Oct. 4, 1966 E. L. KARAS 3,276,243

CHROMATOGRAPHIC THERMAL SYSTEM

Filed Sept. 9, 1963 4 Sheets-Sheet 1

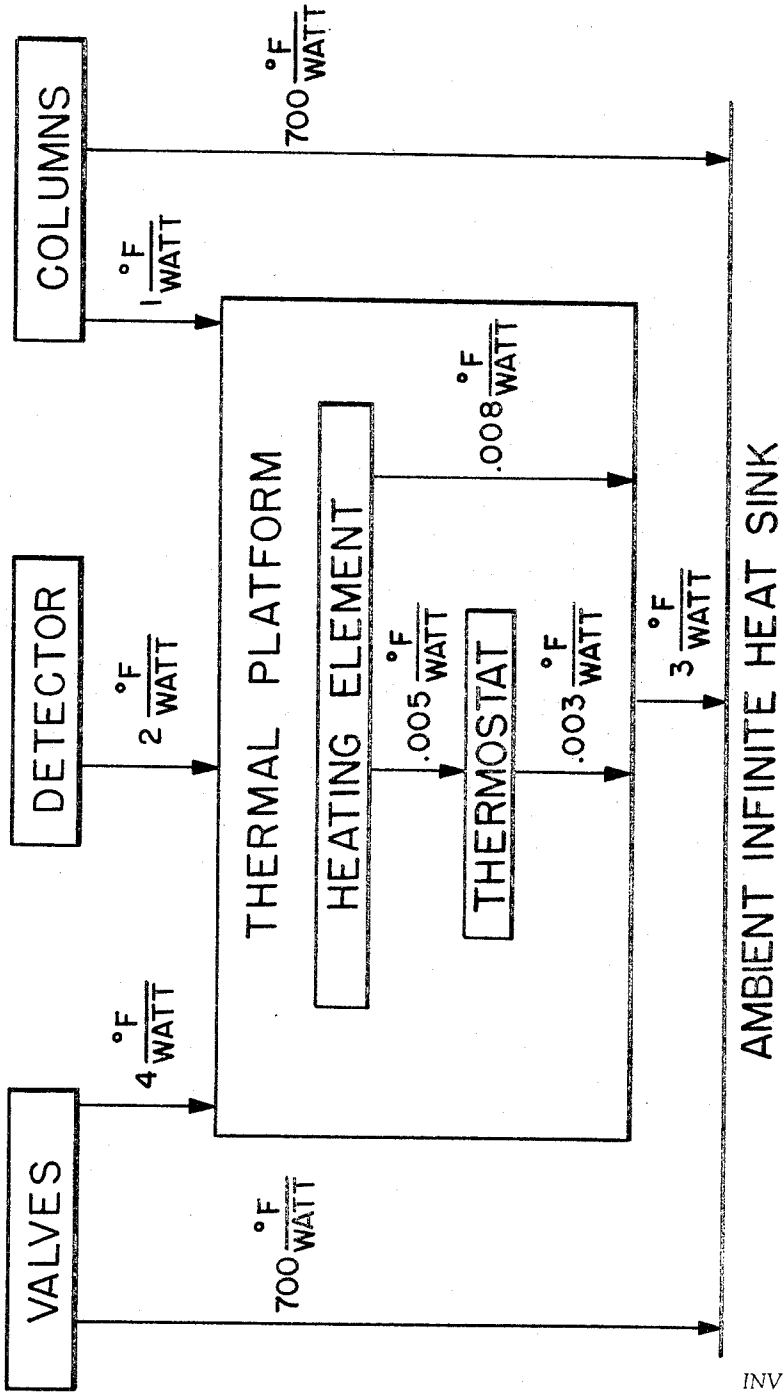


FIG. I

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ISOLATION TECHNIQUE	NOMINAL CONDUCTIVITY BTU/HR °F FT.	APPROX. HEAT LOSS AT 130 °F Δ T WATTS	RELATIVE TEMP. OF INSIDE AIR AT 130 °F Δ T	RELATIVE TEMP. OF COLUMN AT 130 °F Δ T	ATTENUATION OF AMBIENT VARIATIONS
2" THICK FLOUROCARBON FOAM	.013	4 WATTS	-29 °F	-7.5 °F	9:1
GLASS DEWAR	.001	3	-7 °F	-2.6 °F	27:1
STAINLESS DEWAR +1" ASBESTOS WOOL	.001	14	-5 °F	-1.3	54:1
1/8 COPPER CONDUCTOR +3/4" ASBESTOS WOOL.	.030	10	-2.5°F	-.5	140:1
1/4 ALUMINUM CONDUCTOR +1-1/2" CO_2 FOAM	.022	7	-1.5 °F	-.22	320:1
1/4 ALUMINUM CONDUCTOR +1-1/2" FLOURO-CARBON FOAM.	.013	4	0.64 °F	-.09	770:1

FIG. II

TABLE SHOWING EFFECTIVE ATTENUATION OF AMBIENT TEMPERATURE VARIATIONS IN THE CHROMATOGRAPHIC COLUMN, WITH DIFFERENT ISOLATION DESIGNS.

