United States Patent [19]

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[54] **ANALYTICAL APPARATUS AND METHOD OF ANALYSIS**

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Related U.S. Application Data

[63] Continuation of Ser. No. 135,836, April 21, 1971, abandoned.

[30] **Foreign Application Priority Data**

Apr. 28, 1970 United Kingdom 20366/70
Apr. 27, 1970 United Kingdom 41246/70

[52] **U.S. Cl.** **356/85**
[51] **Int. Cl.** **G01j 3/30**
[58] **Field of Search** 356/85, 86

[56] **References Cited**

UNITED STATES PATENTS

3,467,471	9/1969	Greenfield et al.	356/85 X
3,610,759	10/1971	Wood	356/85

OTHER PUBLICATIONS

Dagnall et al.: "Talanta," Vol. 16, No. 7, July 1969, pp. 797–806.

McCormack et al., "Analytical Chemistry," Vol. 37, No. 12, November 1965, pp. 1,470–1,476.

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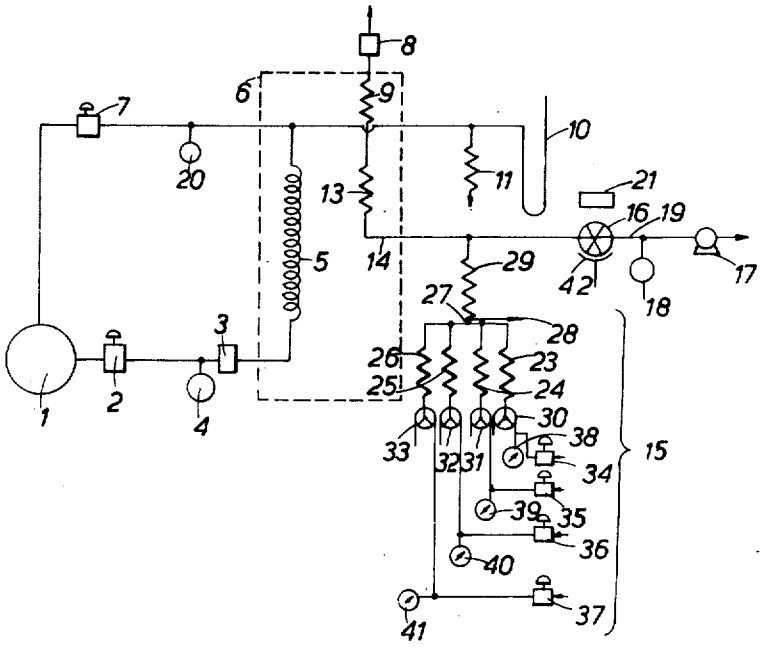
[57] **ABSTRACT**

Elemental analyses of carbon-containing samples are determined from the radiation emitted by them in a plasma which contains a scavenger for carbon.

