

GAS CHROMATOGRAPHY

APPLICATION TO THE STUDY OF RAPID DEGRADATIVE
REACTIONS IN SOLIDSA
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Application of gas chromatography to the study of organic reaction kinetics is clearly a very promising and natural outcome of the recent development of this highly diversified analytical tool^{1,2}. Reaction products of complex gas and liquid phase reactions can be rapidly and accurately determined regardless of the complexity of their composition. With suitable modification for the transferral of materials, any one of the commercially available chromatography units, combined with an infrared spectrometer or a mass spectrograph, provides a means for the complete analysis of practically any imaginable liquid or gas mixture. An application which has received relatively little attention, but which lends itself perfectly to chromatographic methods, involves the determination of the products of rapid degradative reactions of solids or of liquids with low vapor pressures. The essential feature of the method is one of carrying out the reaction directly in the stream of the chromatography carrier gas, through the influence of some external stimulus such as radiation (thermal, nuclear, or radio frequency), electric spark, or simply resistive heating. Examples of reactions which can be studied in this way include the ignition of explosives, the burning of solid propellants, the degradative processes induced in solids by ionizing radiations, and the rapid pyrolysis of organic compounds. In effect the method to be described can be used to study the reactions of any substance whose vapor pressure is small and which decomposes at least partially to gaseous products under the influence of applied stimuli rapidly enough that in an interval of time of a minute or less the reaction has run its course to such an extent that the nature of the reaction can be determined.

The method as it is used in the author's laboratory amounts to exposing an organic solid suspended in the helium carrier gas stream to very intense radiant energy similar in spectral distribution and radiant power to that which is emitted during a nuclear weapon detonation. Such radiation is produced in the laboratory by high-current carbon arcs³. High temperatures are developed in a solid in a very short time when it is exposed to this radiation, and depending upon the intensity of the radiation, the solid may be largely decomposed to vapors in a fraction of a second. Under the proper conditions, in air, the solid would ignite spontaneously and burn. While the subject of radiation ignition is quite beyond the scope of this paper, it should be mentioned that the processes are rather well understood macroscopically⁴,

i.e., ignition behavior in terms of the gross physical properties of the material and the parameters of exposures. Less well understood, however, are the details of the high temperature pyrolysis reactions and the role of changes of composition of the resulting vapors in the spontaneous ignition process.

In the analytical procedure to be described here, the vapors resulting under various conditions of pyrolysis are characterized through the use of two different systems. The first separates the condensibles into rough fractions with dynamic cold traps and analyzes the non-condensibles with suitable solid adsorption chromatography columns. Subsequently, the materials condensed in the cold traps are analyzed by liquid partition methods.

APPARATUS AND PROCEDURES

Exposure equipment

The work to date has been restricted to the study of rapid pyrolysis of α -cellulose in thin sheet form. To simplify the geometry of temperature distribution and, hence, provide a situation which is amenable to heat transfer theory, the material is suspended in such a way that it may be irradiated uniformly over one surface with small conductive loss. This is achieved by cutting the material into a circular wafer whose diameter is no larger than the diameter of the field of uniform irradiance provided by the source of radiation (generally less than 1-in. diameter) and suspending the wafer behind a quartz window in the center of the carrier gas stream with three tungsten needles which pierce the material near its edge (Fig. 1). Liquids, crystalline solids or any substances which cannot be readily produced in sheet form could be handled by saturating thin asbestos or quartz fiber paper with the substance and handling as described above. It is very important in the design of the exposure chamber, as it is in the flow system which follows, that the vapors be moved rapidly and uniformly with little or no "hold up". The resolution of the resulting chromatogram depends to a large extent upon the mixed vapors moving onto the column in a short, sharply-defined interval of time. Moreover, the vapors which arise from the irradiated solid attenuate the incoming radiation and, for this reason, should not be allowed to accumulate between the exposed surface and the quartz window. This requirement necessitated high helium flow rates through the system including the chromatography column. Inasmuch as the exposure chamber cannot be made smaller than about 15 ml capacity, it is necessary to run the carrier gas through at a rate of not less than 150 ml/min in order to carry away the expelled vapors at a velocity in accord with their free-air convection velocity. Since it is also important not to produce excessive forced convective cooling of the irradiated solid, in general the flow rate has been kept between 150 and 200 ml/min. To achieve this flow rate through a 2 or 3 m column packed with 30-60 mesh solid, it is necessary to use a larger-than-ordinary diameter copper tubing for the column (3/8-in. diameter), to avoid excessively high pressures in the exposure chamber and cold-trap train, and to use reduced pressures at the column exit. Generally, evacuating the exit to about 100 mm Hg pressure and supplying the helium at 5 p.s.i.g. provides the desired flow rate.

Cold traps

The cold traps are specially designed to provide turbulent gas flow along the full length of immersed tubing, the length of which was calculated to provide cooling of the emergent stream to approximately 90% of the bath temperature-ambient temperature difference.