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CHROMATOGRAPHIC THERMAL SYSTEM

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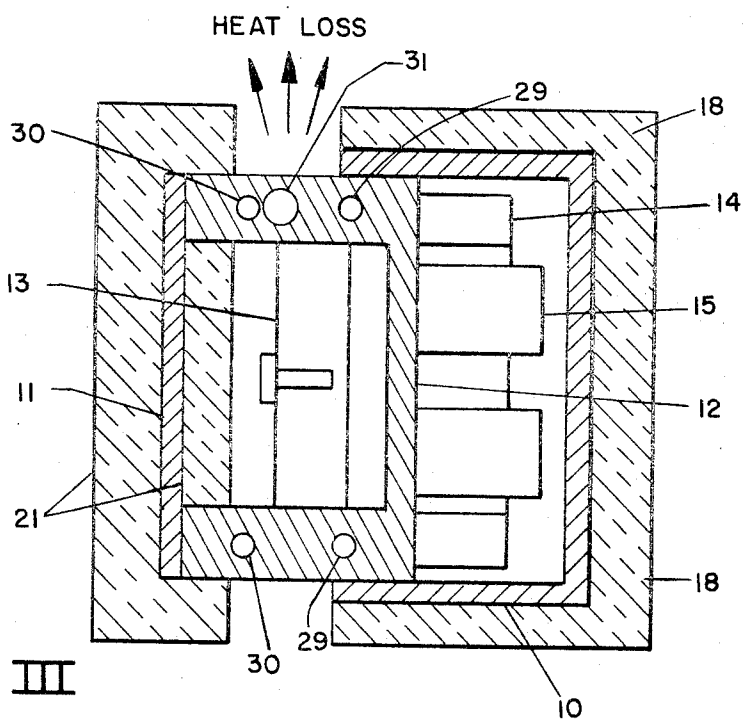


FIG. III

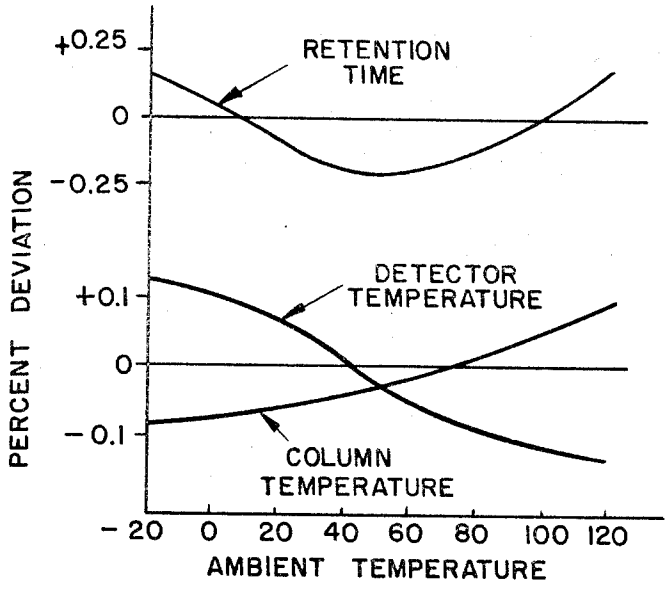


FIG. IV

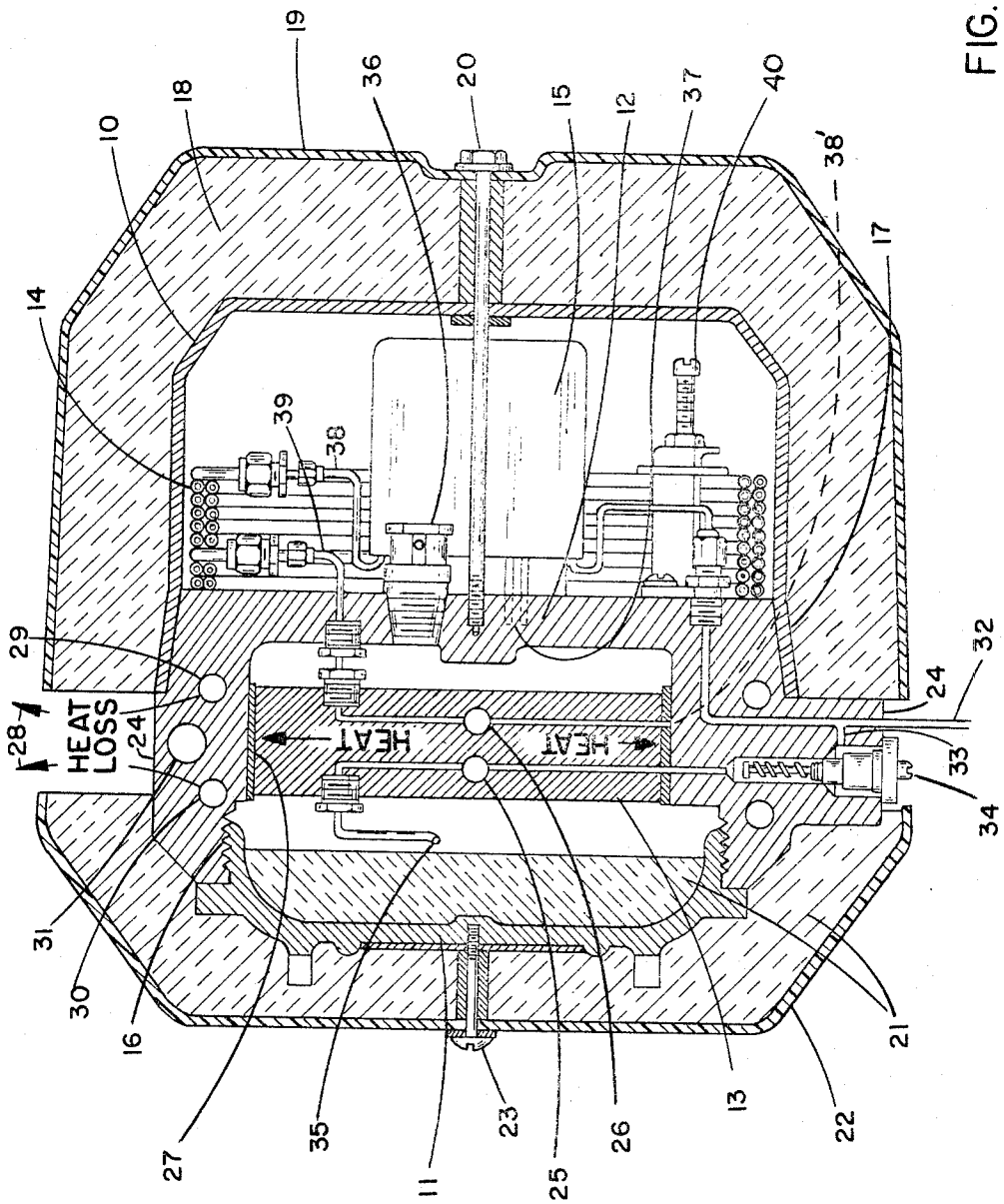
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FIG. V



