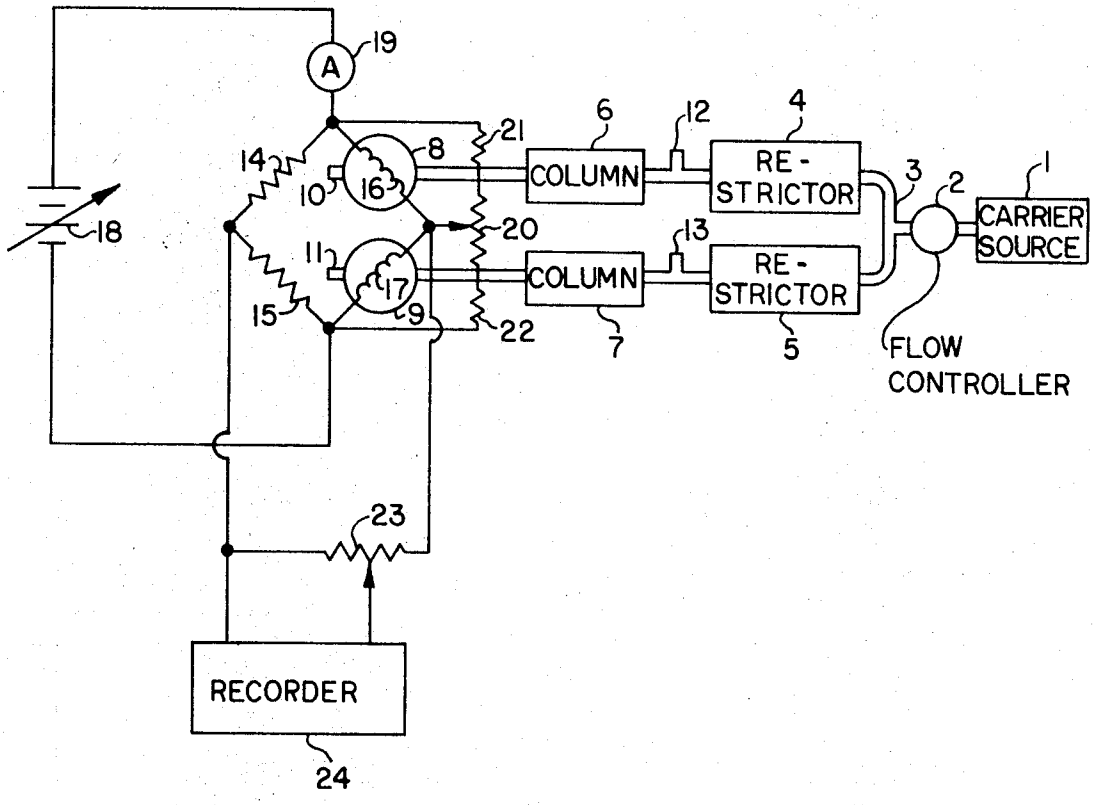
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METHOD OF TREATING THERMAL CONDUCTIVITY DETECTOR FILAMENTS TO AVOID BASELINE DRIFT

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METHOD OF TREATING THERMAL CONDUCTIVITY DETECTOR FILAMENTS TO AVOID BASELINE DRIFT

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ABSTRACT OF THE DISCLOSURE

Discloses a method for improving the baseline stability of chromatograph thermal conductivity detector filaments by reacting them with a volatile hydrocarbon containing at least one atom per molecule of the group of chlorine and fluorine in sufficient quantities to remove baseline drift due to contamination. The method may be carried out by injecting the material to be reacted with the filament into a sample injection port in a chromatograph through the column and into the detector chamber. Normal operating temperatures, pressure, etc. may be employed.

