United States Patent

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[54] **METHOD AND APPARATUS FOR DETERMINING SULFUR CONTENT IN HYDROCARBON STREAMS**
12 Claims, 5 Drawing Figs.

[52] **U.S. Cl.** **250/43.5,** 250/84, 250/106
[51] **Int. Cl.** **G01n 23/12**
[50] **Field of Search** ..... 250/43.5 D, 43.5 R, 84, 106 S

[56] **References Cited**

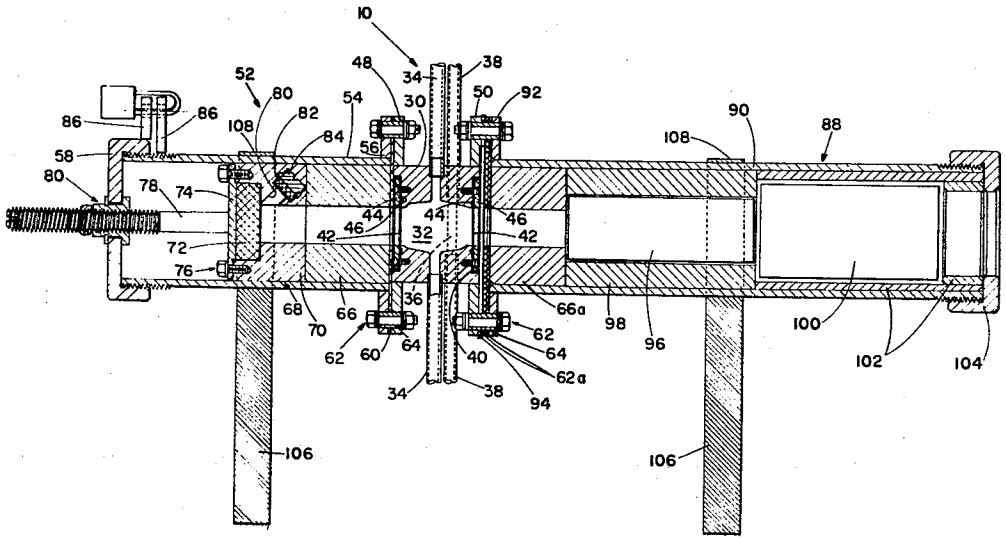
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ABSTRACT: Method and apparatus to accurately determine the percent sulfur content in hydrocarbon process streams comprising the use of radioactive americium-241 and a molybdenum target in reflection mode to produce a narrow X-ray density spectrum at 20 Kev. The equality of the mass attenuation coefficients of carbon and hydrogen at 20 Kev., is utilized to determine the percent by weight content of sulfur in the hydrocarbon stream.



