mentholated), and a hashish sample. A single flake of $\sim 100 \mu\text{g}$ was heated at a rate of $28\text{C}/\text{min}$ for the thermograms. Of the dozen or so tobaccos run thus far, all produced tracings sufficiently similar to identify them as tobacco; at the same time, all were distinctive and reproducible. Note the quite different tracings obtained from the hashish in Fig. 7D.

new double knits, crimped elastomers are twisted into the fiber bundle. To alleviate the necessity of color matching to the fabric, transparent monofilaments of polyester are now commonplace.

Adding to the variations of the base material in the thread, finishes and coatings have become specialized, too. Silicones and waxes lubricate and waterproof the core. Flame retardants add an element of safety. Surfactants facilitate subsequent dyeing and wash-and-wear treatments.

Along with the complexity of the thread itself has come the complexity of the techniques needed to control its quality. Dr. Herman Vant Erve of American Thread Company, Willimantic, Connecticut, recently installed an MP-3 as still another diagnostic tool for quality control and research. One of the strongest assets of the MP-3, he feels, is its ability to separate the thread from its finish. Preliminary tests have shown that by heating the material in the EG section of the MP-3 to a comparatively low temperature, most coating materials are driven off and directed selectively to the GC section. Any differences in the chromatograms not only "flag" the analyst that something is wrong in a production batch but also pinpoint the trouble to the thread or the finish.

Thermal Stability and Weight Loss

Thermal stability of materials can be readily measured by temperature programming a sample in the tube furnace of the MP-3 and observing the volatiles and or decomposition products as they pass through the detector. Such data are comparable to those from TG measurements but with an all-important 100-fold sensitivity advantage. Measurements in TG are, of course, limited by the sensitivity of the microbalance, about 0.1 μg . With a flame ionization detector, the MP-3 picks up changes representing thousandths of a microgram. Although this means that the sample size can be reduced to as little as 0.1 μg with an FID, this is often unimportant. More important is the fact that subtle changes in a material which remain undetected in TG appear in thermal chromatography.

One way of illustrating the extreme sensitivity of the MP-3 with an FID and comparing it with a conventional TG apparatus is with calcium oxalate monohydrate, a substance that decomposes in three discrete stages. The MP-3 achieves essentially identical data as the TG equipped with an optional and expensive accessory, a time-derivative computer. With only 100 μg of sample, peak heights of the MP-3 equal those in the time-derivative mode of TG with a sample size of 10 mg. TG does have the advantage of recording weight loss directly. It is possible and practical, however, to calibrate the MP-3 scale in weight loss terms.

Collection and Study of Volatiles

Residual solvents and impurities can be detected and determined in a manner similar to that described for measuring weight loss. The thermogram yields information related to the amount of the substances present while the subsequent chromatogram yields compositional information. Both can readily be calibrated for quantitation.

Medical Products

A surgical product manufacturer is investigating the MP-3 in two quality control areas. One relates to the determination of monomer ratios in a suture. Currently, analysts laboriously separate the monomers chemically then follow this with gas chromatography. Initial results with the MP-3 were encouraging; chemical separation appears unnecessary as the separation step may be made in the thermal section of the MP-3. Fig. 6 illustrates a similar problem in which the ratio of polyvinyl acetate to polyvinyl chloride in a copolymer was determined in the thermogram itself simply by ratioing peak areas.

The second area of interest to this laboratory is the identification and characterization of natural dyes. Where in the past the Food and Drug Administration stressed the safety of man-made products paying less attention to natural ones, it is now imposing much more stringent controls on the latter as well. Silk sutures are commonly dyed with derivatives of naturally occurring logwood. Preliminary tests with the MP-3 have shown that it is capable of characterizing families of these dyes. To identify individual dyes within these families, further research is anticipated.

IN summary, the MP-3 is an instrument with many features common to TG and pyrolysis/GC but with decided advantages over either. With respect to TG, the following advantages accrue:

1. The sample size can range over at least 6 decades from a microgram or so to several grams. In forensic work where a tiny fragment can loom as an essential piece of circumstantial evidence, the MP-3's ability to work satisfactorily with small samples is a boon. When trace impurities like residues, solvents, inhibitors, stabilizers are to be controlled in manufactured products, the MP-3's ability to work with comparatively large samples is ideal.

2. The concentration of sample in the carrier gas is comparatively small with respect to that needed in TG. This feature facilitates the transfer of the material directly to a mass spectrometer or infrared spectrometer. Excessive dilution by the carrier gas required in TG reduces the sensitivity of subsequent analysis by MS or IR.