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CHROMATOGRAPHIC THERMAL SYSTEM

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Filed Sept. 9, 1963, Ser. No. 307,714
2 Claims. (Cl. 73—23.1)

This invention relates to chromatographic systems and means for providing desired thermal conditions therein.

This invention provides a gas detection system which is held to an essentially constant overall temperature situation, wherein part of the system is explosion-proofed, and the remainder is made readily accessible without disturbing the explosion proofing.

The structure shown in illustration of this invention is a thermally conductive, generally spherical, hollow shell with a central transverse platform which is thermally an integral part of the shell. A chromatographic detector is mounted in one of the chambers formed by the platform, in an explosion-proof situation. Other chromatographic units such as a sampler, a column, and valving, are mounted as a group in the other of the chambers formed by the platform.

These units are established as thermally sluggish within the thermally active shell by thermal capacities of the mass of the units in conjunction with thermal resistances at the mounting interfaces between the units and the shell structure which includes the transverse platform.

A special form of differential detector is provided in that uniform and symmetrical heat flow paths are provided for the measuring and reference cells.

The shell is provided with a temperature sensor and heaters preferably in an on-off control situation. The chromatographic units are essentially isolated from the temperature control flutuations in the shell. Heat losses from the shell to atmosphere as a heat sink are set up as a temperature gradient essentially by-passing the chromatographic units.

The temperature sensor in the shell is placed closer to the outer wall of the shell than the heater elements. Thus the sensor is downstream of the heater units in the temperature gradient heat flow path to atmosphere. Accordingly when there is heat loss from the chromatographic units other than through their mountings, for example directly through the insulation when atmospheric temperature is very low, the relation of the sensor and heaters is a see-saw with the sensor as the fulcrum. Thus low atmospheric temperature drains heat from the shell at a greater rate and causes the heater to raise the whole temperature level of the shell, consequently compensating for the above-mentioned special losses of the chromatographic units.

Thermal insulation is provided about the shell, and a special heat escape may be provided by leaving some of the shell bare of such outer insulation.

Examples of features and advantages of this invention are set forth as follows:

Precise temperature control of the analyzer is essential for repeatable analyses. It is achieved by a unique design which incorporates the desirable features of both metal-to-metal contact and air bath techniques. This design yields a uniform temperature maintained within $\pm 0.1°$ F. over ambient changes from -20 to $+120°$ F.

The explosion proof casting which houses the detector is heated by two heaters, rated 175–250 watts each, operating at less than 70 watts total, cast into the housing. A precision, high-sensitivity, mercury-in-glass thermostat is inserted in the casting at the point of major heat loss so that control action balances heat input with heat loss to maintain the casting at constant temperature.

A highly conductive metal shield is placed in contact with the heated casting and over the section in which the valve and column are located. Thus, the valve, column, detector and other temperature sensitive elements are thermally coupled to the casting and effectively insulated from the amibent so that they stabilize at the fixed casting temperature.

The thermal dome can be removed, columns, valves worked on (or replaced) without turning off electrical power.

Gas flows may be adjusted externally without touching or upsetting thermal system.

Thermal system should have high reliability, for there are few parts that can fail—heater, thermostat, relay.

Instruments on front panel are convenient check on instrument performance.

Instrument combines advantages of both air bath and metal conduction type analyzers:

Simplicity, reliability of solid conduction,
Accessibility, serviceability of air bath.

Entire instrument is weatherproof and may be mounted outdoors on pedestal, pipe or rack.

Temperature control is precise over full outdoor temperature range.

Analyzer accepts either T.C. detector or flame ionization detector.

The thermal platform serves five functions:

(1) Explosionproof thermostated enclosure for electrical elements.

(2) Non-explosionproof thermostated chamber for columns and valves, and other pneumatic element to enable access to these elements without danger.

(3) Mounting platform for all principal components.

(4) Manifold for several gas flows.

(5) Heat exchanger to preheat some gas flows.

Column temperature stability achieved by locating so as to divide the temperature gradient between platform and ambient in the ratio of 1 to 700, or

Column is positioned so that ambient temperature variations will be attenuated at least to $1/700$ its full value, or

Column chamber insulation designed to provide 700 times the average thermal resistance existing between platform and column.

Temperature correction in on-off temperature control—by locating the thermostat on the thermal gradient between heat source and heat sink (ambient), the average heat source temperature will rise when the heat sink temperature falls. This corrects or cancels the normal fall of average heat source temperature when the heat sink temperature falls.

This correction is incorporated in the design of the thermal platform. The action is analogous to a seesaw with the thermostat being the fulcrum, height of each end representing its temperature.

Reduction of thermal drift and noise within differential thermal conductivity detector—each measurement cell and its reference cell are located so that any variations in heat flow affect both cells equally.

This is accomplished by providing a small resistance connecting the cells to their heat sink. This high resistance is distant from the cells, placed symmetrically to both cells.