Cold trap media are selected according to the particular column packing material in use at the time. For example, the high-activity charcoal (Burrell 341-10) column at room temperature resolves the diatomic gases and methane, but ethane is irreversibly adsorbed. The equilibrium vapor pressure of ethane at 100° K is less than 0.1 mm Hg while methane and the diatomic gases, H₂, O₂, N₂ and CO have vapor pressures in the range of 1/4 atm and higher. Hence, liquid nitrogen appears to be a rather ideal cooling medium for the cold trap just preceding the high-activity charcoal column. Similar, though less clean-cut, separations are afforded by other cooling media, such

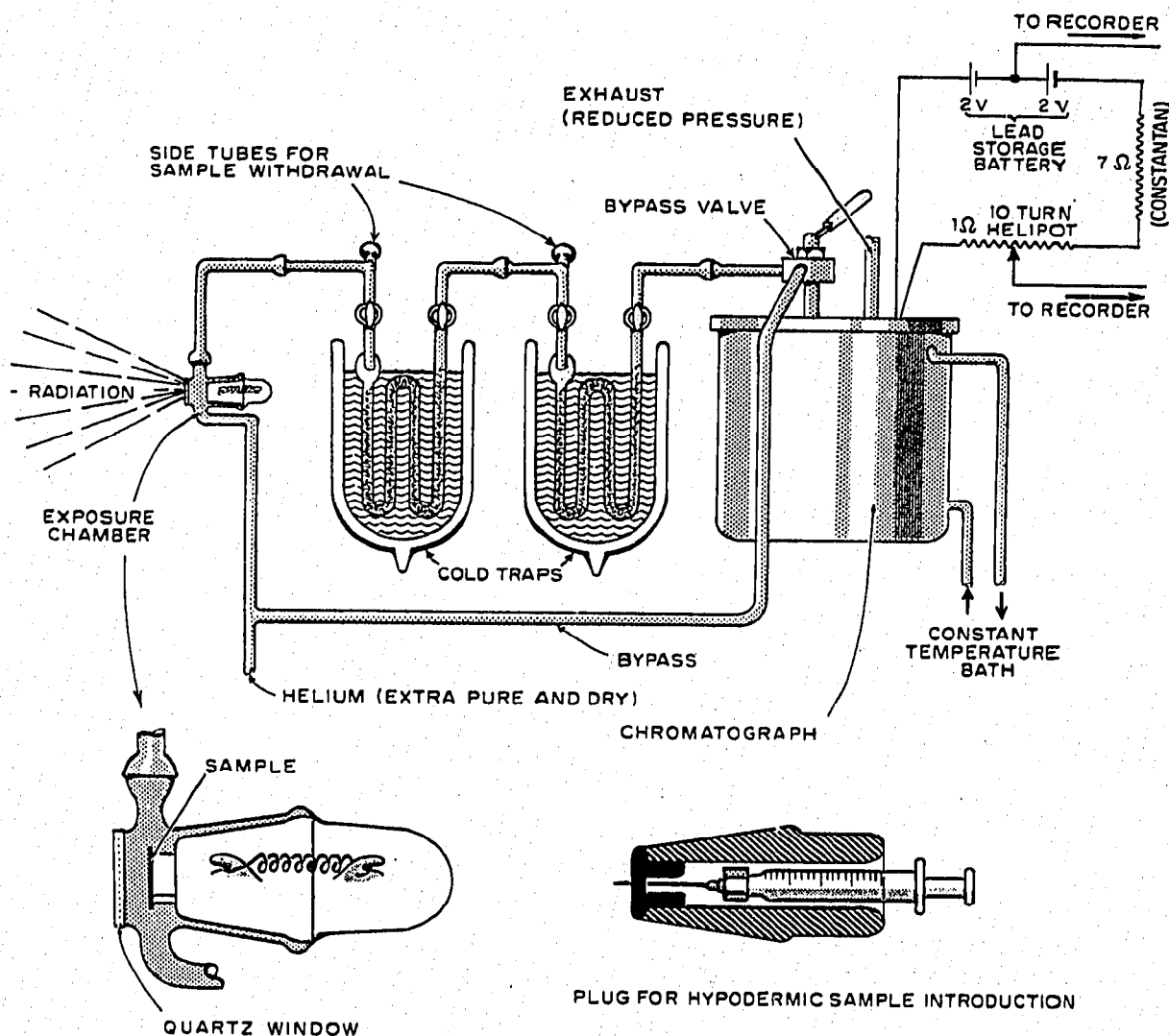


Fig. 1. Diagram of exposure apparatus and gas-solid adsorption chromatograph for the analysis of the non-condensed gases.

as dry ice-acetone or dry ice-ether mixtures, ethanol slush (prepared by mixing the alcohol with liquid nitrogen), and ice-salt mixtures.

Some of the complications inherent in this type of separation should be mentioned. First of all, though an almost immeasurably small vapor pressure may exist for a particular substance at the temperatures achieved by cold trap cooling, the actual efficiency of the trap can never be better and generally will not be nearly as good as the efficiency calculated using the thermodynamic quantity "equilibrium vapor pressure" since the system is far from being at rest. Furthermore, the trap efficiency can never be 100% for any substance, for no matter how small the vapor pressure becomes, it is always finite at any real temperature. Secondly, materials which are supposed to "pass" the trap may be carried down and occluded with condensibles despite the fact that at the trap temperature their vapor pressure may exceed many-fold their partial pressure in the gas phase.

Recognizing these potential sources of error, the following steps have been taken to evaluate their effect and/or to obviate them:

1. A bypass for the exposure chamber and cold-trap train was provided so that at the conclusion of an exposure, as soon as the non-condensibles were on the column, the carrier gas could be diverted directly into the column entrance. In this way, any components of the condensate having appreciable vapor pressures were prevented from migrating out of the cold traps and onto the column.

2. The efficiency of the liquid nitrogen cold trap to retain ethane and ethylene was verified by analyzing the emerging gases with a silica gel column. Likewise the separations afforded with the ethanol slush and with dry ice-acetone were determined with alumina and dinonyl phthalate columns.

3. To test for occlusion the condensate in sealed-off traps was repeatedly vaporized and recondensed slowly, and the non-condensed vapors analyzed with the appropriate column packing.