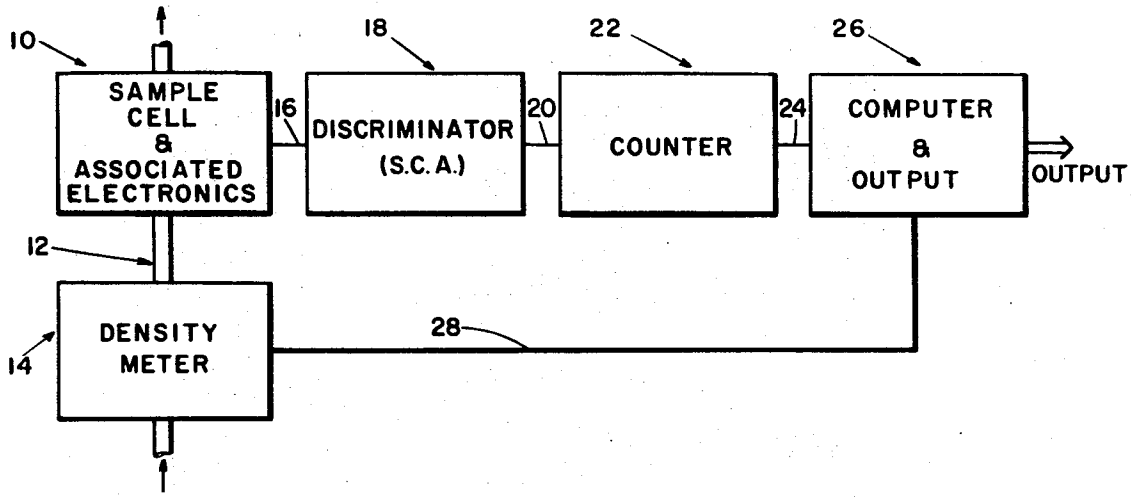


FIG. 1

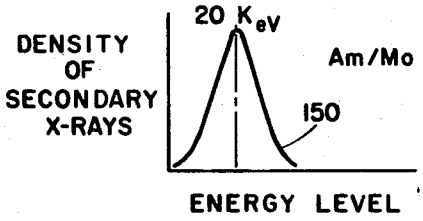


FIG. 3

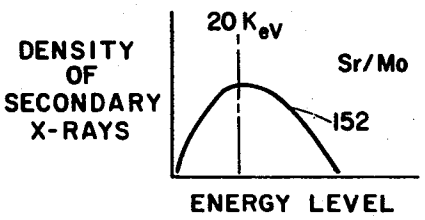


FIG. 4

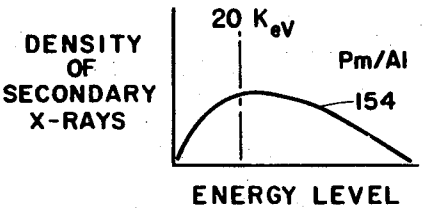


FIG. 5

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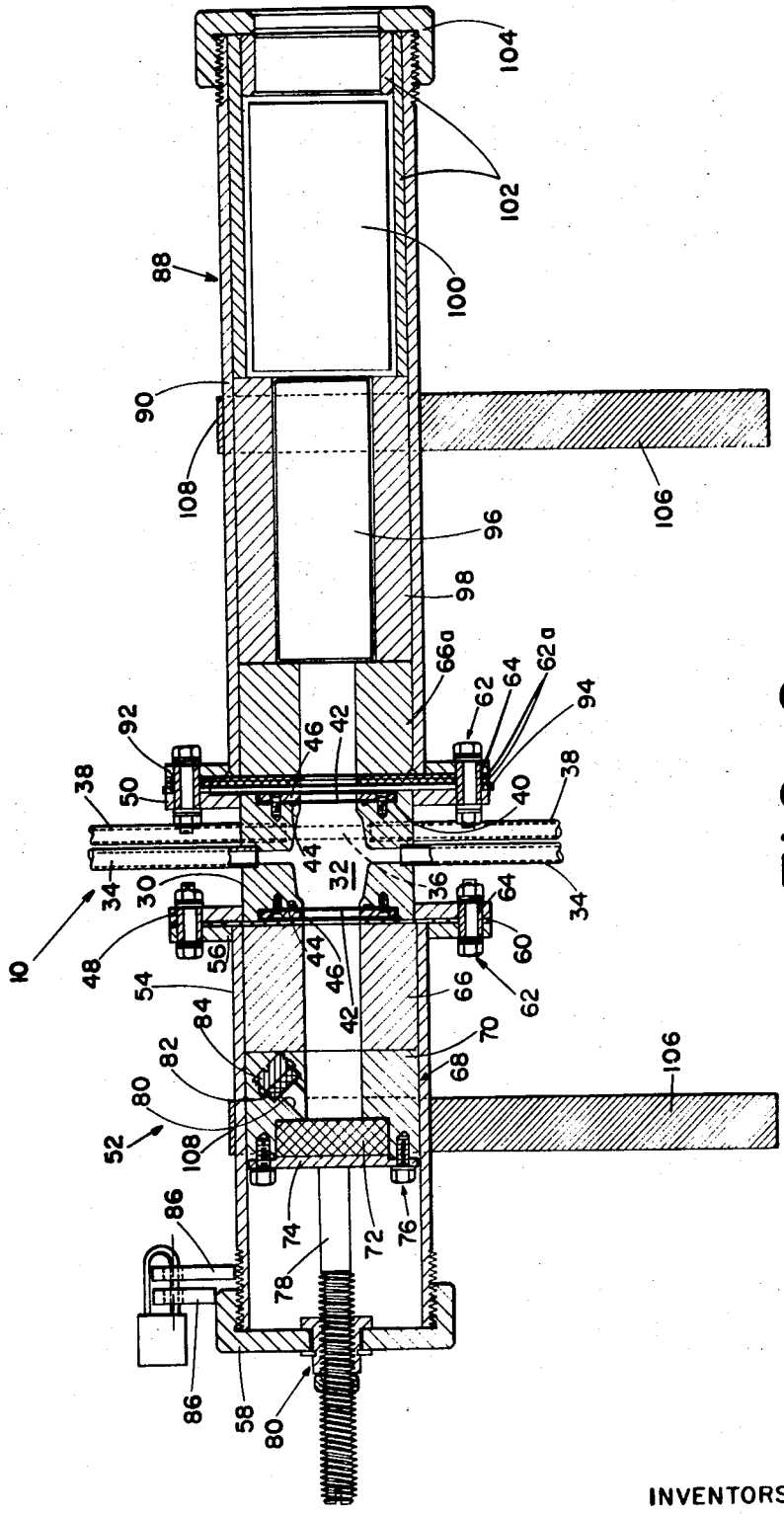