Platform temperature control achieved by system containing:

(1) A thermal capacitor (platform casting) which is thermally charged and discharged through a narrow span.

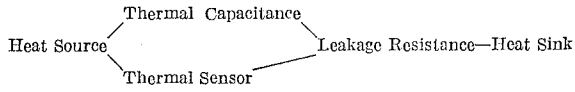
(2) Two integral heat sources to charge the capacitance.

(3) A thermal leakage resistance to discharge the capacitor.

(4) A temperature sensor to regulate charging of the capacitor.

(5) A relay triggered by the sensor to control power to the heaters.

The heat source, capacitance, sensor and leakage resistance are connected in a series parallel arrangement as:



Heat conducting gasket

Consisting of several layers of aluminum foil sandwiched between two parallel surfaces of objects which are to be thermally connected.

The gasket increases the number of contact points between the objects and effectively decreases the thermal resistance between them.

In addition, the two objects are pressed together to increase contact area. In addition, the air in the spaces is replaced by helium which conducts and convects heat more effectively than air.

In a dead air space of a chromatograph analyzer reduction of temperature differences—by replacing the air with helium vapor.

The higher conductivity of helium helps to equalize temperatures within thermostated chambers.

Helium obtained from thermal conductivity detector reference vent.

It is therefore an object of this invention to provide a new and useful chromatographic thermal system.

Other objects and advantages of this invention will be in part apparent and in part pointed out hereinafter, and in the accompanying drawings, wherein:

FIGURE I is a block diagram of the thermal pattern according to this invention;

FIGURE II is a table of temperature variations with different isolation designs;

FIGURE III is an illustrative showing of the main elements of a device according to this invention;

FIGURE IV is a graphic showing of ambient temperature vs. percent deviation; and

FIGURE V is an illustration like that of FIGURE III, in more detail as to the system.

Referring first to FIGURE V is an illustration of the structure and body of this invention:

In FIGURE V, a thermally highly conductive hollow shell, very generally in the form of a sphere, is provided by the combination of a conductive liner **10**, an explosion-proof cover and liner **11** and the outer periphery of a thermal platform **12**. The platform **12** itself provides a transverse partition within the overall thermally conductive shell in identical thermal situation therewith. The partition divides the inside of the hollow shell into two main chambers. In one of these chambers there is mounted a chromatographic detector block **13**, and in the other a chromatographic system combination of a chromatographic column **14**, and a sample selector and other valving assemblage as at **15**.

The explosion-proof cover and conductive liner **11** is mounted on the thermal platform unit **12** by means of a screw thread arrangement as at **16**, providing a highly thermally conductive connection. The conductive liner **10** is mounted on the thermal platform **12** in a conically tapering surface connection as at **17**, wherein there is provided an aluminum foil gasket throughout, for solid highly thermally conductive connection between the platform **12** and the conductive liner **10**. A body of thermal insulation as at **18** is mounted over the conductive liner **10** and is provided with an outer cover **19**. This whole assemblage is removably mounted to the platform **12** by means of a dome mounting bolt **20**. The detector side

of the device is provided with an outer insulation **21** both inside and outside of the cover **11**. Suitable lugs are provided on the cover for unscrewing the cover from the main platform **12**. An outer cover for the insulation is provided at **22**, and a mounting bolt **23** is provided for mounting the outer insulation and the outer cover **22** to the cover **11**.

It will be noted in this illustrative embodiment that the insulation caps do not meet and there is a circular surface area as at **24** of the peripheral portion of the thermal platform **12** which is exposed to atmosphere as a direct heat flow escape path to atmosphere as a heat sink.

The detector block **13** is provided with a detector reference cell **25** and a detector measurement cell **26** which may be heat producing as in the thermal conductivity cells. The detector block **13** is mounted in a cup-like arrangement of the thermal platform **12**. The block **13** is a rectangular cross section bar which has contact only at its ends through thermal resistance such as a layer of rubber at **27**, thus the detector block is thermally isolated on its sides by air or gas and has only an axial heat path of main temperature gradient through the outer periphery of the thermal platform **12** to atmosphere as a heat sink is indicated by the heat loss arrows **28**. Thus the reference and measurement cells are thermally uniform and symmetrical and therefore each side of the cell that is, reference and detector is thermally identical because of this axial flow path. This is an important factor in providing highly precise measurement situations especially in that these reference measurement cells **25** and **26** are in themselves heat producing units and this heat must be taken off in a uniform symmetrical fashion as between the detector and the reference. Because of this actual flow situation as indicated within the detector block **13** by the heat escape arrows, the heat takes the simplest path and therefore the air around the block is strongly, firmly insulative.

With this arrangement the fluctuations in temperature in the thermal platform **12** are filtered out with respect to the detective block **13** so as to maintain a detector block in a constant temperature situation. This detector block is thus in the explosion-proof section of the inside of the overall thermally conductive shell.

In the other chamber of the shell, that is, the chamber outerly defined by the conductive liner **10**, the assemblage of chromatographic units, the column **14** and the sampler unit **15**, are similarly thermally isolated with respect to fluctuations of temperature in the thermal platform **12**. They are mounted on the platform **12** in that the chromatographic column **14** and the sample and valving units rest on the platform. The interfaces of these bodies provide thermal resistance which is sufficient to be comparable to the thermal resistance **27** for the detector **13** in the other chamber. Thus the nonexplosive portions of the chromatographic system are also thermally isolated and filtered from the temperature fluctuations of the thermal platform **12**, and the outside atmosphere.

Thus the main heat loss path from the thermal platform **12** is as indicated by the arrows **28**. Further throughout the outer shell throughout the device there is a heat loss path from the conductive liner **10** and the other chamber conductive liner **11** through the thermal insulation **18** and **21**.