BACKGROUND OF THE INVENTION

The materials most generally used in constructing gas chromatograph thermal conductivity detector filaments, such as tungsten or a tungsten/rhenium alloy, are subject to oxidization at high temperatures. When a sample containing significant quantities of air or oxygen is injected into a gas chromatograph the air or oxygen peak may be followed by a permanent offset of the baseline on the recorder associated with the detector. This would indicate a permanent change in the resistance of the filament or filaments due to the formation of an oxide coating on the surface. Even highly oxidation resistant materials such as platinum or rhodium may exhibit this phenomena although usually to a lesser degree. The phenomena also exhibits itself by a continual drift in baseline when a small leak in the system allows air to diffuse in and cause a continuous oxidation process to occur.

Baseline offset has also been observed following the elution of chlorinated hydrocarbons when using tungsten or rhodium filaments; and in the case of rhodium filaments operated at high filament temperature an offset may occur following the elution of a major hydrocarbon component such as N-decane. At high bridge powers the filaments are as much as 200° C. hotter than the wall of the detector. Actual filament temperatures run as high as 450° to 500° C. In the case of rhodium and platinum such temperatures are high enough to cause catalytic decomposition and deposition of carbonaceous materials on the filament thus changing its emissivity and/or resistance with a resulting shift in the detector baseline.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the invention to provide a method for treating thermal conductivity filaments to minimize or eliminate baseline drift.

This and other objects are achieved by providing a method of treating a thermal conductivity detector filament to overcome baseline drift due to filament contamination comprising the steps of reacting a volatile hydrocarbon containing at least one atom per molecule of the group consisting of chlorine and fluorine with the filament in sufficient amount to effect baseline drift due to contamination and repeating the reaction if necessary until the baseline remains stable.

In a more particular embodiment the above method

may be carried out in a chromatograph under normal operating conditions.

In still another embodiment an oxidization step may be included with the possibility of forming a metallic oxychloride on the filament.

The novel features which are believed to be characteristic of the invention are set forth with particularity in the appended claims. The invention and further objects and advantages thereof can best be understood by reference to the following description and accompanying drawing.

BRIEF DESCRIPTION OF THE DRAWING

The drawing is a diagram, partly in block and partly schematic, of an experimental apparatus in which the method of the invention may be carried out.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Turning now to the drawing there is illustrated a source of carrier gas **1** which is directed through a flow controller **2** and split in a T configuration **3** to go through two restrictors **4** and **5** and through columns **6** and **7** respectively. The output of columns **6** and **7** go through detector volumes **8** and **9** to the atmosphere through vents **10** and **11** respectively. A sample inject port **12** is located between the restrictor **4** and column **6** and a sample inject port **13** between the restrictor **5** and column **7**.

A wheatsone bridge detector arrangement is provided consisting of two fixed resistors **14** and **15** connected in a bridge configuration with thermal conductivity detector filaments **16** and **17**. Filament **16** is in detector volume **8** and filament **17** is in detector volume **9**. The input to the bridge is a source of voltage **18** which is connected in series with a current meter **19** across the bridge at the interconnections of the elements **14** and **16** and the elements **15** and **17**. A zeroing potentiometer **20** is connected in series with two fixed resistors **21** and **22** connected to its extremities across the same bridge interconnections. The variable contact on the potentiometer **20** is connected to the interconnection of the filaments **16** and **17** on the bridge which interconnection is also connected to one terminal of a variable attenuation potentiometer **23** the other terminal of which is connected to the interconnection of resistors **14** and **15** and to an input terminal of the recorder **24**. The variable contact on potentiometer **23** is connected to the other input terminal of the recorder **24**.

Typically the columns **6** and **7** may be 3% SE 30 on chromasorb W six feet long, ⅛ inch O.D. and approximately .025 inch wall thickness. The flow rate through the columns may be 30 cc. per minute, the volumes **8** and **9** may be approximately ½ cc., the resistors **14** and **15**—1,000 ohms, precision resistors having low temperature coefficients, the attenuator **23**—1,000 ohms, the resistors **21** and **22**—3,000 ohms, the potentiometer **20** a 10,000 ohm 10 term potentiometer, and the carrier gas helium. The detector chambers are at atmospheric pressure.