20 Claims, 5 Drawing Figures



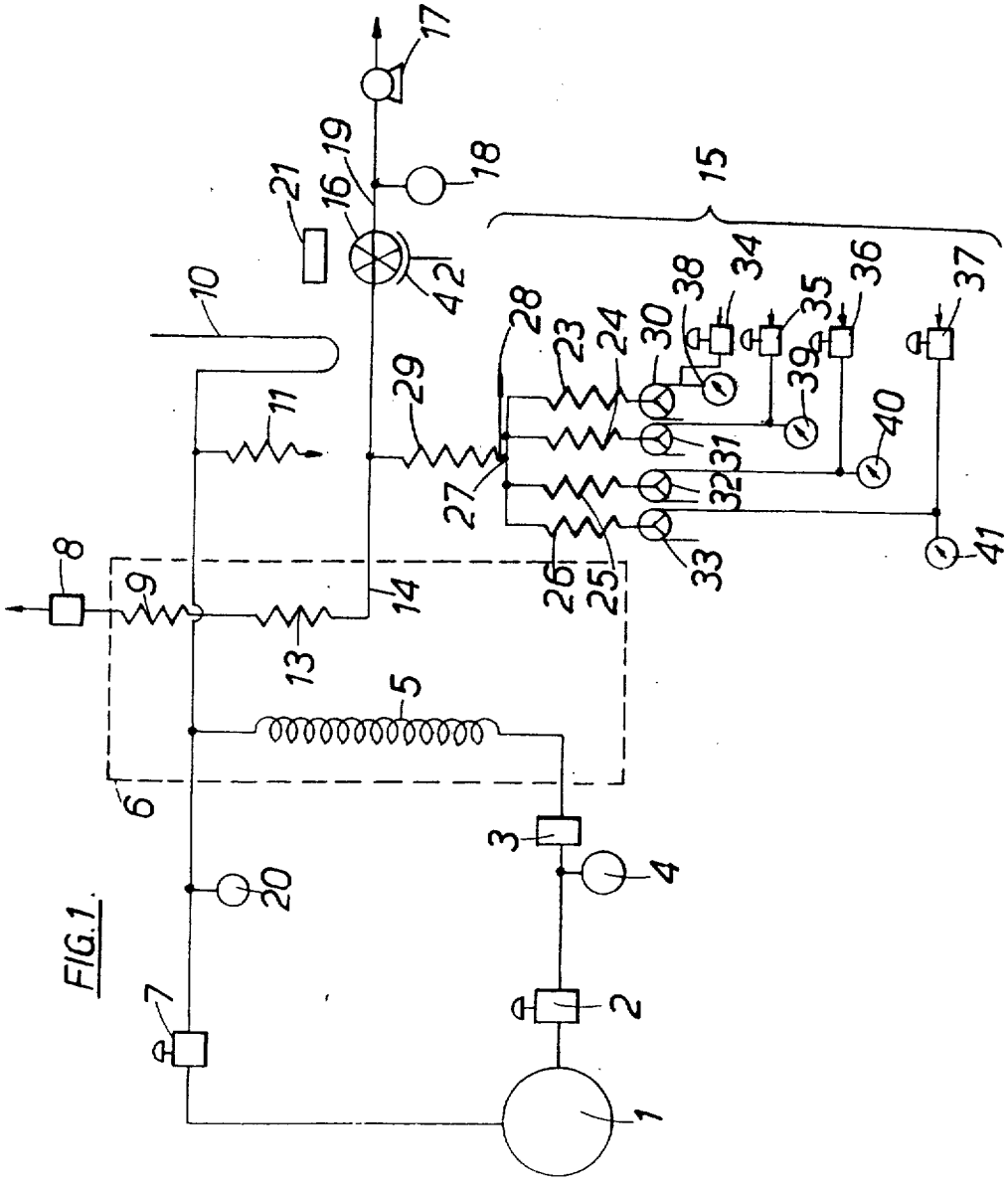


FIG. 1.

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FIG. 2.

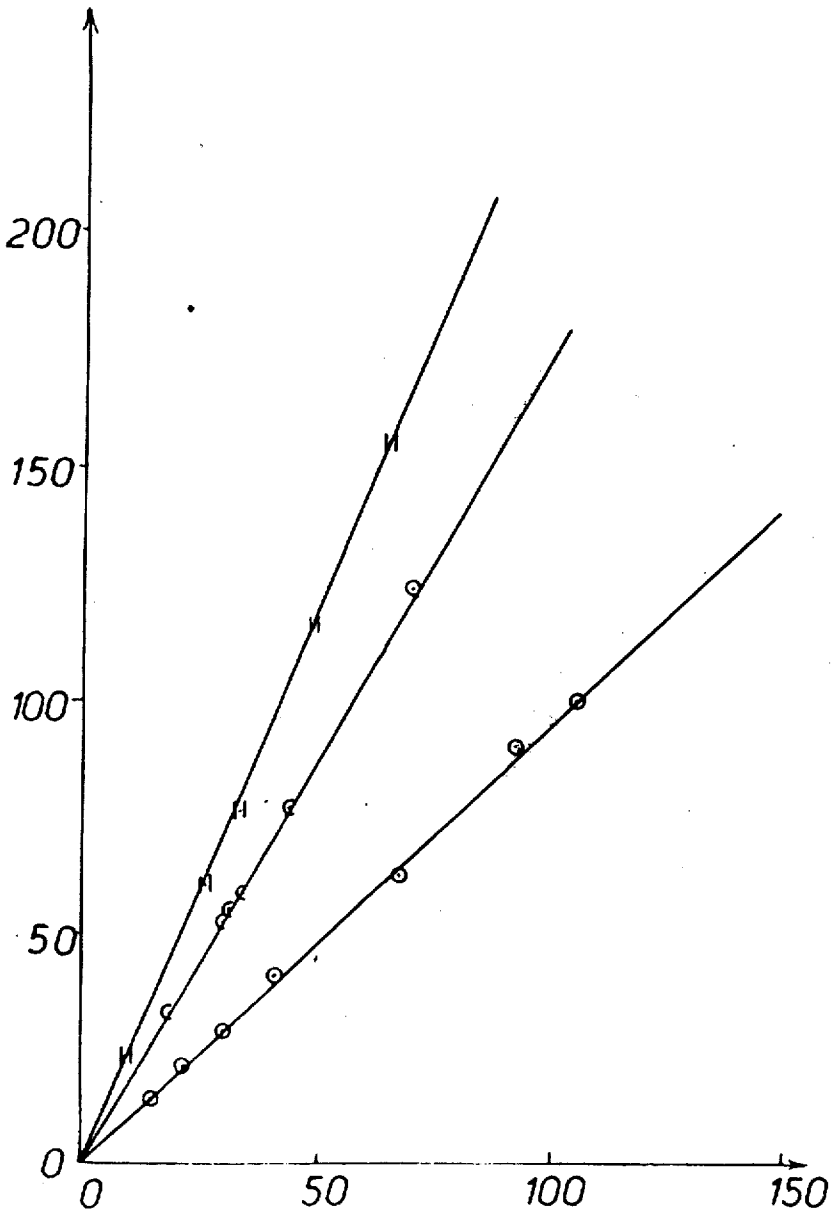

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FIG. 4.