The main heat loss path from either detector block **13** or the chromatographic units **14** and **15** are through their connection to the thermal platform **12** by way of the thermal resistance established therebetween as previously indicated.

There are situations in which the loss from the chromatographic non-explosive units, that is column **14** and in the sampler **15**, is in fact through the surrounding air within the liner **10**, through the liner **10**, and the insulation **18**. Such losses occur for example when the surrounding atmosphere is at a very low temperature. When this happens there is a compensating overall raising of the temperature of the thermal platform **12**.

This is accomplished by an arrangement of a pair of heat sources 29 and 30 arranged on the perimeter of the thermal platform 12. In addition a temperature sensor is provided at 31 in the periphery of the thermal platform 12. Note that the temperature sensor 31 is closer to the atmosphere, the outer space of the thermal platform 12, than are the heat sources 29 and 30. The temperature sensor is downstream in the thermal gradient to the heat sink with respect to the heat sources 29 and 30. Because of this a very low temperature outside will cause the heaters 29 and 30 to stay on for a longer period thus raising the overall temperature of the thermal platform 12, and therefore raising the temperature of the chromatographic unit 14 and 15, to compensate for extra heat loss directly through the insulation 18 under unusual situations such as long term operations or very cold outside conditions.

For the chromatographic systems a carrier gas inlet is provided at 32. This leads in through the thermal platform 12 so that the carrier gas comes to the temperature of the thermal platform before being applied to the sample valve 15 and the columns 14. In a branching arrangement the carrier gas inlet is provided with a passage 33 which leads through a flow adjusting valve 34 to the detector reference cell 25. The reference cell 25 is vented as indicated at 35 into the space around the detector block 13 within the overall shell. This vented gas eventually disperses through a breather vent 36 leading into the space around the non-explosive portion of the column in the other chamber, and then gradually leaks out through the cover mounting of this other chamber past the aluminum foil gasket 17.

For the chromatographic process, passages for the introduction and removal of sample are indicated at 37 with suitable entrances (not shown) like that of the carrier gas. These sample passages also contact the thermal platform 12 so that the sample gas achieves the same temperature as the carrier gas, that is, the temperature of the thermal platform.

From the sampling units into the column there are according to selection, sample and carrier gasses entered by means of a pipe 38. Having passed through the various coils of the column they are exited through a pipe 39 leading to suitable couplings into the explosion-proof section of the device and to the measurement cell 26. From the measurement cell a vent is provided, as indicated by dotted line 38', suitably extending through the thermal platform 12.

Some dummy coils for the purposes of thermal contact as shown below the actual chromatographic column and in actual contact with the thermal platform 12, and a column mounting bracket 40 is provided by holding the column to the platform 12.

Of those characteristics which distinguish process control instruments from all others, reliability stands at the head of the list, with safety, simplicity, and ruggedness not far behind.

The heart of the chromatograph—the column—is a natural for process application, for these qualities are just a few or its inherent properties. Confidence in a chromatographic analyzer then hinges on how well the supporting elements of the system contribute to these characteristics.

The thermal support system plays a determining role in the overall analyzer design, and must in the final analysis answer to the challenging requirements made of it. This paper considers these requirements, and applies a simple analytical approach to evolve a basic analyzer design intended to meet the specific needs of the process industries.

The thermal environment for a chromatograph is one of the more involved elements in the system, due to the strong temperature dependence of gas kinetics in the separating columns, and to temperature sensitivity of certain detectors. Emergence time of components from

separation columns varies from 1 to 3 percent per degree Fahrenheit, requiring stability in the order of ±.1° F. for the analysis repeatability expected of a process control instrument. Thermal conductivity detectors must have stability during a single analysis close to ±.01° F. to avoid baseline shifts, although long term variations are zeroed out before each analysis cycle.

A fundamental principle for holding such components at constant temperature is to couple them to a fixed temperature source and eliminate all other avenues of heat transfer to and from the components. The components must then come to thermal equilibrium with the fixed source, their only environment. The source acts as a collective agent dealing with changing ambient conditions, leaving sensitive components isolated from external conditions.

A number of available thermal systems are capable of fulfilling this function. However, a suitable system for process control instrumentation must meet stringent demands other than temperature stability. Since it is strictly a support system, it should not be the cause of servicing attention or instrument shutdown. Operation outdoors at the process site is oftentimes necessary to avoid dead time in transporting sample to the analyzer. With atmospheres at the process generally considered hazardous, heating and control must be achieved with assured safety.

Fast and direct access to principal components poses the most challenging demand. Explosionproof housings constitute a severe restriction and are not desirable where they would handicap access to harmless pneumatic elements—the major portion of the analyzer. A thermal enclosure for these elements must also be removable to the extent of providing at least three-sided access to the columns and valves.

Two design concepts can be combined to fulfill these requirements. Accessibility and safety can be achieved by localizing electrical heating to a small area and distributing heat over the components by some conductive medium, either fluid or solid. High reliability can be expected in a system which takes maximum advantage of passive elements and minimizes mechanical and other activity. Passive elements are those requiring no energy source to function, performing entirely by use of inherent physical properties, with no chance of failure unless the material is destroyed.

The heart of a chromatograph—the column—owes much of its desirability to the fact that it functions as a passive (reactive) element. Since it is possible to take advantage of passive elements (heat conductors and insulators) to channel heat transfer, we may avoid the mechanical complexity of circulating air baths, and obtain a simple and rugged unit.