Analysis of the non-condensable gases

Fig. 1 is a schematic diagram of the component parts of the chromatography unit designed to analyze the non-condensed fraction of the degradation products. Unlike most systems, there is only a single detector involved. The base line drift, frequently reported as an intolerable feature of single detector units, has not been found to reduce the general utility of the instrument, though at times it is somewhat annoying. The detector element was constructed by removing the envelope from a 6 V pilot light* and sealing the base, vacuum tight, into a 1/4-in. to 1/8-in. IPS reducer threaded into a massive brass block. The detector block along with the column is immersed in water whose temperature is maintained constant and kept stirred through the agency of an external constant temperature bath. The detector element forms one arm of a simple, yet very stable, bridge circuit (Fig. 1). The unbalance of the bridge, produced by the change in temperature of the tungsten filament as the heat transfer property

* General Electric No. 44.

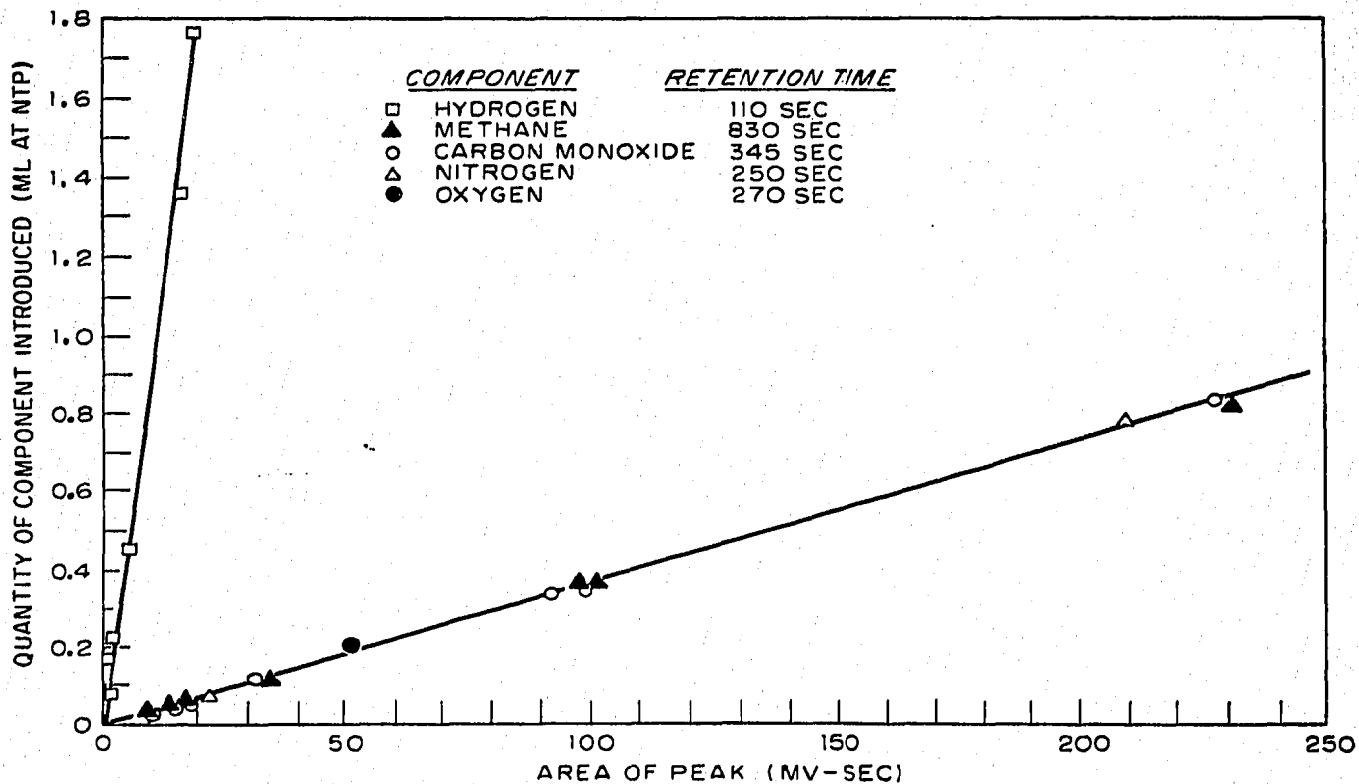


Fig. 2. Calibration of 3-m charcoal column.