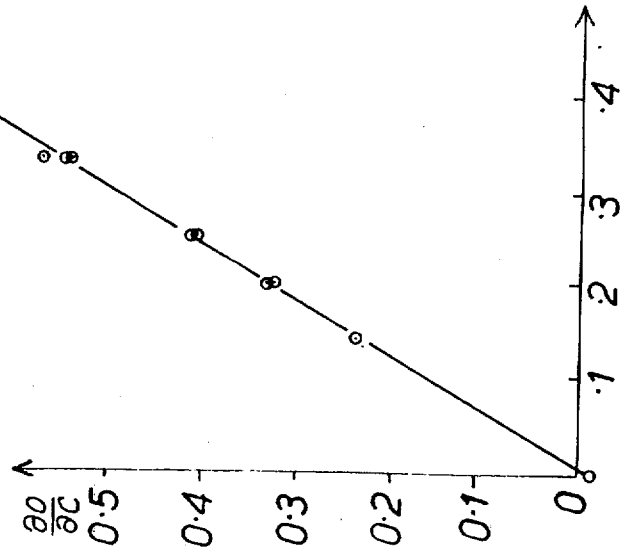

FIG. 3.

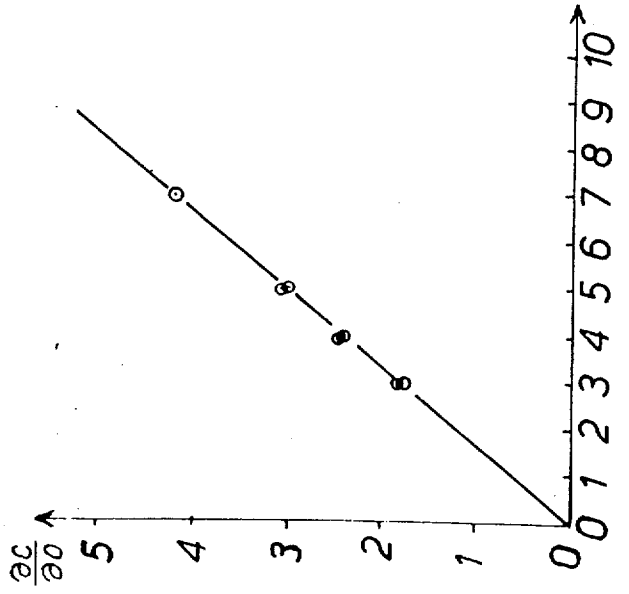

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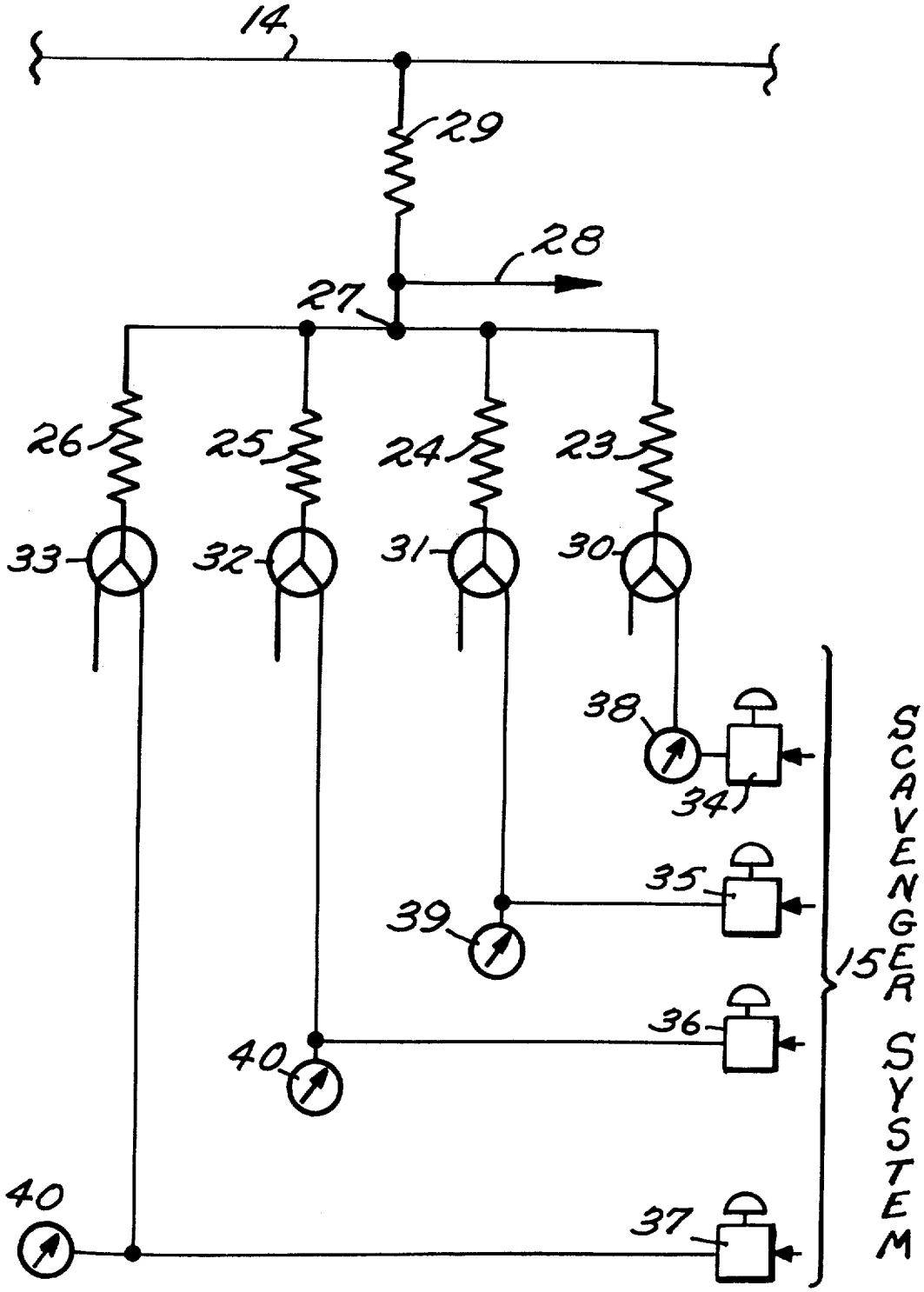
FIG. 5.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SCAVENGER SYSTEM