FIG. 2

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METHOD AND APPARATUS FOR DETERMINING SULFUR CONTENT IN HYDROCARBON STREAMS

Broadly, this invention pertains to methods and apparatus to analyze a hydrocarbon stream also containing some heavier, by atomic weight, element for the percent by weight content of said heavier element. More specifically, this invention relates to the determination of the sulfur content in flowing streams of hydrocarbon fluids.

The invention will be described with regard to analyzing a hydrocarbon stream to determine the percent content of sulfur in said steam. However, as will appear more clearly as the description proceeds, the invention can be used to analyze for the percent content of any element in a hydrocarbon stream so long as the mass attenuation coefficient of said third element is substantially different from the mass attenuation coefficients of hydrogen and carbon at 20 Kev. It will therefore be understood that the use of the word "sulfur" should not be construed as limiting the invention to sulfur analysis but shall also include all such heavier elements which may be found in hydrocarbon streams, such as lead, nickel, iron, and vanadium.

In the refining of hydrocarbons, it is important to know, as precisely as possible, the percentage sulfur content of many process steams for many different reasons. In some situations it is necessary to know the percentage sulfur content because a certain minimum sulfur content is required. An example of this situation is where a catalyst must be used in the presence of a certain amount of sulfur in order to partake in the reaction. When hydrocracking materials such as furnace oils and gas-oils into gasoline using Group VI and Group VIII metals on cracking carriers, certain minimum quantities of sulfur are sometimes desirable in the feed stock. An example of such catalyst is a Nickel-Tungsten catalyst on a silica-alumina carrier. In these kinds of situations, if there is not sufficient sulfur in the process stream, additional sulfur must be added to bring the sulfur content to the desired level.

In other situations it is necessary to know the sulfur content for the opposite reason. No more than a certain maximum sulfur content is permissible, and if there is too much sulfur in the process stream it must be removed. Examples of this situation include, for example the production of certain special lubricants such as refrigerator or transformer oils, wherein a product sulfur content above a certain level may cause the formation of sludges in the oils, and/or may disturb oxidation stability. Another example where excess sulfur is undesirable is where the catalyst will be poisoned by too high a sulfur content. An example of this situation is in reforming using a platinum an alumina catalyst. Still another example of where sulfur content must be known in order to keep it below certain minimums is in the manufacture of certain oils, particularly No. 2 fuel oil, wherein the sulfur content must be kept below certain minimum levels since, upon combustion, the sulfur will produce compounds which are undesirable in the atmosphere.

The invention provides means to accurately, rapidly and inexpensively determine the sulfur content of many different hydrocarbon steams by the use of a radioactive energy source in such a manner as to cause cancellation of the hydrogen and carbon contents in the process stream, whereby the apparatus of the invention is sensitive to only the percent sulfur content.

The apparatus of the invention utilizes a radioactive americium-241 source, the radiations from which bombard a molybdenum target to obtain fluorescent X-rays having a narrow energy spectrum peak and an average energy at 20 Kev. Several advantages over prior known atomic sources flow from this particular combination of source and target. Americium-241 has a half-life of 458 years. This exceedingly long half-life obviates the need for the heretofore usual source decay corrections, obviates the need for frequent recalibration, and provides a substantially completely maintenance free apparatus.

A second important advantage is that a very narrow, i.e., sharp, energy distribution occurs at 20 Kev. with this particular combination of source and appear The sharp energy distribution is important in the method of the invention because the mass attenuation coefficients of hydrogen and carbon are virtually identical at 20 Kev., thereby permitting the absorption effects of the hydrogen and carbon to be considered together, leaving the sulfur content solely responsible for variations in transmitted X-rays As is known, the mass attenuation coefficient of a material is a number representative of the total probable ability of that material to reduce the intensity of the transmitted beam by compton scattering or photoelectric absorption. The manner of the operation of the invention will appear more clearly in the detailed description below.