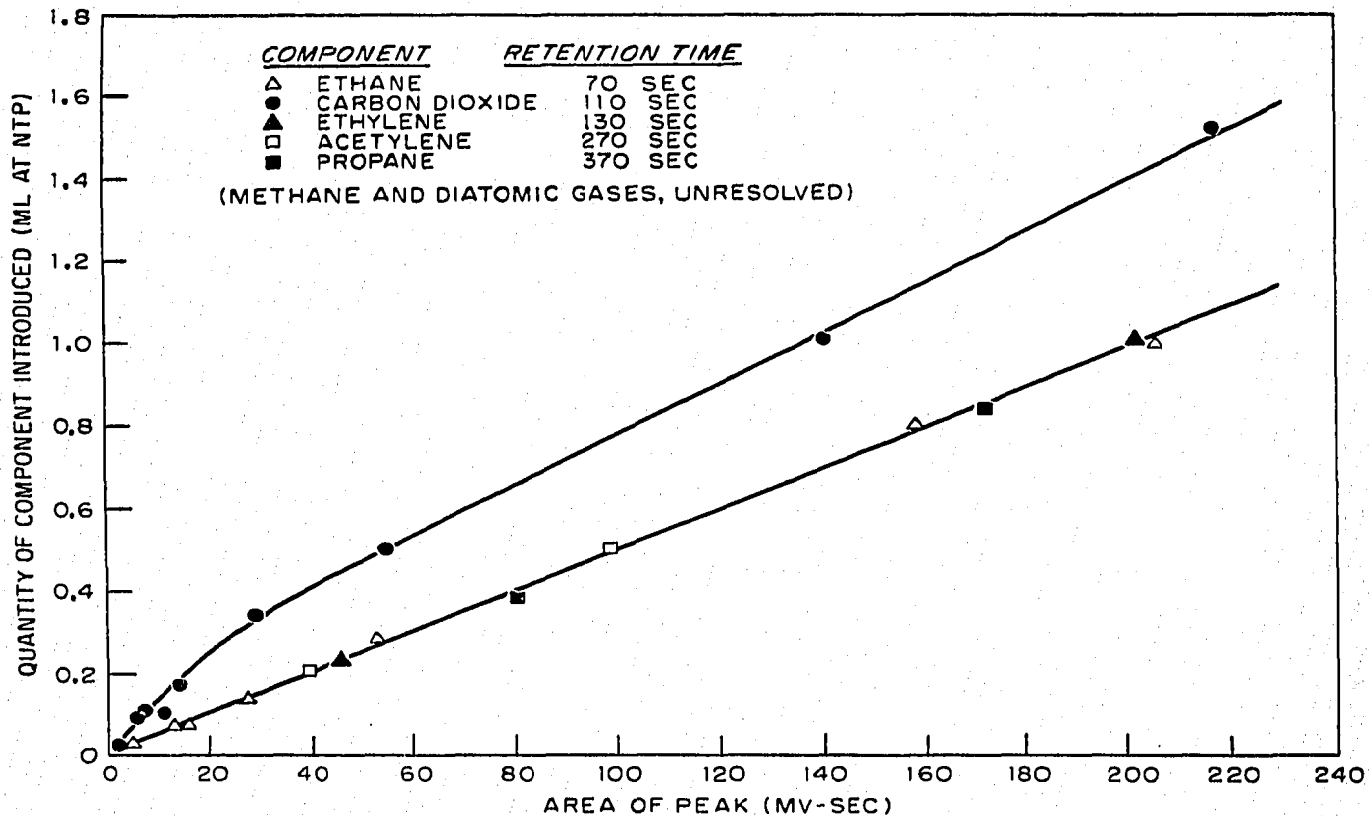


Fig. 3. Calibration of 2-m silica gel column.

of the gases in which it is immersed changes with changes in composition, is recorded on a chart-type potentiometer recorder having 0.5, 2.5, 10 and 50 mV full-scale sensitivities.

The system is calibrated by introducing with a hypodermic syringe through a special fitting in the exposure chamber (see Fig. 1) measured quantities of either pure gases or gas mixtures whose composition has been measured with a mass spectrometer. Example calibration curves are given in Figs. 2 and 3.

Table I lists the combinations of chromatography columns and cold trap media presently in use along with a brief description of the separations afforded by each. It

TABLE I
COMBINATIONS OF COLD TRAPS AND COLUMNS

Cold trap-column combinations a. Higher temp. trap b. Lower temp. trap c. Column packing	Materials retained by cold traps	Analysis provided by column	Comments
a. Dry ice-acetone b. Liquid nitrogen c. High-activity charcoal	a. Hydrocarbons except C ₂ and C ₃ and most oxygenated compounds b. C ₂ and C ₃ hydrocarbons plus CO ₂ and ketene	H ₂ , N ₂ , O ₂ , CO, CH ₄	Contents of trap a. analyzed by aliphatic phthalate stationary phase and with polyglycol stationary phase columns. Trap b. with silica gel column as well as with a polyglycol column as a check for the highly volatile oxygenated compounds, e.g., CH ₂ O, CH ₂ CO
a. Dry ice-acetone b. Liquid nitrogen c. Silica gel	Same as above	(H ₂ , N ₂ , O ₂ , CO)*, CH ₄ , C ₂ H ₆ , C ₂ H ₄ , C ₂ H ₂ , CO ₂ and C ₃ hydrocarbons	Same as above. Used as a check on efficiency of liquid nitrogen to stop C ₂ hydrocarbons
a. Sodium chloride-ice b. Dry ice-acetone (or ethanol slush) c. Silica gel	a. All normal liquids b. C ₄ hydrocarbons plus volatile oxygenated compounds including CH ₂ O, CH ₃ CHO, and CH ₃ OCH ₃	Same as above	Both traps analyzed as trap a. above
a. Sodium chloride-ice b. Dry ice-acetone (or ethanol slush) c. Dinonyl phthalate on C-22	Same as above	General for aliphatic compounds above C ₂ or C ₃ and for many oxygenated compounds, particularly esters and ketones	Used only to check efficiency of cold traps to stop intermediate range of compounds
a. Sodium chloride-ice b. Dry ice-acetone (or ethanol slush) c. Activated alumina	Same as above	Same as above	Same as above

* Not resolved.