ANALYTICAL APPARATUS AND METHOD OF ANALYSIS

This is a continuation, of application Ser. No. 135,836 filed Apr. 21, 1971, now abandoned.

This invention relates to analytical apparatus and a method of analysis.

The invention comprises apparatus for determining the elemental analysis of a carbon containing sample which comprises means for introducing the sample, preferably in a gas stream, to a plasma in the presence of a scavenger for carbon, means for resolving radiation emitted by the plasma according to its frequency and means for detecting the intensity of radiation of frequencies characteristic of one or more individual elements.

The carbon-containing sample may contain one or more compounds of carbon. If the sample contains only one organic compound and all of the elements present in it are determined, the empirical formula of the compound may be calculated. The sample is preferably introduced as a gas to the plasma. Compounds dissociate in the plasma.

By "plasma" is meant a mixture of electrons and gaseous ions optionally together with neutral atoms. The plasma may suitably be formed by providing for the presence of neon, argon, or preferably helium and exciting the gas, for example, by subjecting it to an electric discharge, microwave radiation and/or high frequency induction.

The scavenger for carbon may be, for example, oxygen or nitrogen. If either of these elements is present in the compound the other is preferably used as the scavenger in order to avoid the production of radiation of the characteristic frequency by the scavenger. If the same element is used, allowance must be made in calculations for the effect of radiation due to the scavenger. If both of these elements are present in the compound a determination may advantageously be carried out with oxygen and nitrogen as scavengers sequentially. Hydrogen may be used as a scavenger, and enables determinations of carbon, nitrogen and/or oxygen to be performed simultaneously.

The means for resolving the radiation emitted according to its frequency may comprise a prism spectrometer or filter, but more preferably comprises a diffraction grating spectrometer.

The means for detecting the intensity of radiation of frequencies characteristic of different elements may be of a single channel spectrometer but it is more preferably, when a prism or diffraction grating is the means for resolving the radiation, a multichannel spectrometer. This may comprise a number of photo detecting devices, for example photo multipliers, positioned so as to detect radiation of the desired frequencies.

When a multichannel spectrometer is used for detecting radiation from the plasma, detection may conveniently be done automatically by sensing radiation of a frequency which is not required for the analysis and which is characteristic of an element which is common to the compounds under investigation (which is conveniently the second order radiation from carbon as its frequency is suitable and carbon will always be present in the analysis) and, when this is above a specified intensity, detecting radiation of frequencies characteristic of the desired elements, for example by switching currents representative of the intensities of spectral

lines characteristic of such frequencies into integrators during the period when the second order carbon radiation is above the specified intensity, and detecting the integrated values. The integrators may comprise capacitors, the potential across which is determined after each reading.

Part of radiation which is used in the analysis, which may be the first order carbon radiation, may be used to control detection as above if desired by physical splitting of a beam of the radiation if the apparatus is calibrated on this basis.

If peaks occur close together so that the integrators would be required for re-use before a sufficient interval has been allowed for reading, two or more sets of integrators may be provided for use in turn.

The apparatus may, if desired, comprise means for establishing the ratios of atoms of the elements present by comparing the intensities of radiation of frequencies characteristic of different elements automatically.

The plasma may be at a pressure of 10^{-8} to 2 bars and preferably 10^{-4} to 1.5 bars, for example 10^{-3} to 1.5 bars. When helium is present a more preferred pressure is in the range 0.1 to 10 millibars and when argon is present a more preferred pressure is 1 to 100 millibars.