3. Material may be trapped over a long period of time. In curing rubber, for example, the end point is the disappearance of hydrogen sulfide which may take many hours.

Over pyrolysis/GC, other advantages obtain:

1. Because the heating rate of the MP-3 is carefully controlled, its thermograms are much more reproducible. Fingerprints, never quite acceptable in pyrolysis, are excellent in the MP-3.

2. The MP-3 has the ability to monitor the onset of phase changes, determine their temperatures as well as that of the final temperature of decomposition. It can also distinguish among impurities such as surface water, residual organics, solvents, etc., which elute prior to the decomposition of the base material.

3. The MP-3 can selectively trap at any point in the decomposition process for study of each species independently.

4. The material may be decomposed under any atmosphere because the thermal stage is barred from the gas chromatographic stage by a trap. Conventional pyrolyzers cannot work in a reactive atmosphere such as oxygen because the oxygen would ruin the GC column.

Over both TG and pyrolysis/GC, the MP-3 claims another significant advantage: ease of operation. After but a few hours of training, any technician can turn out excellent data that are reliable and reproducible but above all economically and scientifically meaningful in diverse and proliferating analytical problems.

DEVELOPMENT of the MP-3 Thermal Chromatograph involved more than the breakthrough of an idea by Don Paul. Coaxing the instrument from the abstract image to a time-tested, human engineered, debugged commercial instrument, took the cooperation of a number of people urged on by Don's enthusiasm. These included C.E. Bennett, D.J. Brindle, L.J. Levasse and J.A. Wegener. A deep debt of gratitude is owed the late Professor C.W. Meade of the University of Massachusetts who devoted the last months of his life to a comprehensive study of the MP-3. Unfortunately all that remains are reams of raw data on a host of organics and metallo-organics, unjelled information that only he could have integrated for publication.

—AJM

MP-3 THERMAL CHROMATOGRAPH SPECIFICATIONS

An instrument for obtaining a thermogram (evolved gas record) and a gas chromatogram sequentially on a solid, liquid or gas sample. A trap and specialized plumbing between the two halves of the instrument assure attaining a representative chromatogram while permitting great flexibility in the analysis of separate thermal fractions of the sample.

FLOW SYSTEM: 3 separate gas flow paths with individual flow controllers and rotometers. Solids flow path has a carrier gas shutoff valve. Maximum operating temperature 250C (Optionally 300C).

TEMPERATURE PROGRAMMER: The same programmer controls either the thermal (EG) section or the GC section.

Type	Linear
Operating Modes	Three (isothermal, programmed to hold at limit or off at limit)
Programming Rates	4 to 40C per min in 4° steps
Control	Proportional with feedback loop from Chromel-Alumel thermocouple
Program Range	Ambient to 800C

SOLID SAMPLE FURNACE:

Temperature	Ambient to 800C
Sample tube	Fused silica or Pyrex, 5-1/2" long x 1/8" id
Sample size	5 g (approximate maximum)

DETECTORS:

Thermal Conductivity	
Type	Wheatstone bridge
Filaments	4, W-2 tungsten
Current Range	50-150 mA
Attenuator	1 to 1024 in factors of 2
Flame Ionization	
Electrometer Sensitivity	Three settings: 2.5×10^{-12} , 2.5×10^{-10} , 2.5×10^{-8} A/mV

TRAP: Externally located; may be operated at ambient or down to 77 K if immersed in LN₂.

Power	Variable transformer
Limit control	Relay pyrometer with adjustable set point

GC OVEN:

Internal dimensions	10" W, 10" D, 8" H
Temperature Range	Ambient to 400C
Cooling Rate	400 to 40C in 6 minutes
Air Circulation	Internal centrifugal blower
Construction	Stainless steel with heavy-duty insulation

TEMPERATURE MONITORING:

Indicator	Thermocouple pyrometer; also direct-reading dial on programmer
Range	0-1000C; accuracy $\pm 2\%$ FS
Sections monitored	Sample Furnace, GC oven, detector casting, transfer lines, and provision for auxiliary thermocouple (10-ohm iron-constantan)

RECORDER RECOMMENDATIONS: Potentiometric, 1 mV FS, 0.5 sec cross-chart; single pen with thermal conductivity or FI detector, double pen with dual detectors.

ELECTRICAL REQUIREMENTS:

Power	115 V., 50-60 Hz, 15 A
Fuses	Three 2 A, one 8 A, one 3/8 A, one 15 A

DIMENSIONS:

Overall	33" W, 18" D, 18" H
GC oven	14" W, 14" D, 18" H (attached by transfer line)

WEIGHT: Net	91 lb
Boxed	130 lb