SPECIFIC EXAMPLES

Example 1

Two tungsten filaments of 200 turns of .001 inch diameter wire with a resistance of approximately 22.55 ohms each at 22° C. were run with a recorder sensitivity of 5× with a voltage of source **18** of 22 volts and a current through meter **19** of 180 milliamps. This corresponds to a bridge power of 3.9 watts. The current was adjusted to give a Dimbat-Porter-Stross sensitivity of approximately 1,000. This measure of sensivity is described in an article entitled "Apparatus Requirements for Quantitative Application of Gas-Liquid Chromatography" pub-

lished in Analytical Chemistry, vol. 28, pp. 290–297, 1956. The temperature of the detector chambers **8** and **9** was 250° C. The filaments 16 and 17 were therefore approximately 450° C. (calculated).

Using the two sides of the detector alternately as reference and sample sides, a 5 microliter air sample injected in sample port **12** gave 1½% offset or 1.5 divisions on the 100 division recorder scale. A one microliter standard sample consisting of one microgram of N-C_{16} per microliter of N-C_{10} was then injected in port **12** with no offset resulting. Three 5 microliter samples of methylene chloride were then injected into port **12**. The first time 2¼ turns of the potentiometer **20** were required to zero the recorder. The second time ¼ turn was required to zero and the third time ¼ turn. Subsequently 5 microliters of air were injected five times into port **12** with no resulting offset.

The bottom inlet **13** was also treated with 5 microliters of air sample and 1 microliter of standard sample similar to the top inlet. After this three 5 microliter samples of methylene chloride were injected into port **13**. The first time 3 turns of the potentiometer were required to zero. The second time ½ turn and the third time ⅛ turn. Subsequently four injections of 5 microliters of air each were made into port **13** with no resulting offset and then one injection of 30 microliters of air was made into port **13** with no resulting offset.

Example 2

Example 2 was run under the conditions above except that 200 turns of .0013 inch diameter filaments having 12.65 ohms resistance at 22° C. each, a voltage of 17.7 volts and a current of 250 milliamps were used for a bridge power of 4.4 watts. The same standard sample injected into the top inlet **12** gave a permanent two division upscale baseline offset after the C_{10} peak. Six repetitive 30 microliter air samples injected into port **12** gave upscale baseline offsets of 1.1, .4, .4, .4, .4 and .3 divisions each. Two 30 microliter O_2 injections gave upscale offsets of 1 division each. This was then followed by an injection of standard sample and the C_{10} peak was followed by a 1.5 division upscale offset.

A standard sample was then injected into the bottom inlet **13**. The air peak was followed by a 4.5 division downscale offset and the C_{10} peak followed by a 3 division downscale offset (or 1.5 divisions higher than after the air peak) which slowly drifted up to the original baseline. Two successive injections of standard sample 6 minutes apart resulted in 4 division and 2 division downscale offsets respectively. A third injection of standard sample 20 minutes later yielded 1.5 division offset. Repetitive 30 microliter air samples into port **13** gave upscale offsets of about 1 division average. A standard sample injected 20 minutes after the last air sample gave a 4 division downscale offset after the air peak and an additional 1 division offset after the C_{10} peak. The injection of a standard sample in the inlet **12** then yielded an upscale offset after the C_{10} peak of about .9 division. Repetitive injections of 5 microliters of methylene chloride were then injected into the bottom inlet **13**. The first yielded a downscale offset which required 3 turns of the potentiometer **20** to rezero. Subsequent injections gave upscale offsets of 26, 17, 7 and 5 divisions. When the standard sample was then injected in inlet **13** no baseline offset was observed indicating that the methylene chloride had cleaned or conditioned the filament. The above procedure was repeated in the top inlet with substantially the same results.

Five successive 30 microliters air injections showed no baseline offset after the methylene chloride treatment. To test whether a large sample would uncondition the filaments, a 5 microliter sample of N-decane was injected with no resulting baseline offset. This was followed by

a 1 microliter injection of standard sample, again with no baseline offset. The detector compartment temperature was then reduced to 150° C. and the current increased to 275 milliamps at 17.7 volts (4.9 watts). The standard sample was then injected with no resulting baseline offset and four 30 microliter air samples were injected with no offset.

Almost any volatile chlorine containing hydrocarbon such as carbontetrachloride, chloroform and ethylene trichloride should also yield approximately the same results. Fluorine containing compounds such as Freon should also be effective. Other suggested filament materials are tungsten/rhenium or platinum. The filament temperatures which have been employed in other tests have ranged from approximately 330° C. up to 450° or 500° C., both for tungsten and rhodium. These have been employed since they are approximately as low as we normally operate the detectors up to a temperature which is close to the point where the filament might become brittle. The carrier employed was always helium, however, other inert carriers should function similarly.

Filaments treated as above have been tested after treatment for several months and showed no degradation of baseline stability. This could conceivably be limited to running the same type of samples such as organics. Rhodium filaments treated with only three 1 microliter samples of methylene chloride were stable for a time but did not remain so indefinitely.

The reaction may create a layer of film of metal chloride on filaments but since the filaments were often oxidized prior to reaction with the methylene chloride it is also possible that the end product is a metal oxychloride. A metal chloride film may be functioning to kill the catalytic character of the filament and thus reduce carbonation as well as to resist oxygen penetration and resulting oxidation. Some metal oxides are also catalytic whereas the chlorides are not.

Since the principles of the invention have now been made clear, modifications which are particularly adapted for specific situations without departing from those principles will be apparent to those skilled in the art. The appended claims are intended to cover such modifications as well as the subject matter described and to only be limited by the true spirit of the invention.

What is claimed is:

1. A method of treating a thermal conductivity detector filament formed of at least one of the metals from the group consisting of tungsten, rhodium, platinum and tungsten-rhenium alloy to overcome baseline drift due to filament contamination comprising the steps of:

reacting a volatile hydrocarbon containing at least one atom or molecule of the group consisting of chlorine and fluorine with the filament raised to a temperature of at least 330° C. in sufficient amount to remove oxidation from the surface of said filament and condition said surface to prevent further oxidation thereby to reduce baseline drift due to contamination,

repeating the reaction if necessary until the baseline remains stable.

2. The method of claim **1** in which the filament is partially oxidized prior to reacting it with the volatile hydrocarbon thereby forming a metal oxychloride or oxyfluoride metal coating on said filament.

3. The method of claim **1** in which the hydrocarbon is methylene chloride.

4. The method of claim **1** in which the filament is reacted at temperatures from 330–500° C. in a detector chamber.

5. The method of claim **4** in which the volatile hydrocarbon is introduced into the detector chamber through a regular sampling means of an associated chromatograph column and through the column.

6. The method of claim **5** in which the filament is partially oxidized by the introduction of a sample con-

taining oxygen prior to reacting it with the volatile hydrocarbon.

7. The method of claim 6 in which the normal operating conditions include the use of a helium carrier and atmospheric pressure.

8. The method of claim 7 in which the filament is rhodium, the detector chamber volume containing the filament is approximately ½ cc., the flow rate is approximately 30 cc./min. and at least three/one microliter amounts of methylene chloride are reacted.

9. The method of claim 8 in which the filament is partially oxidized by the introduction of a sample containing oxygen prior to reacting it with the methylene chloride.

References Cited

UNITED STATES PATENTS

3,130,073 4/1964 Van Der Linden et al. _ 117—231

OTHER REFERENCES

Harrison: Vapor Phase Chromatography Symposium, London, 1956, D. H. Desty, ed., Academic Press Inc., London, Butterworth Scientific Pub., 1957, pp. 332, 333.

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