Apparatus according to the invention may comprise a gas chromatographic system which serves to provide a gas stream as an effluent, the stream being fed into the plasma, the system being provided with means for introducing a scavenger for carbon before the compound is so dissociated. It is preferred that the carrier gas used in such a system should be argon, or more preferably helium, and it is preferred that the scavenger be introduced after the passage of the compound through the chromatographic column. However, the scavenger may be introduced before passage of the compound through the chromatographic column especially if it is nitrogen. In order to achieve the preferred pressures for the plasma it is desirable to feed effluent from the chromatographic column through a resistance to gas flow into a vessel in which the plasma is formed, which vessel is continuously evacuated by a pump. It is also usually desirable to feed additional carrier gas to the outlet of the column to maintain the pressure at the outlet at above atmospheric pressure but at less than that fed to the inlet of the column and to let effluent escape through, e.g. a conventional detector as well as through the plasma as this maintains pressure control and improves general stability and the precision of separation of components.

If it is desired to separate a mixture into its components by gas chromatography and to analyse a minor component when another component is present in a very much greater concentration it may not be possible to introduce sufficient sample to give a high sensitivity with the minor component without requiring so much scavenger to deal with the said other component that the analysis becomes unstable.

This problem may be overcome by providing means for by-passing the plasma when the said other component would otherwise pass into it or by reducing the concentration of the said other component passing through the plasma.

The plasma may be by-passed by providing a vessel in which the plasma is produced with a by-pass and providing a valve which is adapted to block the path through the vessel or the by-pass alternatively, the valve being controlled by a detector for the said other

component (for example, a flame ionisation or hot wire detector) so as to by-pass the vessel in response to detector readings above an acceptable value.

The concentration of the said other component can be reduced in response to a detector reading above an acceptable value by bleeding off a proportion of the gas flow from the scavenger is added whilst maintaining the pressure by feeding in carrier gas from a pressure controller.

In normal gas chromatographic analysis the sample to be analyzed is passed through the gas chromatographic system as such. However, more information may be obtainable if instead of, or in addition to, passing the sample through as such it is reacted with a gas in a reactor (which may contain a solid catalyst) and the product of the reaction is passed through a chromatographic column.

Suitable gases may be, for example hydrogen (including deuterium), oxygen, or chlorine. The effluent from the reactor may very suitably be injected into the chromatographic column using apparatus as described in our co-pending Pat. application No. 59912. It is found that the gas of the block of sample injected in general separates from the other sample components and thus does not interfere with the determinations, since the sample components enter the plasma in the appropriate carrier gas rather than in the said gas.

The concentration of scavenger should preferably be in the range of one atom of scavenger per million atoms present to one atom of scavenger per thirty atoms present. This is usually found to be sufficient to avoid quenching of the major spectral lines by more than 50% whilst overcoming laydown of carbon. Preferably, if oxygen is the scavenger, the plasma should contain 0.01 to 10% of oxygen (expressed as atoms). The maximum concentration of carbon compounds which it is desired to detect should be at most sufficient to provide 1 carbon atom per oxygen atom and preferably is at most 1 carbon atom to 2 oxygen atoms.

If nitrogen is the scavenger, the plasma should contain 0.03 to 30% of nitrogen (expressed as atoms). The maximum concentration of carbon compounds which it is desired to detect should be at most sufficient to provide one carbon atom per three nitrogen atoms, and preferably at most one carbon atom per five nitrogen atoms.

The presence of deuterium can be detected separately from hydrogen according to the invention, and this is useful in the identification of hydrocarbon types by deuteration.

The invention also provides a method of analysis which comprises dissociating an organic compound in a plasma in the presence of a scavenger for carbon, and determining the quantity of one element present relative to another element present by comparing the intensities of radiation of frequencies characteristic of the said elements.

The present invention may be better understood by reference to the following figures therein;

FIG. **1** is a diagrammatic illustration of the preferred embodiment of the present invention;

FIGS. **2**, **3**, and **4** are graphs of analysis results of Example **2**; and

FIG. **5** is another embodiment wherein the scavenger system is shown coupled to feed line **14**.

One form of the invention will now be described with reference to the accompanying diagram.

A carrier gas cylinder **1** containing helium feeds a constant pressure controller **2**, and a sample injector **3**, a pressure gauge **4** being provided for facilitating the setting of the constant pressure controller. The outlet of the sample injector **3** feeds a chromatographic column **5** which is contained in an oven **6**. The outlet of the chromatographic column **5** is fed by a second constant pressure controller **7** with helium derived from the cylinder **1**. A pressure gauge **2** is provided for checking the pressure at the outlet of the chromatographic column. The outlet of the chromatographic column **5** feeds a flame ionisation detector **8** through a restriction to gas flow **9**, and a manometer (which, to prevent back diffusion of mercury vapour, is provided on its inlet side with a vent to the atmosphere through a resistance to gas flow **11**. The outlet from the chromatographic column **5** also feeds a resistance to gas flow **13** which in turn feeds a line **14** which is also fed by a system **15** for bleeding a mixture of helium and nitrogen, oxygen or other scavenger into the line.