Prior known combinations of radioactive sources and targets do not produce a sharp energy distribution at 20 Kev., or do not have the advantage of the long half-life of the americium/molybdenum combination of the invention, or lack both of these advantages. For example, the use of radioactive strontium-90 and a uranium target produces X-rays having a maximum intensity at about 100 Kev., with a low intensity tail to 2.2 Mev., thus rendering it unsuitable for use in the invention. Another prior known combination is a radioactive promethium **147** source and an aluminum target. This combination has a relatively short half-life of 2.6 years and, although it does have an energy peak at 20 Kev., the peak is quite broad with an average value of about 25 Kev. With the americium/molybdenum combination of the invention, both the average value and the maximum value of density of secondary X-rays produced by the target falls at 20 Kev. The advantage of the source combination of the invention and the shortcomings of the prior known sources is illustrated in the drawing and detailed description below.

The above and other advantages of the invention will be printed out or will become evident in the following detailed description and claims, and in the accompanying drawing also forming part of the disclosure, in which:

FIG. **1** is a block diagram of the apparatus of the invention;

FIG. **2** is a longitudinal, elevational, cross-sectional view through the sample cell, the source, and associated apparatus; and

FIGS. **3**, **4** and **5** are curves illustrating the energy distribution of the source combination of the invention and the energy distribution of two prior source combinations.

Referring now in detail to FIG. **1** of the drawing, block **10** represents the sample cell and associated apparatus and electronics. A pipe or other suitable conduit **12** feeds the process stream whose sulfur content is to be determined into sample cell **10**. Conduit **12** also passes through a density meter **14**, shown positioned before sample cell **10** in the process stream. The density meter may be either before or after the sample cell in the stream.

The electronics included within block **10** produces a train of pulses the rate of which is related to sulfur content of the process steam. The height of each pulse is directly proportional to the energy of the X-ray initiating the pulse. The pulses are transmitted through a line **16** to a Single Channel Pulse Height Analyzer, S. C. A. **18**, which serves to remove spurious portions of the signal, and to limit the signal in line **16** to that portion thereof which is produced by the transmitted energy in the sample cell at 20 Kev., as will appear in more detail below. The S. C. A. contains two discriminators set to bracket the peak at 20 Kev. The process stream flows continuously through the sample cell. S. C. A. **18** produces an output signal in a line **20** similar to the signal in line **16** but modified by the exclusion of portions of the signal other than those produced by 20 Kev., energy in the sample cell, by action of the bracketing discriminators. Thus, the S. C. A. **18** serves as a kind of filter to produce a signal in line **20** related only to the quantity of sulfur in the process stream.

The signal in line **20** is fed into an array of circuits and devices designated by reference numeral **22** and labeled "-

COUNTER". The function of block 22 is to total the series of pulses received from the S. C. A., the number of which is related to sulfur content. In general terms, counter 22 comprises a scaler, a timer and interfacing apparatus to join block 22 to computer 26. The scaler serves as an intermediate storage buffer. In digital operation data from the scaler and the density meter are fed periodically into a digital computer. From these data the concentration of sulfur is computed.

In the analog mode, counter 22 would consist of a ratemeter and an interface to an analog computer. The ratemeter converts the train of pulses from the S. C. A., to a voltage which is proportional to the number of pulses. This voltage is fed through the interface to an analog computer along with a signal from the density meter. FRom this information the sulfur concentration is computed.

The output of counter 22 of whatever form, is present in a line 24 which feeds a computer and an output device generally designated by reference numeral 26. It will be understood that the computer may be either digital or analog, and the output means may be any of the commercially available and well-known devices such as a strip chart, a cathode-ray tube display, an electronic readout or printout device, and the like, and combinations thereof. The particular readout device or devices will be selected according to the needs of the installation, as is well known to those skilled in this art. The output is indicated on FIG. 1 by the double arrow extending to the right out of block 26.

The method of the invention requires that the density of the process stream be known in order to produce a final output in percentage by weight content of sulfur in the process stream. To this end, a conventional density meter 14 is located in conduit 12 in closely adjacent sample cell 10. Density meter 14 produces an output signal in a line 28 proportional to the density of the process stream. The details of the nature of the density signal in line 28 will be dependent upon the details of the computer and the other components in output block 26. That is, if it is desired to produce a continuous analog output signal, then density meter 14 will produce a continuous analog signal in line 28 appropriately scaled to mesh with the sulfur content signal in line 24 being fed to computer 26. If it is desired to have an intermittent digital printout, density meter 14 may be caused to periodically produce a signal in line 28 proportional to density and appropriately scaled to mesh with the sulfur content signal in line 24 being fed to the computer. For example, as will appear more clearly in the operative example given below, if the nature of the process and the possible speed with which the sulfur content can change is of the appropriate character, then a density measurement can be made once per hour while sulfur measurements are made continuously and the hourly density measurement used at no cost in accuracy for that hour, after which density will be again measured, and a new density value may be supplied for the following hour. As will be made clear by the analysis of the method of the invention below, the density determination is required to remove another variable in the equations in order to accurately determine weight percent sulfur in the process stream.