Use of insulation does not eliminate all heat loss from sensitive components, but simple analysis shows to what extent components should be isolated. Consider a thermal platform, maintaining an absolutely fixed elevated temperature. Mounted to it are components expected to remain within a ±.1° F. temperature. These are covered by insulation separating them from an environment varying from 120° F. to −20° F., or ±70° F. We will require, then, that the components vary only $1/700$ of environment variations. For one dimensional heat transfer, this means the thermal resistance between components and ambient must be 700 times greater than between components and platform. This is directly analogous to a voltage divider, set at 700 to 1 attenuation of noise amplitude. An electrical analogy is valid, for one-dimensional heat flow obeys an Ohm's law relationship with temperature and thermal resistance. Other criteria concerning detector and platform thermal impedances and heater control combine to establish a coupling relationship diagrammed in FIGURE I. A hybrid resistance unit is used because it makes thermal magnitudes more apparent.

A design model was built to express the relationships in FIGURE I and given thermal tests to arrive at the prescribed isolation for the column and valve chamber. The initial approach used only foam insulation of very low conductivity. Results were quite poor, yielding ambient sensitivity in the column fifty times too great. Since high vacuum provides a much better insulation value, Dewar flasks were next tested. Results improved slightly but were far from satisfactory, due to an excessive amount of heat conducted from the inner to the outer shell at the neck of the shallow Dewar. The thermal platform could not provide this heat flow directly without excessive temperature drop, for good thermal coupling to the Dewar is not easily accomplished. In addition, the outside of the Dewar becomes quite hot and difficult to handle.

Since insulation alone is inadequate, it was combined with a conductive liner, capable of delivering the amount of heat lost through the insulation, directly from the cast platform. Results were far better, leading to a final design of foamed-in-place fluoro-carbon blown foam over an aluminum conductive liner. The foam is completely encased in Fiberglas and aluminum which retards outgassing of the foam to maintain the original low conductivity. The highly conductive liner gives the advantage of distributing heat in a way which tends to equalize temperatures throughout. This minimizes the effects of non-uniform heat loss from the exterior of the enclosure which could cause internal gradients.

FIGURE II traces the results of these isolating techniques. Generalizations from this data should be made with caution, for these results pertain to a unit of certain size, proportion, and design characteristics. Extrapolation to systems with different parameters may not be valid, and would require specific tests with that system.

A vital requirement of this conductor-insulator design is that there be no temperature drop between the thermal platform and the conductive lining. Since metallic interfaces make contact at relatively few points, they create a significant thermal resistance. Heat transfer area must be generous, and a thermal gasket plus clamping pressure are required to minimize this resistance. An effective heat transfer gasket consists of 4 to 12 layers of common aluminum foil, depending on surface flatness. This increases the number of contact points considerably, with surprisingly effective results. Six layers are used in this system, reducing the temperature drop below our ability to measure it.

In an operating analyzer, the air enclosed under the isolating cover is replaced by helium venting from the detector's reference cells. Helium's high thermal conductivity would further reduce the inside air temperature drop, but was not used in these tests. The slow helium purge also minimizes corrosion and hazard from any leakage of sample.

Shaping the isolating cover in the form of a shallow dome permits a relatively simple mechanical design for the thermal platform and component mounting, as shown schematically in FIGURE III. The right side of the platform **12** under the removable isolating dome accommodates pneumatic components—columns **14**, valves and flow restrictors. The left side forms an explosionproof enclosure for the detector **13** and heater connections. A flat cover **11** completes the explosionproofing and also serves as a thermal conductor for heat lost through the cover insulation **21**.

The heated platform completely encloses and isolates the thermal conductivity detector from the ambient, as prescribed by FIGURE I. Heat generated by the detector conducts out each end directly to the thermostated walls of the platform, where it is used constructively in helping the heaters provide for external heat losses.

The platform is self temperature controlled by means of integral electrical heaters and thermostating. Several types of heating elements may be used, but cast-in heaters provide optimum performance. This results from the close thermal bond between the heaters and platform, causing heat to diffuse rapidly and evenly into the platform metal. Non-uniform gradients are eliminated, and the thermostat is able to respond within fifteen seconds, each time heat is applied. During warmup, this close bond and the high thermal diffusivity of the platform prevent heater cycling until the control temperature is reached, at which time control commences smoothly as in a critically damped system. With columns, valves and detector also closely coupled to the platform, there are no long time constants to retard stabilization from warmup, which occurs in two to three hours from a cold start.

Two heating elements, each forming an 8-inch ring, follow the perimeter of the platform in the area of external heat loss. An uninsulated band around the platform perimeter is used to channel the principal external heat loss in a symmetrical and predictable pattern. The heat flow path from the heaters to the platform edge is very short, and the heat transfer area wide, to reduce gradients within the platform. Even in solid aluminum, a low heat flux of one watt per square inch would cause a gradient of .6° F. per inch—far beyond the tolerances allowed in a chromatograph.

The total heat loss from the platform must be sufficient to dissipate the detector heat output and discharge some of the platform heat capacity each heater cycle for on-off control. Numerically, a heat capacity of one watt-hour per degree F. requires a six watt heat loss to discharge 0.1° F. per minute. The design resistance to ambient of 3° F. per watt provides satisfactory discharge out to both extremities of the analyzer operating range.

Heater wattage rating can similarly be defined with simple calculations, for recharging in the same length of time requires a heat input twice the loss. Heaters rated 125 watts each are connected in series to produce 62 watts for low control temperatures, and in parallel for 250 watts in high temperature analyzers. Development tests have established these ratings sufficient for the full range of operating conditions, including fast analyzer warmup.

Relatively low heater power is desirable just from general principles, for it lessens thermal gradients, and generally creates fewer problems. The long length of perimeter heaters reduces wattage densities at the heater's surface to very low levels, resulting in low operating temperatures of the elements and virtually unlimited life span. Tubular heaters have long proved their reliability in severely demanding service, such as electric range surface elements. Cast in, they ensure a rugged reliable unit.