System **15** takes the form of four resistors to gas flow **23**, **24**, **25**, **26** which are fed by helium, nitrogen, oxygen and another scavenger (which may be hydrogen) respectively. The inlet of each is fed through a three-way tap **30**, **31**, **32**, **33** arranged to connect the resistor to the atmosphere or to a gas source feeding through an adjustible pressure controller **34**, **35**, **36**, and **37**. Pressure gauges **38**, **39**, **40**, and **41** are provided to determine the outlet pressure of the pressure controller. Resistor **23** is of low resistance and the others are of high resistance. The resistors feed junction **27** which in turn vents to the atmosphere through narrow bore tube **28**, and feeds line **14** through resistor **29**. The composition of the gas at junction **27** may be set by appropriately adjusting the pressures at the inlets to resistors **23**, 24, 25 and **26** and directing the three-way taps to feed from the desired gas source. The gas flow through the resistors can be calculated. Gas of this composition is drawn into line **14** at a rate which depends on the pressure in it, and the amount of scavenger bled into line **14** is set by varying the composition of the gas passing junction **27**. The line **14** feeds a vessel **16** which is surrounded by a suitably designed and tuned cavity **42** which can be supplied with microwaves at a frequency of 2450 megacycles/second and a power up to 200 watts. The vessel is evacuated via a line **19**, by a pump **17**, which is provided on its inlet side with a pressure gauge **18**.

A manually tuned single channel or a multichannel diffraction grating spectrometer **21** is positioned so as to detect light from the vessel **16**.

EXAMPLE 1

The apparatus may be operated as follows: helium is fed at an absolute pressure of 3.5 bars to the chromatographic column **5**, the temperature of which is controlled by means of the oven **6**. The pressure at the outlet of the column **5** is set at 1.15 bars by means of the constant pressure controller 7 and gas flowing from the column is split. One part flows through a flow restrictor to the flame ionisation detector **8** and a second part flows through the restriction to gas flow **13** to line **14**. Oxygen or another scavenger is bled into the line **14** in admixture with helium (1 part of oxygen to 10 of helium) to provide a final ratio in the vessel **16** of 1 part of oxygen per 1000 parts of helium (the ratios being by volume). The vessel **16** is pumped down to maintain a

steady pressure of 5.5 millibars; microwaves are supplied to the cavity **42** and a plasma initiated by a Tesla coil. The spectrometer **21** is then operated.

The apparatus may be calibrated as follows: One or more known compounds are injected into the chromatographic column and the intensities of radiation of frequencies characteristic of the desired elements are noted. This process is preferably carried out with a number of suitable compounds. Calibration factors for the elements of interest are calculated.

The sample containing the compound to be investigated is then injected into the column. The radiation intensities of interest are noted. Background contributions to these intensities are deducted. The stoichiometry of the compound is obtained by multiplying the corrected intensities by the calibration factors to give atomic concentrations. Concentrations in terms of the absolute weight of the compound may also be obtained.

The flame ionisation detector is useful in assessing chromatographic performance during setting up and for comparison of results with other chromatographic systems.

If a single rather than multichannel spectrometer is employed the flame ionisation detector is used to determine the sample sizes so as to enable the above data to be obtained. The data may be obtained without the use of the flame ionisation detector when a multichannel spectrometer is used. With single channel spectrometers, only one element can be determined at a time, and determination of the empirical formula of a compound will require as many analysis as there are elements in the compound, the intensities of the radiation being corrected for any variation in sample size.

EXAMPLE 2

The use of the apparatus above described with reference to FIG. **1** will now be described for the analysis of a number of organic compounds for oxygen and carbon.

Quantities of the compounds in the following list chosen so as to produce comparable peak heights in a flame ionisation detector were mixed together and injected into column **5** by sample injector **3.** Column **5** was three metres long and had an internal diameter of 2.5 mm; it was packed with a chromatographic support of 60/80 mesh particle size, sold under the trade name "Chromasorb" G by the Johns Mansfield Products Corporation, which support contained 5% by weight of polyethylene glycol of an average molecular weight of 20,000. The sample injection temperature was 200°C and the temperature of the column was 85°C. The compounds investigated were:

	% by weight
1. diethyl ether	2.2
2. propylene oxide	4.0
3. acetone	4.7
4. nonane	2.9
5. benzene	4.7
6. butan-2-ol	6.4
7. toluene	6.1
8. allyl alcohol	12.3
9. heptanone-4	12.6
10. 2-methyl butan-1-ol	18.1
11. normal pentanol	26.0

The pressure at the outlet of column **5** was set at 1.20 bars absolute which gave an approximately equal flow rate of effluent from column **5** through restrictors **9** and **13.** The pressure at the preheater was set at 2.3 bars absolute, this giving optimum separation efficiency.

Flame ionisation detector **8** was operated in the normal way. The scavenger bleed system **15** was operated as follows:

0.21 litres of helium/hour were passed through restrictor **23** to junction **27,** and 0.125 litres/hour of nitrogen were passed through restrictor **24** to junction **27,** taps **32** and **33** being connected to atmosphere so that no flow occurred through restrictors **25** and **26.** The desired rates of flow through restrictors **23** and **24** were secured by an appropriate adjustment of the pressure controllers **34** and **35** to provide the desired rate of flow through the restrictors, the requisite pressures being calculated from a knowledge of the resistance to gas flow of the resistors. 1.5 litres/hour of gas flowed through resistor **13** into line **14** and the pressure in vessel **16** was set at 0.3 millibars by the operation of pump **17.** It was calculated that the flow of gas from junction **27** where it was at atmospheric pressure because of capillary **28** through resistor **29** was 0.125 litres/hour, the concentration of nitrogen in the gas at junction **27** being 37% as calculated from a knowledge of the relative rates of flow of nitrogen and helium into junction **27.** Total rate of flow of gas to vessel **16** was 1.625 litres/hour of which approximately 1.575 litres/hour was helium and 0.05 litres/hour was nitrogen. All of the above flow rates given in litres/hour are calculated as at 20°C and at atmospheric pressure.

The quantities of mixed sample injected into preheater **3** were set such as to give a maximum flow rate of 1.33 micrograms/second of sample through the plasma, the flow rate of nitrogen through the plasma being 0.62 micromoles (expressed as N_2) per second.

The vessel **16** was a quartz capillary tube having an internal diameter of 2 mm. and an external diameter of 9 mm. It passed through a microwave cavity **42** to which a power of 170 watts was fed. A plasma was induced by means of a Tesla coil.

A manually tuned single channel diffraction grating spectrometer **21** was aligned with the plasma tube **16** and adjusted to detect a wave length of 777.2 nanometres for oxygen measurements, 247.8 nanometres for carbon measurements and 656.2 nanometres for hydrogen measurements, a red filter being used for the oxygen and hydrogen measurements. Light from the plasma was focused with a lens on to the entrance slit of the spectrometer **21** for the oxygen and hydrogen measurements but this was unnecessary for the carbon measurements.

Oxygen results results were first obtained by tuning the spectrometer **21** to the oxygen wavelength and passing samples through column **5** at different concentrations. A peak corresponding to each oxygen-containing component was obtained from both the spectrometer **21** and the flame ionisation detector **8.** For each component the peak height from the spectrometer was graphed against the peak height from the flame ionisation detector. Similar results were obtained for carbon and hydrogen. A typical graph showing results for acetone is shown in FIG. **2,** the upper graph being for hydrogen, the lower graph being for oxygen, and the middle graph being for carbon. Since the peak height of the flame ionisation detector is known to vary linearly with the concentration of the sample passing through the detector, it is clear that the peak height

from the spectrometer behaves similarly. The graph is in arbitrary units.

Having carried out the above procedure for a number of known compounds the intensity ratios of oxygen to carbon may be calculated, i.e. detector responses for oxygen and carbon may be related to the oxygen to carbon atomic ratio in the compound which is investigated. FIG. 3 shows intensity ratios of carbon to oxygen ($\delta C/\delta O$) graphed against the carbon to oxygen atomic ratio of a number of compounds and on the right hand of FIG. 3 the reciprocals, i.e. the intensity ratio of oxygen to carbon ($\delta O/\delta C$) is graphed against the oxygen to carbon ratio. It will be seen that the calibrations are linear. $\delta O/\delta C$ and $\delta C/\delta O$ are in arbitrary units.

For an unknown compound a determination is carried out twice calculating for an equivalent size of sample the radiation produced characteristic of oxygen and of carbon, and the ratio of the two when multiplied by the appropriate calibration factor as shown in the graphs gives the atomic ratio of oxygen to carbon.

Similar determinations may be carried out for different pairs of elements and in particular a hydrogen to carbon, or hydrogen to oxygen atomic ratio may be determined.

EXAMPLE 3

In this Example the empirical formula of two unknown compounds are determined using a multichannel spectrometer in the apparatus described with reference to FIG. **1**. A sample was injected into preheater **3** and a chromatographic separation under the same conditions as before, except that the column temperature was 100°C, was carried out. Ten microlitres of the sample were injected.

The pressures throughout the system were the same as in Example 2 except that the plasma pressure was 4 millibars and the bleed system **15** was set to give a concentration of 2% of oxygen in the plasma by atoms, instead of using nitrogen as scavenger. The microwave power fed to the cavity was 160 watts. The plasma tube had an internal diameter of 1 mm.

The spectrometer was previously aligned and adjusted to detect the following wave lengths:

	Wave Length Å
C	2478.57
H	4861.33
D	6561.00
O	7772
N	7468.79
F	6854.02
Cl	4794.54
Br	4704.86
I	5161.19
G	5452.00
P	2535.7
He	3875.6
C(second order)	4957.14

The spectrometer contained photo multiplier tubes positioned to respond to each of the above wave lengths and the voltages applied to each photo multiplier were separately adjusted to make the output signal comparable to that of the other photo multipliers.

The second order carbon signal was used to activate a series of relays to connect a condenser with each of the photo multiplier tubes in use when it rose above a threshhold value and, when the signal fell below this value it initiated a digital display of the voltages accumulated on the condensers in turn, being an integrated record of the radiation which was produced characteristic of each element during passage of the component of the sample through the plasma. The condensers were then discharged to permit fresh readings to be taken of the next component.

The values thus obtained consist of two parts; a signal component and a background component which is produced irrespective of the presence of any sample in the plasma. The background signal is proportional to the time taken to integrate the signal and the normal level of background is measured when no component of the sample is present in the plasma. The background signal is deducted from the integrated value to give a pure signal component.