Referring now to FIG. 2, the sample cell and the associated apparatus and electronics are shown in detail. The sample cell is built around a sample chamber forming member 30, formed with sample chamber 32 which is of generally cylindrical shape. In the successfully constructed and used embodiment of the invention, chamber 32 is one inch in diameter and about two inches long. Means are provided to flow a process stream through chamber 32. To this end, a pair of process stream conduits 34 are joined in fluid communication with chamber 32 by means of passageways formed in member 30 and suitable sealing means such as welding or the like. The outer ends, not shown, of the conduits 34, may be tapped into any suitable process stream the sulfur content of which it is desired to determine.

Because certain hydrocarbon fluids with which the invention is used are viscous at room temperature, means are provided to heat member 30 and chamber 32 to permit ready flow of the process stream through the apparatus. So long as the temperature to which the process stream is brought is held constant, there will be no differential changes in density, and the heat will not have an effect on accuracy. Member 30 is of a diameter substantially larger than the diameter of the chamber 32. A passageway 36 is formed through member 30 separate from chamber 32 but closely adjacent thereto. A pair of conduits 38 connect to the opposite ends of passageway 36. By supplying steam or other suitable heated fluid through conduits 38 and passageway 36, the entire member 30 and chamber 32 may be held at some constant high temperature to permit easy flow of the process stream through the apparatus without effecting accuracy.

Means are provided to seal the ends of chamber 32. To this end, each end face of member 30 is formed with a recess 40 in which is seated a "window" 42 formed of beryllium. An O-ring or other suitable sealing means 44 is provided between the inner face of recess 40 and the inner face of the window 42 to seal this plane against fluid leakage. The window is held in fluidtight relation in the recess by a sealing plate 46 which is held in place by suitable screws. A source assembly mounting flange 48 is provided at the left-hand end of member 30, and a detecting assembly mounting flange 50 is provided at the right-hand end of member 30. The flanges 48 and 50 are of ringlike configuration and formed with a row of openings.

Beryllium is chosen as the material for the windows because it is relatively transparent to X-rays. Any other material having this property could be used for the "windows."

The source assembly 52 comprises a main housing cylinder 54 formed with a mounting flange 56 and a threaded end cap 58. Means are provided to thermally isolate member 30 and the process stream handling portion of the apparatus from the source assembly 52. To this end, a sheet 60 of heat insulating plastic or other suitable material, is provided between the mounting flanges 56 and 48. A plurality of nut and bolt assemblies 62 are seated in the registering openings in the flanges 48 and 50, and each comprises a suitable thermal insulation sleeve 64 of Bakelike or the like heat insulating material around the shank of the bolt. Within main housing 54, adjacent insulation 60, is a source spacer or X-ray collimator 66. Next adjacent collimator 66 is a source mounting assembiy 68 comprising a mounting block 70 formed with a central opening in registry with the opening in collimator 66 through which the X-rays pass in a beam from the collimator. Block 70 is formed with a recess at its rear end in which is mounted a block of molybdenum 72, which is joined at its rear or outer face to a mounting plate 74, held in place on block 70 by suitable mounting screw and washer assemblies 76. Extending rearwardly from plate 74 is a threaded adjusting rod 78 which passes through a suitable guiding nut and locking means 80 formed in end cap 58. In spaced relation to the front face of the molybdenum target block 72, block 70 is formed with a 45° passageway 82 in a rear enlarged portion of which is seated the radioactive americium 241 source, held in place by a threaded locking plug 84. End cap 58 and body 54 are formed or provided with cooperating perforated hasps 86 adapted to receive a suitable lock to prevent unauthorized opening of the source assembly 52.

To assemble the source for use, the americium and molybdenum active elements are mounted into block 70 with the use of the usual precautions when handling radioactive materials. Plate 74 is secured behind the molybdenum target by the bolts 76. The remainder of the apparatus has been meanwhile positioned in relation to the process stream and all connections made and checked. With the use of a suitable long handled device or the like on the end of threaded rod 78, not shown, block 70 with the assembled radioactive source and with the end cap 58 on the rod 78 is inserted into main housing 54. The end cap is secured on its threads, the lock put on the hasps 86, and assembly is complete.