Since on-off control of heaters has proved to be a reliable, simple and inexpensive means of temperature control, it has been integrated with the heat transfer pattern in this system. However, the manner of integration to the thermal system is critical for satisfactory control at chromatograph tolerances and several requirements must be considered analytically.

First, the thermostat must be closely coupled to both the heat source and the ambient heat load, in order to limit heater excursion by a short cycle and to minimize temperature offset resulting from load variations. The static operating differential of the thermostat is .05° F., but its thermal capacitance and coupling resistance to the heater create a response time lag which increases the platform temperature excursion. In typical operation, where heat loss may be 15 watts, heater power 60 watts, and the heater is on 22 seconds each cycle, the net energy input to the platform is 45 watts for 22 seconds, or .27 watt hour. Treated as a single heat capacity of 1.5 watt hour per degree F., the platform would rise 0.18° F. This amplitude remains fairly constant with heaters on from 6 to 94 percent of each cycle.

A second requirement is that the thermostat sensing

element lie on the same isotherm controlling both critical components—the columns and detector, regardless of the temperature variations in between. Because of the characteristic linearity of conduction heat transfer, several points located on one isotherm during one ambient load condition will remain on an isotherm under other load conditions, provided non-linear effects (radiation, mass transfer) are not introduced.

One end of the detector is located right at the thermostat to satisfy this requirement. The other end is identically controlled through platform symmetry. This symmetry also insures that the local region sensed and controlled by the thermostat is representative of the entire platform perimeter, which mounts the columns.

A third requirement in relating the thermostat to the system is caused by finite response times of thermostats, which allow the cast platform to have temperature excursions of fairly constant amplitude. But as ambient loads vary, the heat capacity of the platform charges and discharges thermal energy at different rates, so that the allowed excursion is greater downward during cold ambient conditions and greater upward in warm conditions, though always including the thermostat set point. To compensate for this shift, the thermostat is located on the thermal gradient between the heaters and load. This elevates the platform temperature band slightly with colder conditions, and negates the natural downward shift. The mean temperature then stays fixed. It is possible to adjust this compensation during factory performance tests to achieve required temperature stability.

This compensation technique is further extended to the column to minimize the effect of the slightly lower air temperature under the isolating dome. The column, coupled to the platform but also exposed to the chamber air, assumes a temperature somewhere between the two. By elevating the mean platform temperature slightly more the column temperature rises closer to the thermostat setting. In terms of the voltage divider analogy, the center tap is moved closer to zero for lower signal level or higher noise attenuation.

The measured temperature stability in an analyzer incorporating the foregoing design relationships is shown in FIGURE IV as a function of outdoor temperature. The analyzer was operated at 130° F. and contained an 8-foot coiled column and a two-filament thermal conductivity detector. The retention time deviation is of a butane peak in helium carrier, and is due to ambient temperature effects only, for the test prevented deviations due to possible flow changes. Peak size variation would be similar to that of retention time.

This degree of independence from outdoor temperatures is both necessary and sufficient to locate the analyzer at the process, where a process instrument belongs. Thermal system reliability should be high, for the major portion of the system works with passive conducting and insulating materials. The four active elements each have high reliability figures. The mercury in glass thermostat has a minimum of five million cycles (equivalent to five years operation); its hermetically sealed relay 100 million cycles; while the two heaters have a very long, but unknown, life as used. Failure of either of the two heaters still allows operation on the remaining heater, but with a widened platform temperature band. For percent type analyses, this would be satisfactory.

The differential thermal conductivity detector is another critical element whose stability must be assured in analyses used for process control. At maximum sensitivity, hot wire filaments each produce nearly one watt of heat, dissipated through some fixed resistance to a constant temperature sink. The direction and nature of this heat dissipation have a marked effect on the detector's thermal noise level and stability.

Reference filament matching attenuates sensitivity to changes in overall block temperature, but does not reduce response to changing thermal gradients between cells. These result from coupling the detector to its environment, whose very slight temperature fluctuations can introduce significant heat flow changes, resulting in signal noise. To eliminate this source of noise, thermal resistances between each cell and the environment should not differ by more than 1 percent, requiring absolute symmetry in relating referenced pairs of cells to the pattern of heat transfer. Both these requirements may be met by symmetrically locating the two or four cells in the center of a long block, with cell heat output passing axially out both ends of the block through resistance gaskets. A long flow path is necessary to assure similar heat flow patterns from each pair of cells.

The gaskets serve a dual function, for their resistance can give the block a thermal time constant sufficient to dampen out response to heater cycling. The allowable limit for short term detector cycling may be derived from its temperature uncertainty coefficient which averages 167 micro volts per degree F. For ¼ percent noise limit into a one millivolt full scale readout, or 2.5 microvolts, the maximum temperature variation is ±.017° F. A ten to one attenuation is required from the platform cycle, which ranges to ±0.12° F. The detector may be considered a single capacity system, with a thermal time constant represented by its heat capacity times coupling resistance to the platform. To attenuate by ten to one, a time constant slightly greater than the longest heater cycle is needed, and was chosen to be approximately seven minutes. This has been validated in sensitive chromatographic analyses where no heater cycling was evident in the detector output at five minute cycles or less, but was evident beyond eight minute cycles. Longer detector time constants are neither necessary nor desirable for a process analyzer, for warmup time and drift are adversely affected with loose detector coupling.

Using the two end gaskets as seals for gas flow permits a plug-in design for the detector. This feature is useful in the field, for detector filament life is limited in certain applications, so simple, fast replacement is desirable.