The sample was found to contain two peaks. The first had intensity ratios of 1.173 for hydrogen to carbon and 4.26 for chlorine to carbon. The second had intensity ratios of 0.601 for hydrogen to carbon and 0.986 for sulphur to carbon, no other elements being detected in either case. Multiplication of these values by calibration factors derived by experiments with known compounds gave atomic ratios for the first component of 1.99 for hydrogen to carbon and 2.01 for chlorine to carbon. For the second component the atomic ratio for hydrogen to carbon was 1.03 and for sulphur to carbon was 0.249. The empirical formula were, therefore, for peak one CH_2Cl_2 and for peak two C_4H_4S. Subsequent work confirmed the above empirical formulae and the identities of the compounds were later found to be methylene dichloride and thiophen.

It is normally possible for an experienced chromatographer to make a reasonable estimate of the molecular weight of the component from a consideration of the retention time of the component in the column in conjunction with the empirical formula; thus a molecular formula may normally be deduced for the compound. It may in addition be possible to form conclusions in some cases as to the structure of the compound based on gas chromatographic considerations and it may be possible to identify the compound unambiguously from a knowledge of its empirical formula and its retention time.

The wave lengths given in these Examples may be converted to the corresponding frequencies by the furmula $\lambda\nu = C$ where λ is the wavelength, ν is the frequency and C is the velocity of light in vacuo.

I claim:

1. A method of analysis which comprises introducing a carbon-containing sample to a plasma in the presence of helium and a carbon lay-down suppressing amount of a scavenger for carbon, said scavenger being introduced separately before the sample is dissociated, resolving radiation emitted by the plasma according to its frequency, detecting the intensity of radiation characteristic of an element and determining the quantity of the element present from the intensity of radiation so detected.

2. A method as claimed in claim **1** wherein oxygen is the scavenger and the plasma contains 0.01 to 10% of oxygen expressed as atoms.

3. A method as claimed in claim **1** wherein nitrogen is the scavenger and the plasma contains 0.03 to 30% of nitrogen expressed as atoms.

4. A method as claimed in claim **2** wherein the maximum concentration of carbon compounds is sufficient to provide one carbon atom per oxygen atom.

5. A method as claimed in claim 3 wherein the maximum concentration of carbon compounds is sufficient to provide at most one carbon atom per 3 nitrogen atoms.

6. A method as claimed in claim 1 wherein the pressure of the plasma is 10^{-8} to 2 bars.

7. A method as claimed in claim 1 wherein the pressure of the plasma is in the range of 0.1 to 10 millibars.

8. A method as claimed in claim 1 in which a mixture is separated into its components by gas chromatography to provide a gas stream as an effluent, the effluent therefrom is passed into the plasma and one or more individual components are analysed.

9. A method as claimed in claim 8 in which the component to be analyzed is present in a much small concentration than another component and the plasma is by-passed when said other component would otherwise pass into it.

10. A method as claimed in claim 8 in which oxygen is determined, the scavenger for carbon being nitrogen.

11. A method as claimed in claim 8 in which nitrogen is determined, the scavenger for carbon being oxygen.

12. A method as claimed in claim 8 in which oxygen and nitrogen are determined and in which the scavenger is hydrogen.

13. The method of claim 1 wherein the carbon-containing sample contains oxygen, the scavenger for carbon is nitrogen and the quantities of carbon and oxygen present in the sample are determined.

14. The method of claim 1 in which the carbon-containing sample contains nitrogen, the scavenger for carbon is oxygen and the quantities of carbon and nitrogen present in the sample are determined.

15. Apparatus for determining the empirical formula of an organic compound which comprises means for dissociating the compound in the gas phase in a plasma in the presence of a scavenger for carbon, means for resolving radiation emitted by the plasma according to its frequency and means for detecting the intensity of radiation of frequencies characteristic of individual elements.

16. Apparatus as claimed in claim 15 in which the means for resolving the radiation emitted by the plasma according to its frequency and means for detecting the intensity of radiation of frequencies characteristic of one or more individual elements is a multichannel diffraction grating spectrometer.

17. Apparatus as claimed in claim 15 which comprises a gas chromatographic system which passes its effluent to the plasma, the system being provided with means for introducing a scavenger for carbon before the compound is dissociated.

18. A method of determining the elemental analysis of components present in a mixture in which the components are separated by gas chromatography to a stream of helium, passed into a plasma in the presence of a carbon lay-down suppressing amount of a scavenger for carbon, resolving radiation emitted by the plasma according to its frequency, detecting the intensity of radiation characteristic of the elements present in the component and determining the quantity of the elements present in the component from the intensity of radiation so detected.

19. Apparatus for determining an elemental analysis of a carbon-containing sample which comprises means for introducing a scavenger for carbon, additional means for introducing the sample to a plasma in the presence of the scavenger for carbon, means for resolving radiation emitted by the plasma according to its frequency and means for detecting the intensity of radiation of frequencies characteristic of one or more individual elements.

20. Apparatus as claimed in claim 19 which comprises a vessel in which the plasma is formed, a chromatographic column for feeding the vessel, a resistance to gas flow between the chromatographic column and the vessel, and a pump for continuously evacuating the vessel.

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