To the right, FIG. 2, of the sample chamber member 30 is a detector assembly 88 comprising a tubular housing 90, formed with a mounting flange 92, which is secured to flange 50 with

thermally insulated nut and bolt assemblies **62, 64**, identical to those described above with regard to the source assembly **52**, but with the change that they are slightly longer. The additional length is required to accommodate the double sheets of thermal insulation **62***a* and an airgap **94** which are useful in preventing overheating of the preamplifier **96**.

Within housing **90** next adjacent the insulation **62***a* is a spacer and beam collimator **66***a*, similar to member **66** described above. Next adjacent collimator **66***a* is an X-ray detector and preamplifer **96**, housed within a suitable spacer assembly **98**. Next adjacent preamplifier and detector **96** is an amplifier **100** which is held in place by suitable amplifier spacers **102**. The detector assembly **88** is closed off by an end cap **104**. The various electrical leads, electrical interconnections, and associated details, are well known to those skilled in the art and are not shown.

Support means are provided, and comprise a pair of stands **106** formed with cutouts to receive the housing **54** and **90** respectively, which are held in the cutouts by a pair of top straps **108** and suitable securing means not shown.

The use of the radioactive source combination of the invention to produce a narrow band of energy at 20 Kev., is critical because the mass attenuation coefficients of carbon and hydrogen are virtually identical at 20 Kev. The basic equation is as follows:

$$(1) \qquad I = I_o e^{-t(u_H W_H + u_C W_C + u_S W_S)p}$$

Wherein I is the amount of X-rays transmitted through the sample cell, I_o is the amount of X-rays incident on the sample, e is the natural log base, t is the sample thickness presented to the X-rays, u_H, u_C, and u_S are the mass attenuation coefficients for hydrogen, carbon, and sulfur respectively, W_H, W_C, and W_s are the weight fractions of hydrogen, carbon, and sulfur in the sample, respectively, and p is the density of the sample. In this equation, I, I_o, and p are measured quantities, and t is a known quantity. The assumption is made that there is nothing in the process stream other than carbon, hydrogen, and sulfur, which assumption is valid for the reasons set forth above. The sulfur content of typical refinery process streams with which the invention has been used have been on the order from about 1 percent to about 3 percent, although there is theoretically no upper limit on the amount of sulfur that can be detected by the apparatus of the invention. In any case, since in use, u_H is equal to u_C, Equation (1) above can be rewritten and slightly rearranged as follows:

$$(2) \quad \mathrm{Log}_e I/I_o = tp(u_H(W_H+W_C)+u_S W_S)$$

Since the sample has appreciable quantities of only carbon, hydrogen, and sulfur the following equation is valid: (3) $W_S + W_H + W_C = 1$

rearranging:

$$(4) \quad W_S = 1-(W_H+W_C)$$

Substituting Equation (4) into an rearranging only the right-hand side of Equation (2):

$$(5) \quad tp(u_H(1-W_S)+u_S W_S)$$

$$(6) \quad tp(u_H - W_S u_H + u_S W_S)$$

$$(7) \quad tp(u_H - W_S(u_H - u_S))$$

Since the t, p, u_H, and u_S all have known values, it is valid to substitute the following constants K_1 and K_2.

$$(8) \quad K_1 = tpu_H$$

$$(9) \quad K_2 = tp(u_H - u_S)$$

Substituting Equations (8) and (9) into Equation (7), Equation (2) appears as follows:

$$(10) \quad \mathrm{Log}_e I/I_o = K_1 - K_2 W_S$$

Thus, the amount of transmitted X-rays is directly proportional to only the weight percent of sulfur in the process stream. It will be understood by those skilled in that art, that Equation (10) above can be normalized to some standard material having properties closely related to those of the process streams with which the invention will be used.

The term "appreciable quantities of only..." as used in the specification and claims herein means that any minute or trace quantities of any other additional substance which might also be present is not large enough to adversely effect operation of the invention. As is known, such spurious substances are sometimes present in hydrocarbon streams in insignificant amounts.

The invention is highly sensitive to changes in the weight fraction of sulfur in the process stream, and insensitive to changes in the weight fractions of hydrogen and/or carbon in the process stream. As stated above, u_H is almost identical to u_C at 20 Kev. Additionally, the value of u_S at 20 Kev., is on the order of about 18 times as great as the value of u_H or u_C at 20 Kev. Therefore, a change of, for example 1 percent in either W_H or W_C, as by the addition of a sulfur free hydrocarbon to the process stream, will have a much less than 1 percent change on W_S. Therefore, the apparatus of the invention is highly sensitive to changes in W_S in the process stream.