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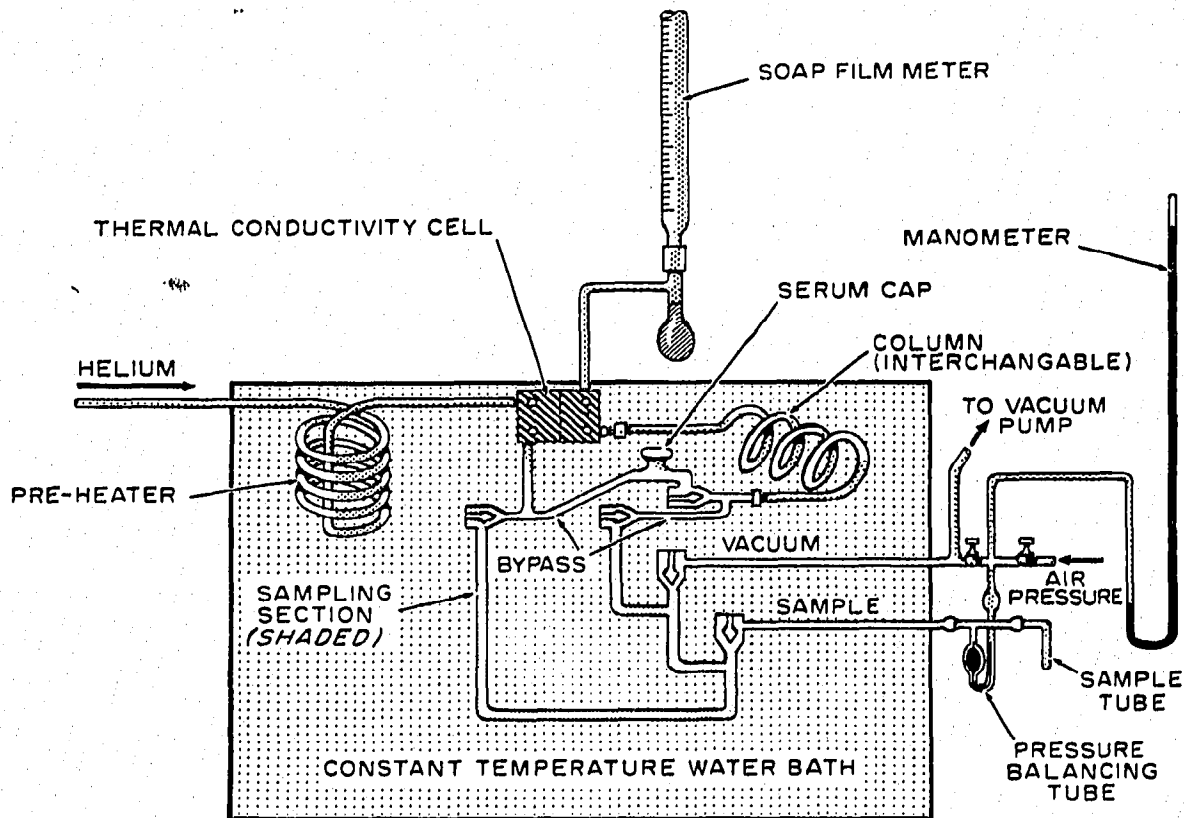


Fig. 4. Schematic diagram of gas-liquid partition chromatography apparatus.

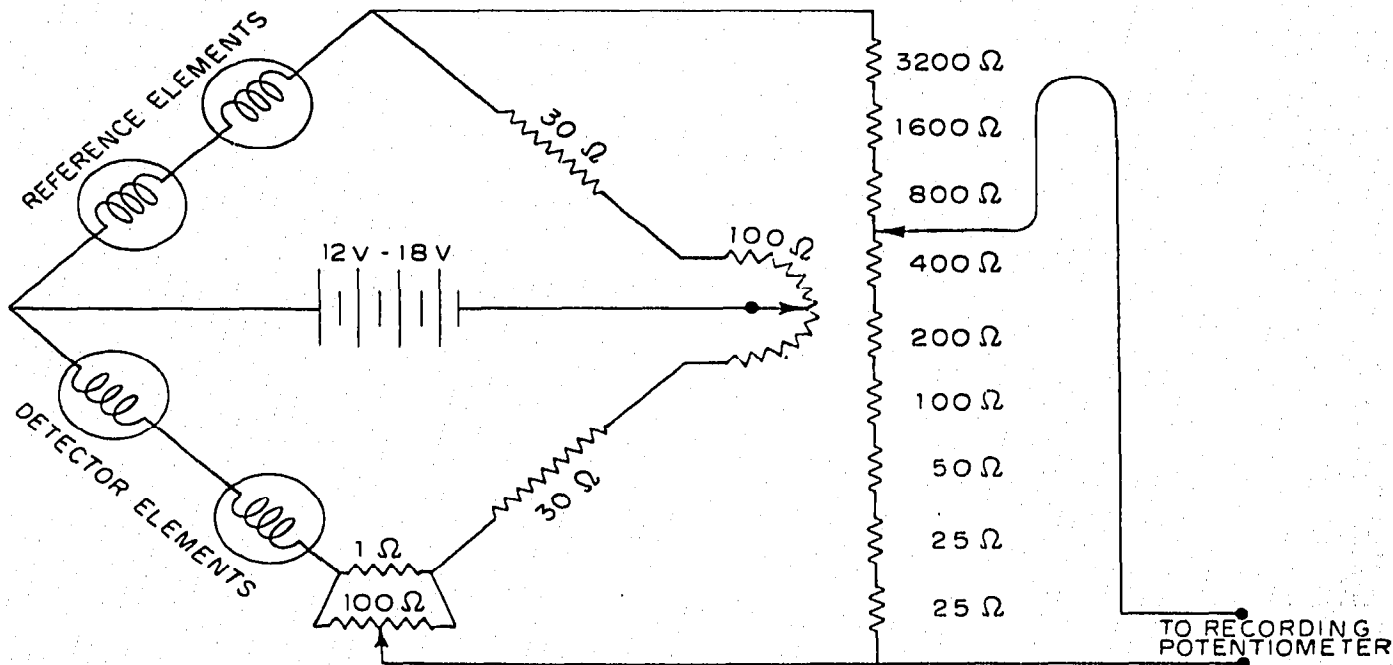


Fig. 5. Schematic diagram of bridge circuit for the gas-liquid partition chromatography system.

will be noticed that there is some overlap of utility. This provides a valuable check of one on another. The columns most often used are the high-activity charcoal and the silica gel. It is much more convenient to analyze the higher molecular weight materials in a more conventional chromatograph.