The often complex traffic of binary gas mixtures in the analyzer has caused concern for how cumulative valving and tube connections affect process analyzer performance. A promient effect is peak tailing, which necessitates greater peak separation and longer analyses to overcome. Another effect is peak shadows or memory, which must be eliminated for reproducible analyses. Investigations have shown both are usually attributable to side capacities or cavities in binary gas flows, and have pointed out the need for extremely careful valve, tubing, and connection design.

Binary gas flow Reynold's numbers, representing the ratio of inertia to viscous forces, range from 20 to 40 in a chromatograph, so that inertia forces in the gas predominate even though the flow is completely laminar in straight passages. For this reason the gas cannot quickly change direction to sweep out sudden increases in flow area, or side capacities, or other misalignments in flow geometry.

To avoid tailing due to this source, tube connections in sampler and other valves are brazed in, using careful brazing techniques to eliminate even minute side cavities at tube ends. Tube connectors are minimized in the system, and those remaining are chosen to have the least side capacity. The fitting leading into the measurement side of the detector is particularly critical and is specially made for its function. Standard tube to pipe thread connectors at this point distort eluted peaks.

Interconnecting tubing lengths generally are kept short to reduce dilution of the sample in carrier gas. Some carrier flows not containing sample are manifolded in the thermal platform to preheat the gas and to further simplify connections. When so manifolded at constant wall temperature gases preheat to operating temperature within an inch of entry at chromatograph flow rates. Flow restrictors, manifolded in the platform edge, allow

flow adjustments without entering or upsetting the thermal system. Flows of pure sample are not manifolded, nor do they ever enter the explosionproof enclosure where leakage might create a hazard.

Columns can often be given longer life spans and perform faster analyses with a design optimizing technique resulting in relatively low analyzer temperatures for many high boiling samples. Low operating temperatures benefit the chromatograph user in several less obvious ways also. A wider choice of column partitioning liquids is available for low temperatures. The column partitioning liquid volatilizes at a slower rate, allowing an extended working range in flame ionization detectors—sensitive to such low flows as a background signal. The flame ionization detector is enclosed in the analyzer system when an analysis of very high sensitivity is required. In addition, maintenance requirements on the system are likely to be lower, for valve life is extended and corrosion rates are lower.

As a result of pursuing the objectives set forth at the beginning of this paper, several secondary benefits accrue in the resulting instrument. The supporting systems are built with relatively few components, most of them intuitively understandable to technicians. As a result, trouble shooting is direct and straightforward. Once connected to power, the thermal system can be forgotten, for it needs no adjustment, no start-up procedure, or other consideration.

The compact size of the analyzer "head" unit permits a self-contained analyzer system in one enclosure, with design freedom to include convenience features such as indicators for monitoring operation. The vertical platform principle of double sided accessibility has been carried into the enclosure for similar access to accessory components. Full covers on both sides hinge downward to form trays during servicing.

Air supply for the analyzer is used only for valve operation, and need not be specially cleaned or regulated. Power consumption is low, making lesser demands of electrical power connections to the instrument. The 80-pound instrument weight lightens the task of installation.

This invention, therefore, provides a new and useful chromatographic thermal system.

As many embodiments may be made of the above invention, and as changes may be made in the embodiments set forth above without departing from the scope of the invention, it is to be understood that all matter hereinbefore set forth or shown in the accompanying drawings is to be interpreted as illustrative only and not in a limiting sense.

I claim:

1. A thermal system for a chromatographic device wherein said device includes a sampling unit, a column, and a detector, suitably interconnected as a chromatographic system,

said thermal system comprising a thermal housing, two separate chambers within said housing, and a thermal platform forming a wall fully separating said chambers,

said sampling unit and said column being mounted on one side of said platform in one of said chambers, said detector being mounted on the other side of said platform in the other of said chambers, and said detector chamber being explosion proofed,

means for opening said sampling unit and column chamber without opening said detector chamber,

means for opening said explosion proofed detector chamber without opening said sampling unit and column chamber,

said thermal housing comprising a first thermal insulation cover unit defining the chamber of said sampling unit and said column with said thermal platform,

a second thermal insulation cover unit defining the chamber of said detector unit with said thermal platform, said cover units each having a thermally conductive inner lining thermally contacting said thermal platform,

a spacing between said cover units such that said thermal platform is exposed in a full peripheral outer wall strip area directly to atmosphere as a heat sink,

heater means in said thermal platform essentially directly between said detector and said exposed thermal platform outer wall strip,

and heat sensor means in said thermal platform essentially directly between said heater means and said exposed thermal platform outer wall strip.

2. A thermal system according to claim 1, wherein

said thermal platform is in the form of a thick walled cup, with said outer wall strip area provided by a portion of the outer face of the sides of said cup,

said heater means and said heat sensor means being mounted in the sides of said cup in the area of said exposed outer wall,

said detector being in the form of a bar, mounted only on said thermal platform within said cup, spaced from the bottom of said cup, and extending transversely of said cup, with both ends mounted on the inner walls of said cup, with substantial air space between said detector and the bottom of said cup, and between said detector and said second cover,

said detector being provided with thermal resistance means at its mounting interfaces with said thermal platform,

said chromatographic column and said sampling unit also being mounted only on said thermal platform, with substantial air space between them and said first cover, and being provided with thermal resistance means at their mounting interfaces with the underside of the bottom of said thermal platform cup,

whereby said thermal system is established as a highly thermally active shell made up of the said linings of said covers, joined by said thermal platform, with said sampling unit, said column, and said detector as thermally sluggish units within said shell, whereby heat generated by said detector is applied to said thermal platform,

and whereby close and rapid control of the temperature of said thermal platform is provided by said arrangement of said heat sensor located essentially directly between said heater means and said heat sink exposed thermal platform outer wall strip.

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