As the above line of reasoning clearly shows, the invention is adaptable to analyze for any element so long as its mass attenuation coefficient is substantially different from that of hydrogen and carbon at 20 Kev.

As stated above, the method of the invention utilizes the fact that the mass attenuation coefficients of hydrogen and carbon are almost identical at 20 Kev., which is the energy level produced by the source of the invention. If another source which produces an energy peak and average value close to 20 Kev., were used, the accuracy of such a device would depend upon how close to 20 Kev., the energy was. If it were very close, for example 20.01 Kev., as an extreme, the accuracy would still be acceptable for all uses. The invention encompasses all such sources that produce an energy level so close to 20 Kev., that the resulting accuracy will be sufficient for the purposes for which the hydrocarbon stream is being analyzed. The range of energy which will produce acceptable accurate results for most purposes is thought to be 20 Kev. ± 3 Kev. Even larger ranges can be used if corresponding lower accuracy can be tolerated.

Referring to the curves of FIGS. **3** to **5**, the advantageous energy spectrum obtained with the americium/molybdenum source of the invention is compared to the energy spectrum of other sources. The curve **150** of FIG. **3** shows the relationship of density of secondary X-rays produced by the molybdenum target as the ordinate against energy level on the abscissa. It is noteworthy that curve **150** has a relatively sharp peak at 20 Kev., and that both the average density and the peak density of curve **150** occur at 20 Kev. Curve **152** of FIG. **4**, to the same ordinate and abscissa, shows the spectrum produced by a stontium-90 radioactive source and a molybdenum target. The peak energy is not as sharply defined at 20 Kev., and hence the average energy may or may not be at 20 Kev. The curve **154** of FIG. **5** shows the spectrum produced by a promethium-147 radioactive source and an aluminum target. The peak of curve **154** is still flatter than that of curve **152**, and the disadvantages inherent in the strontium/molybdenum combination are even more pronounced here.

The density peak obtained with the source of the invention is an important factor in the exceedingly high accuracy of the invention in determining percent sulfur content. As explained above, the invention depends upon the fact that the mass attenuation coefficients for hydrogen and carbon (u_H and u_C) are about equal at 20 Kev. If the source does not produce a sharp peak at 20 Kev., then u_H will only be approximately equal to u_C, dependent upon how close to 20 Kev., the average energy of the spectrum is.

In use, apparatus embodying the invention has been found to be accurate within 1 percent of the sulfur content. Such apparatus has determined sulfur content from as little as about 0.05 percent up to about 15 percent, and measurement up to 100 percent is theoretically possible.

The accuracy of an apparatus embodying the invention is shown by the following table and explanation:

TABLE I

Test Number	Prepared %Sulfur	Average Counts Per Hour
1	0.04	451×10^4
2	0.25	443×10^4
3	0.50	424×10^4
*4	0.75	404×10^4
5	1.00	388×10^4
*6	1.25	369×10^4
7		352×10^4
*8	1.75	338×10^4
9	2.00	323×10^4
*10	2.25	309×10^4
11	2.50	294×10^4
*12	2.75	280×10^4
13	3.00	268×10^4

Heretofore, the commonly used laboratory techniques for determining percent by weight sulfur content in hydrocarbon process streams involved laboratory chemical reactions to isolate the sulfur. The accuracy of the best of these techniques is in the range of ±10 percent of the sulfur content. Hence, in order to prove the accuracy of the present invention, laboratory techniques could not be relied on since it was desired to prove that the accuracy of the invention is in the range of ±1 percent of the sulfur content. In order to prove accuracy therefore, 13 samples were prepared with known percentages of sulfur added to them by dry weight. By this technique, the percentage sulfur content is accurate to the third decimal place of one percent of the sulfur content. These 13 test samples and their known sulfur contents are given in Table I above. All the samples except the five indicated by an asterisk (*) were run through the apparatus of the invention and the average number of counts per hour, measured on counter **22**, noted. From this data a calibration curve was generated with counts per hour on the ordinate on a logarithmic scale, and with sulfur content on the abscissa on an ordinary scale. After the calibration curve was made, the remaining test samples 4, 6, 8, 10 and 12 were run through the apparatus of the invention, and the measured counts, 404, 369, etc., found on that curve. The percent sulfur content found on the curve from these counts was precisely the respective known percentages, i.e., 0.75, 1.25, etc. The calibration curve generated was a straight line on the semilogarithmic paper used, which corresponds to the theoretically expected result.