Analysis of condensed materials

The chromatography equipment used to analyze the mixtures of substances condensed in the various cold traps is essentially that which was reported by DIMBAT, PORTER

TABLE II
ELUTION DATA FOR TYPICAL COMPOUNDS IN THREE TYPES OF COLUMNS

Compound	Vacuum pump oil 1-m column at 40° Inlet pres., $P_i = 1.2$ atm Exit pres., $P_o = 1$ atm Flow rate, $f = 0.83$ ml/sec Volume of liquid phase $v_l = 4.9$ ml			Dinonyl phthalate 2-m column at 70° $P_i = 1.7$ atm $P_o = 1$ atm $f = 0.83$ ml/sec $v_l = 4.7$ ml			Polyethylene glycol 2-m column at 70° $P_i = 1.5$ atm $P_o = 1$ atm $f = 0.85$ ml/sec $v_l = 3.7$ ml		
	* t_e (sec)	** v_e (ml)	*** h	t_e	v_e	h	t_e	v_e	h
Ethane				12	7	1			
Propane				38	22	5			
Isobutane				70	41	8	20	13	3
n-Butane				105	62	13	30	20	5
2,2-Dimethyl-butane	350	265	132	355	210	43	125	82	21
Isopentane	125	95	48	205	121	25	55	36	9
n-Pentane	165	125	64	255	151	31	70	46	12
2-Methylpentane				485	287	59	155	101	26
3-Methylpentane				530	314	64	155	101	26
n-Hexane	490	371	186	645	382	78	155	101	26
n-Heptane	1450	1099	550						
Dimethyl ether	35	27	14	85	50	10	35	23	6
Diethyl ether	185	140	70	350	207	43	130	85	22
Dipropyl ether	1020	773	386	1510	894	184	520	340	89
Isopropyl ether	420	318	159	705	417	86	245	160	42
Methanol	80	61	30	320	189	39	520	340	89
Ethanol	135	102	51	600	355	73	850	555	145
n-Propanol	520	394	197	1510	894	184	1860	1215	317
2-Propanol				820	485	100	850	555	145
2-Butanol				1940	1148	236	1940	1267	330
2-Methyl-2-propanol							850	555	145
Acetaldehyde	40	30	15	195	115	24	100	65	17
Propionaldehyde	110	83	42	520	308	63	235	153	40
Acetone	120	91	46	605	358	74	315	206	54
2-Butanone				1250	740	152	670	438	114
3-Methyl-2-butanone				2200	1302	267	1000	653	170
3-Pentanone				3400	2013	413	1250	816	213
Methyl formate				215	127	26	125	82	21
Ethyl formate				590	349	72	300	196	51
Ethyl acetate				1250	740	152	600	392	102
Water				430	255	52	1140	744	194
Benzene	810	614	307	1850	1095	225	780	509	133
Toluene	2640	2001	1000	4700	2782	571	1700	1110	289

* Elution times, t_e , measured from air peaks.

** Elution volumes, $v_e = 3/2 t_e f \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1}$.

*** Partition coefficient, $h = v_e/v_l$.

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AND STROSS⁵ except that constant temperature environment has been provided by building the system into a large constant temperature water bath (Labline No. 3052).

The chromatograph is provided with a serum-cap sample-introduction port, but is designed primarily for the analysis of vaporized samples introduced from an internal, constant volume sampling section which can be bypassed by the carrier gas stream while it is being evacuated and filled. The chromatograph may be operated in the temperature range 10° to 90° with a high degree of temperature control and constancy. See schematic diagram, Fig. 4.

Because of the high-temperature limitation of the water, this system does not permit the analysis of tarry materials which are formed in greater proportions in exposures of the lower levels of radiant power.

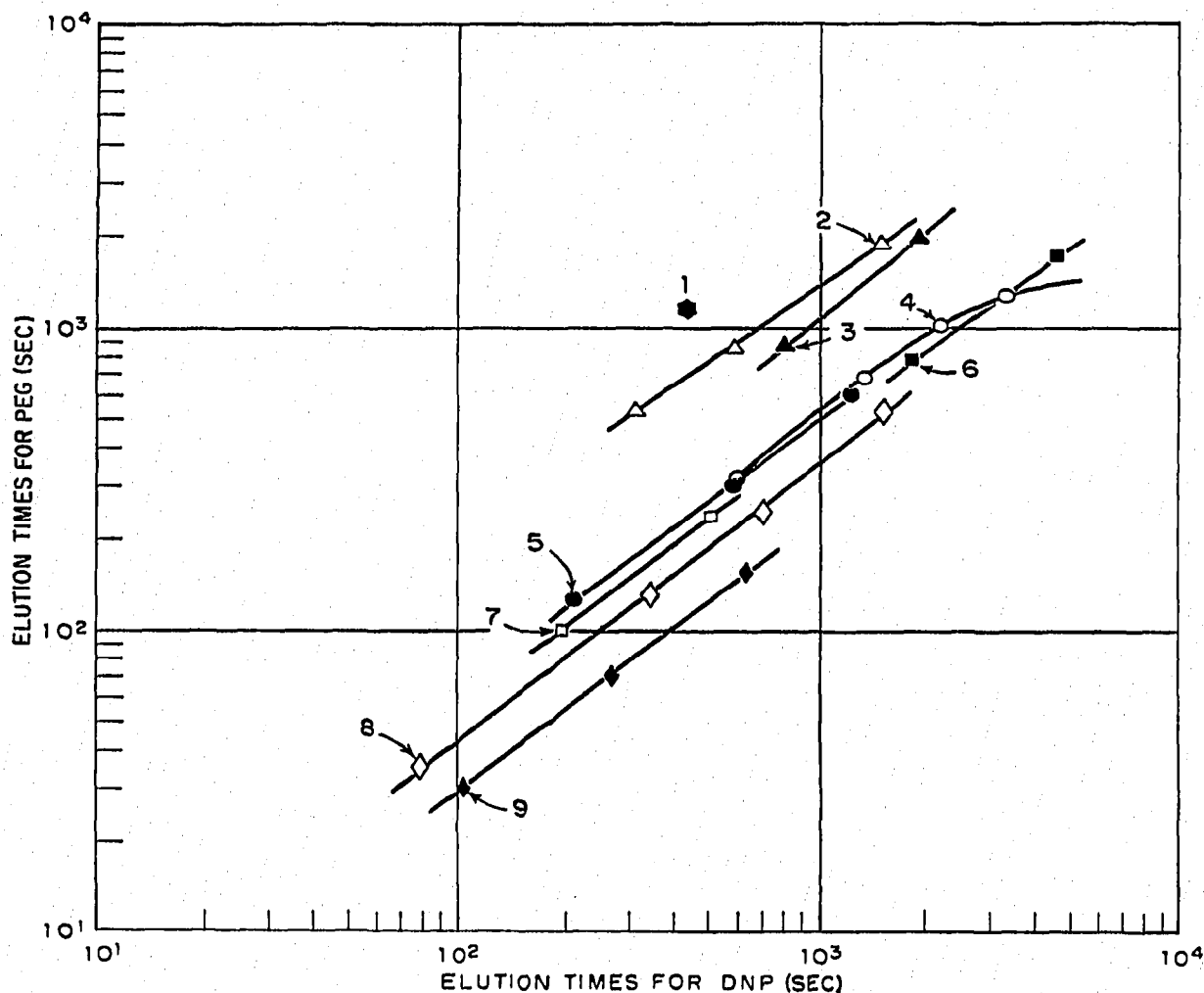


Fig. 6. Relative elution times for polyethylene glycol (PEG) and dinonyl phthalate (DNP) columns. 1. Water. 2. Primary alcohols: methanol, ethanol and *n*-propanol. 3. Secondary alcohols: isopropanol and *sec.*-butanol. 4. Ketones: acetone, 2-butanone, 3-methyl-2-butanone and 3-pentanone. 5. Esters: methyl formate, ethyl formate and ethyl acetate. 6. Aromatic hydrocarbons: benzene and toluene. 7. Aldehydes: acetaldehyde and propionaldehyde. 8. Symmetric ethers: methyl ether, ethyl ether, isopropyl ether and propyl ether. 9. Alkanes: *n*-butane, *n*-pentane and *n*-hexane.

Interchangeable columns of 1/4-in. O.D. copper tubing of lengths ranging from less than 1 m to greater than 20 m in length may be used. The solid support packing is crushed C-22 firebrick (Johns Manville) wet-sieved with running water to 40-60 mesh. Many different stationary liquid phases have been used including dinonyl phthalate, polyethylene glycol, dimethyl sulfolane, vacuum pump oil, and tetraethylene glycol dimethyl ether. In general, two meter columns of the first two of these packings are capable of resolving the composition of the condensate from cellulose pyrolysis.

The carrier gas is helium whose flow rate is kept at 50 ml (N.T.P.)/min. The flow rate is determined by the soap film method as described by JAMES⁶.

The detector is a commercially available thermal conductivity cell (TE-II geometry, 4 GT-T filament, GOW-MAC Instrument Co., 100 Kings Road, Madison, N.J.) which was potted in apiezon hard wax to obviate possible effects of continued submersion in water. The electrical circuitry is shown in Fig. 5.

Elution data and k values corrected for the pressure drop across the column⁷ are listed in Table II for three of the columns used, a 1-m column with vacuum pump oil (Cenco Hyvac) at 40° and two 2-m columns of dinonyl phthalate (Morton-Withers Morflex 190 DNP) and polyethylene glycol (Dow Polyglycol P-400) both at 70°. Following the suggestion of LEWIS, PATTON AND KAYE⁸ on the use of two columns of different characteristics as a convenient means of qualitative analysis, the elution time values for the dinonyl phthalate and polyethylene glycol columns have been plotted on log-log paper in Fig. 6 to indicate the separations afforded.

Transfer of samples

At the conclusion of an exposure, after the cold traps have been bypassed and individually isolated, their contents are transferred to small volume sample tubes which are kept at liquid nitrogen temperature until ready for analysis. Because the total condensate in any one cold trap may be as small as 10 mg and may contain a dozen or more components, it is quite important that extreme care be exercised in the handling of the sample to prevent any loss or contamination. Also it is essential to keep the volume of the sample introduction and associated pressure measuring equipment small by comparison to the volume of the actual sample introduced. The sequence of operations is depicted in Fig. 7. After the cold trap has been isolated, the sample tube is connected and communicated through the three-way stop cock of the cold trap to a vacuum pump. After the tube has been thoroughly outgassed, it is communicated to the trap section, immersed in liquid nitrogen and the trap is allowed to warm up until the condensate has been entirely transferred to the sample tube. The sample tube stop cock is then closed and the tube is transferred to the chromatograph where it is communicated to the sampling section of the chromatograph through a small-volume pressure balancing tube. The entire sampling system is then evacuated and the sample vaporized completely by warming the sample tube, maintaining the mercury level in the pressure balancing tube by continually increasing the opposing pressure. Once at equilibrium, the pressure in the sampling system is ascertained by reading the

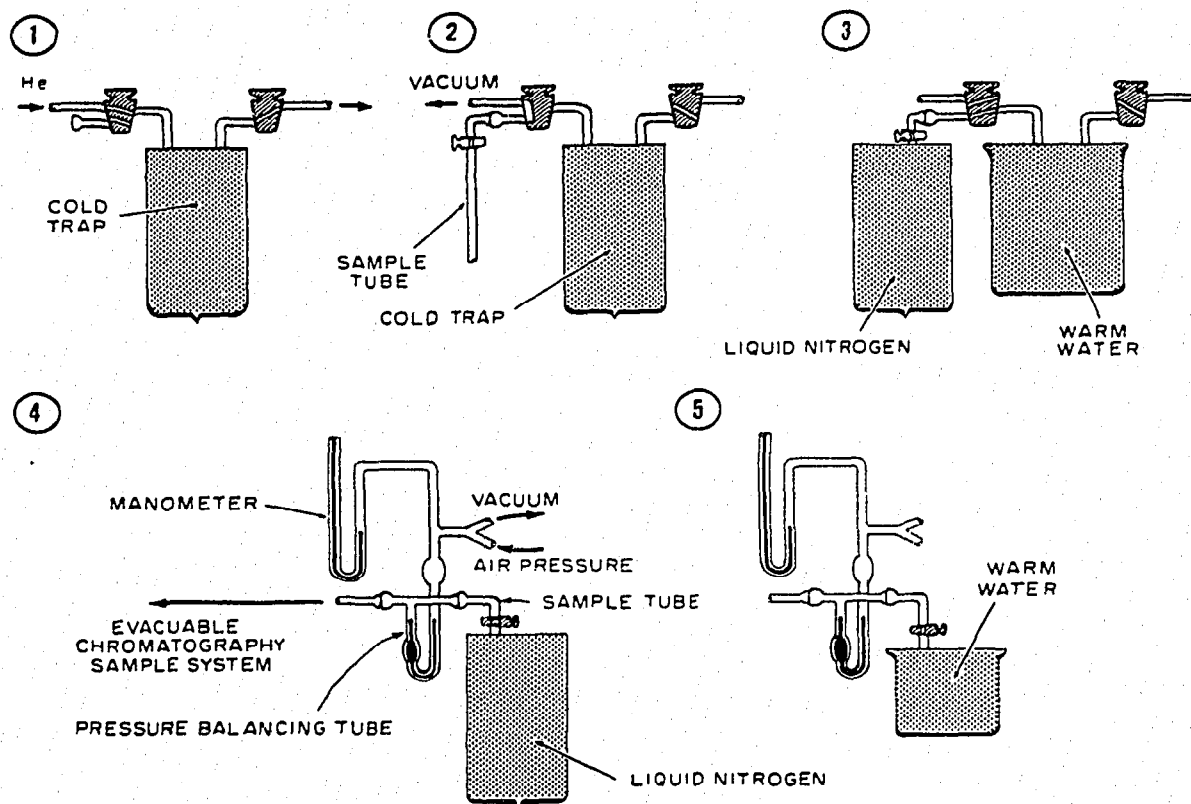


Fig. 7. Series of schematic drawings depicting sequence of operations in transfer of sample from cold trap to chromatograph.

opposing external pressure which just balances the mercury levels. Knowing the volume of the sample section of the chromatograph and its temperature, the total quantity of sample can be readily calculated. The sample is then isolated and swept onto the column and analyzed.

DISCUSSION OF RESULTS AND CONCLUSIONS

The methods described have proven to be quite satisfactory in their present application, *i.e.*, investigation of the reaction products of the pyrolysis of cellulosic solids irradiated by intense radiant energy. Products of low molecular weight (up to about 50) can be analyzed directly by a chromatograph incorporated into the exposure equipment. This chromatograph, generally utilizing gas-solid adsorption chromatography, is designed to quantitatively determine the composition of the gases which are not condensed by the cold traps which precede it. The possibility of overlooking a substance which is not retained (or of underestimating the amount of a substance which is only partially retained) by the cold trap and for which the column packing is not a suitable partitioning medium is obviated by repeating the experiment using different combinations of column packing and cold trap media. This procedure also provides a valuable check of the reproducibility of the experimental results and a means for evaluating comparisons of the quantity of substances which appear in the chroma-

tograms of different columns by the comparison of the amounts of a single substance which appear in the chromatogram of both columns.

This apparatus when used in connection with the conventional chromatograph, permits the complete separation of all of the many products occurring in the evolved vapors of cellulose pyrolysis.

SUMMARY

Gas chromatographic methods are described for determining the products evolved by organic solids (or liquid with small vapor pressure) when rapidly decomposed directly in the carrier gas stream by suitable external stimuli. The method, presently employed to study the chemical reactions accompanying the ignition of cellulosic solids by intense radiant energy, utilizes special dynamic cold traps to separate the complex products into fractions which can be conveniently analyzed by the various gas-solid adsorption and gas-liquid partition columns.

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