The above tests performed for calibration purposes were run with a sample having a known density of 0.900 gr./cm.^{3}, at a temperature of 215° F., with no motion of the sample. Additional tests were run while flowing these same calibration samples through the apparatus of the invention at random speeds in the range of 0 to 100 cc. per minute, and no changes in counting rate larger than the 1 percent instrument plus statistical source emission error were noted.

In the completed and successfully used embodiment of the invention, the following parts and components were used for fabrication.

TABLE II

Component	Description	Manufacturer	Model No.
96	(detector, preamplifier)	Harshow Chemical Co.	Type 5SM
100	(amplifier)	Nuclear Chicago	27001
100	(preamplifier)	Nuclear Chicago	10-17
22	(scaler)	Nuclear Chicago	27104
22	(timer)	Nuclear Chicago	27101
18	(single channel pulse height analyzer	Nuclear Chicago	27352
82	(source)	Radiochemical Center	AMC-7

While the invention has been described in detail above, it is to be understood that this detailed description is by way of example only, and the protection granted is to be limited only within the spirit of the invention and the scope of the following claims.

We claim:

1. Apparatus for determining the amount of an element in a hydrocarbon stream containing appreciable quantities of only hydrogen, carbon, and said element comprising a sample chamber for containing a sample of said hydrocarbon stream, a radioactive source comprising radioactive americium-241 and a molybdenum target arranged in reflection mode to produce a relatively sharp energy peak at about 20 Kev., means to subject a sample in said sample chamber to fluorescent X-rays produced by said source, and means to use the amount of X-rays transmitted through the sample in a calculation to determine the percent by weight content of said element in said hydrocarbon stream.

2. The apparatus of claim **1**, and means to heat said sample in said sample chamber.

3. The apparatus of claim **1**, and means to continuously flow a portion of said stream through said sample chamber.

4. A method of determining the percent content of an element in a hydrocarbon stream containing appreciable quantities of only hydrogen, carbon, and said element, comprising the steps of generating fluorescent X-rays having a relatively sharp energy peak at about 20 Kev., directing said X-rays through a sample of said stream having a predetermined thickness, determining the density of said sample, and determining the weight fraction of said element in said sample according to the relationship:

$$\mathrm{Log}_e I/I_o = K_1 - K_2 W_x$$

wherein $K_1 = tpu_H$, $K_2 = tp(u_H - u_X)$, I is the amount of X-rays transmitted through the sample, I_o is the amount of X-rays impinging upon the sample, e is the natural log base, t is the sample thickness, u_H is the mass attenuation coefficient for hydrogen and carbon, u_X is the mass attenuation coefficient for said element, W_X is the weight fraction of said element in the sample, and p is the density of the sample.

5. The method of claim **4**, wherein said element is sulfur.

6. The method of claim **4**, wherein said element is lead.

7. The method of claim **4**, wherein said sample is heated to a temperature sufficient to permit said sample to flow continuously.

8. The method of claim **7**, wherein said density determination is made in said stream in closely spaced relation to said sample.

9. Apparatus for determining the content of an element in a hydrocarbon stream containing appreciable quantities of only hydrogen, carbon and said element, comprising a sample chamber adapted to contain a sample of said stream, a source of fluorescent X-rays adapted to produce X-rays having a relatively sharp energy peak at about 20 Kev., means to transmit said X-rays through said sample, means to determine the energy of the X-rays transmitted through said sample, means to generate a first signal proportional to the energy of the transmitted X-rays, means to measure the density of said sample, means to generate a second signal proportional to the density of said sample, and means to calculate the percent by weight content of said element in said stream from said first and second signals.

10. The combination of claim **9**, wherein said source comprises radioactive americium-241 and a molybdenum target arranged in reflection mode.

11. The combination of claim **9**, and means to heat said sample in said sample chamber.

12. The combination of claim **11**, and means to continuously flow a portion of said stream through said sample chamber and through said density measuring means.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,602,711 Dated August 31, 1971

Inventor(s) Sudesh Kumar Arora and Donald F. Rhodes

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 5, line 49, in Equation 3, the right side of the equation should be --1-- and not "11", as printed.

Column 7, in Table No. 1, in the line for Test No. 7, the number --1.50-- has been omitted in the "Prepared % Sulfur" column.

Column 7, in Table No. 1, in the line for Test No. 8, the number "1.75" has not been lined up with the remainder of the column.

Signed and sealed this 28th day of March 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents