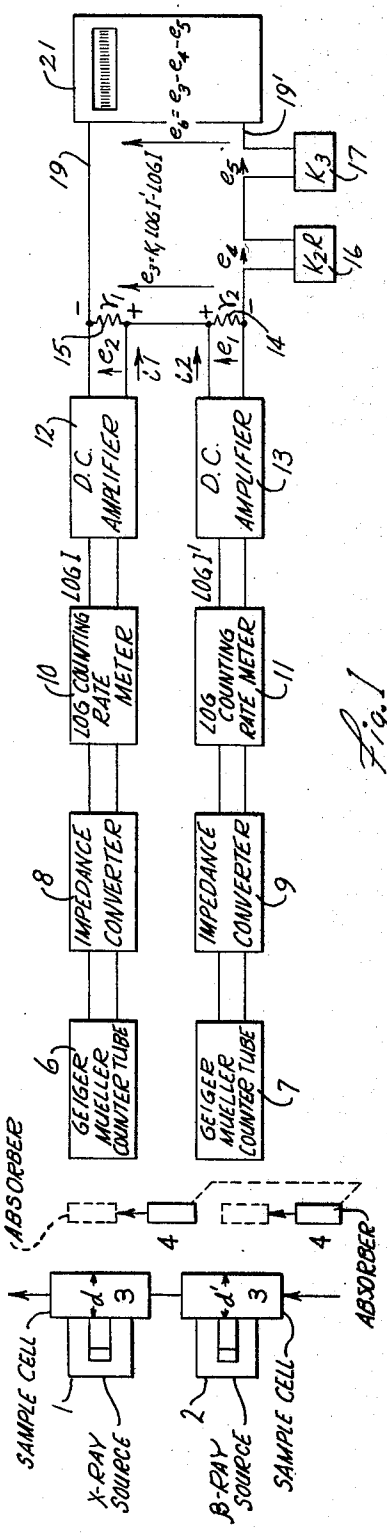
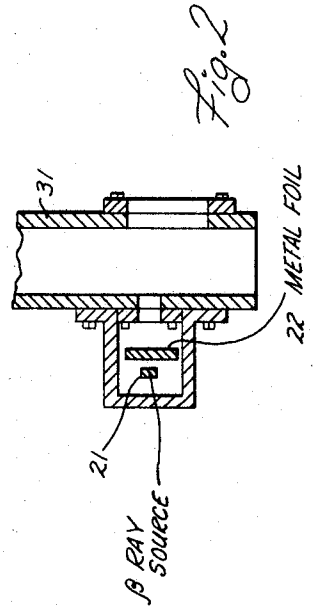
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SYSTEM FOR THE CONTINUOUS AND AUTOMATIC MEASUREMENT OF THE SULFUR CONTENT OF PETROLEUM FRACTIONS

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SYSTEM FOR THE CONTINUOUS AND AUTOMATIC MEASUREMENT OF THE SULFUR CONTENT OF PETROLEUM FRACTIONS

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5 Claims

ABSTRACT OF THE DISCLOSURE

A system for continuously and automatically measuring the sulfur content of petroleum products continuously flowing through a pipe having an X-ray sample cell, a beta ray sample cell provided in association with the pipe, an X-ray source and X-ray detector on opposite sides of the X-ray sample cell, a beta ray source and a beta ray detector on opposite sides of the beta ray sample cell, a metal foil positioned between said beta ray source and said beta ray sample cell and a computer connected to said detectors for receiving separate signals therefrom indicating the transmission intensities of the sample by X-rays and beta rays, respectively, said computer being operative to provide an output signal indicative of the sulfur content of the sample and means responsive to said output signal for continuously and automatically indicating the sulfur content calculated with said computer.

This application is a continuation-in-part of our pending application Ser. No. 518,358, filed Jan. 3, 1966, now abandoned.

This invention relates to a system for continuously, automatically, accurately and quickly measuring and analyzing the sulfur content of petroleum products during the flow of products in a process of refining petroleum or a process of mixing petroleum products and, more particularly, it relates to a system for automatically and continuously calculating and indicating the sulfur content by means of circuitry capable of detecting the penetrabilities of petroleum samples by two kinds of radiation sources, namely, X-rays and beta rays.

As is well known, almost all petroleum fractions contain sulfur. However, generally, the presence of elemental sulfur and sulfur compounds in petroleum products is undesirable. Therefore, a considerable part of the sulfur must be removed by suitable desulfurization treatments and the sulfur content of petroleum products must always be kept under strict control. It is therefore evident that, if the sulfur content of petroleum products can be continuously, automatically, accurately and quickly measured as the products flow through the refining or mixing processes so that steps can be taken, if necessary, to maintain the sulfur content within suitable values, it will be possible to improve greatly the quality of the products, to reduce the operating costs and to prevent the production of faulty products.

Previously there have been suggested many methods of measuring the sulfur content of petroleum products. Suitable procedures are mentioned in various publications of the ASTM, IP and JIS. However, such procedures, which generally involve combustion steps, generally require a long time and considerable skill and, therefore, are not adapted to achieve the objects of the present invention. Further, recently there have been developed methods of measuring the sulfur content of petroleum products by using radioactive isotopes. For example, there is known a method of calculating sulfur content from a value of

density of the petroleum product measured by a separate means and from the amount of X-rays absorbed by the petroleum product, utilizing the property that X-rays emitted from ^{55}Fe, ^{3}H or ^{147}Pm are absorbed by sulfur much more than by hydrogen and carbon, which are principal constituents of petroleum. The measurement of density has been made by batch procedures, such as by placing a sample into a cylinder and measuring its density with a hydrometer. However, needless to say, it is impossible to incorporate such a measurement into a continuous petroleum refining process to obtain a continuous measurement. In this connection, there is already known a density-compensating-type, sulfur content measuring method wherein density compensation is made by a mechanical process by utilizing the variation of the height of a liquid surface by the density variation of a sample caused when a predetermined weight of a petroleum fraction is taken into a particular sample container. In such method, the response time of the density compensation measurement of a petroleum fraction of a high viscosity is so slow and the measured value has so many errors that it is impossible to quickly measure the sulfur content as the petroleum flows, using an apparatus adapted to measure selected portions of the petroleum stream.

The object of the present invention is to improve such sulfur content measuring methods and to make it possible to accurately measure the sulfur content of petroleum products, even petroleum products of a high viscosity, and to continuously, automatically, accurately and quickly measure the sulfur content generally with an apparatus adapted to be applied to a continuously flowing stream of petroleum products.

According to the present invention, it is possible to quickly provide measured sulfur content values of high accuracy, using a sulfur content measuring apparatus which is small and light, by relating the absorption of X-rays and the absorption of beta rays by the petroleum products with each other. It is very simple to incorporate the measuring system of the present invention into any petroleum refining apparatus. For X-ray sources there can be used ^{55}Fe, ^{3}H and ^{147}Pm. The absorption of X-rays will be influenced by the density, sulfur content and carbon/hydrogen ratio of the sample. For beta ray sources there can be used ^{90}Sr and ^{144}Ce. The absorption of beta rays will be influenced by the density and carbon/hydrogen ratio of the sample but same will not be influenced by the sulfur content. Further, the variation of the carbon/hydrogen ratio in a petroleum fraction in any given process of petroleum refinement is so small that only the variation of density need be taken into consideration in relation to the compensation for the absorption value of X-rays. The apparatus of the present invention is characterized by using a beta ray source as a means of such density compensation. If any other radiation source such as, for example, a gamma radiation source, is used the size of the sample required to measure the gamma ray absorption will be far larger than in the case of beta rays. Therefore, not only the apparatus itself will have to be made so large as to be inconvenient to handle, but also a sample will be required which is of much larger size than the sample needed for the X-ray measurement. Thus, a time lag will occur in the measurement and the measured value will have errors. Therefore, in the present invention, a beta ray source is used for density compensation. However, if this beta radiation source is directly applied to the petroleum product, the density of the petroleum product cannot be measured accurately because the beta rays will be greatly influenced by the carbon/hydrogen ratio. In this connection, we have discovered that if the beta rays are shielded by a metal foil of a thickness of 20 to 80 mg./cm.^{2} or preferably 30 to 50 mg./cm.^{2}, beta rays can be used effectively. It is preferred that the metal foils

be made of tin, aluminum or cadmium. For example, if ^{90}Sr is shielded with an aluminum foil of 40 mg./cm.^{2} thickness, the influence of the carbon/hydrogen ratio in the density measurement will be reduced to one-tenth as much as when there is no shield. Further, thereby the density can be represented by a linear formula of the beta ray penetrability and density compensation can be simply made.

In the present invention, a sample cell to be transmitted by X-rays is made of an anticorrosive metal and has an X-ray penetrable part or window made of a beryllium plate. The proper transmitted thickness of the sample cell is from 2 to 6 mm., preferably 3 to 4 mm. The strength of the X-ray source is more than 4 millicuries, usually 5 millicuries for ^{55}Fe.

The proper transmitted thickness of the sample cell for beta rays is from 2 to 10 mm., preferably 4 to 5 mm. The strength of the beta ray source is from 0.5 to 5 millicuries, usually 2 millicuries.

From many experimental values, we have determined by the method of least squares that the logarithm of the intesity of the X-ray transmission (I) of any given petroleum sample is represented approximately by a linear formula based on the density (φ) of the sample, the carbon/hydrogen ratio (C/H) of the sample and the sulfur content (percent S) of the sample and that the logarithm of the intensity of the beta ray transmission (I') of a sample is represented approximately by a linear formula based on the density (φ) and the carbon/hydrogen ratio (C/H) of the sample. That is to say, we have found experimentally that the transmission intensities can be represented by the following equations:

$$\log I = a\varphi - bC/H - k \text{ percent } S + c$$
$$\log I' = a'\varphi + b'C/H + c'$$

wherein a, a', b, b', k, c and c' are constants determined by the strength of the radiation source, thickness of the window, characteristics of the detector and other factors. By solving both equations for density (φ), this factor can be removed. For example, in one specific example wherein ^{55}Fe was used for the X-ray source and ^{90}Sr was used for the beta ray source, the following formula was obtained:

$$\text{Percent } S = \frac{1.3286 \log I' - \log I - 0.837\ C/H - 6.583}{0.295}$$

which could be represented by the following general equation:

$$\text{Percent } S = \frac{K_1 \log I' - \log I - K_2 R - K_3}{K_4} \quad (1)$$

wherein $R = C/H$ and K_1, K_2, K_3 and K_4 are constants.

In the apparatus of the present invention, the values of the transmission intensities I and I', obtained with an X-ray detector and a beta ray detector, respectively, as described above, are introduced into an operation circuit which is constructed so as to operate in accordance with the above-mentioned Formula (1), and this operatoin circuit is connected to a sulfur content indicator so that the sulfur content in the sample may be automatically and continuously indicated. If an automatic recorder is connected to the circuit, the sulfur content will be able to be automatically recorded.

That is to say, the present invention provides a system for continuously and automatically measuring the sulfur content of petroleum products, which system comprises an X-ray transmission sample cell and a beta ray transmission sample cell provided in a pipe through which a sample flows. An X-ray source and an X-ray detector and a beta ray source and a beta ray penetrability detector are provided in association with the respective sample cells and a shielding metal foil of a thickness of 20 to 80 mg./cm.^{2} is positioned between the beta ray source and its associated sample cell. The two detectors are connected to an operation circuit for calculating the sulfur content of the sample from the X-ray transmission intensity and beta ray transmission intensity through the sample so that the sulfur content calculated with said circuit may be indicated by a sulfur content indicator and recorder connected to said circuit.

The apparatus and method of the present invention shall be explained in the following with reference to the accompanying drawing in which:

FIGURE 1 is a schematic block diagram of the system.

FIGURE 2 is a central sectional view through the beta ray cell.

In the drawing, **1** and **2** are ray source containers each having a collimator in the direction of permeating a petroleum fraction. An X-ray source and a beta ray source are respectively provided in them.

The radioactive rays radiated from the ray sources **1** and **2** will permeate sample cells **3** and **3'** and will enter radioactive ray detectors, for example, Geiger Mueller counter tubes **6** and **7**, respectively.

At the time of measurement, an oil to be measured is made to continuously flow to the sample cells **3** and **3'**. (The thicknesses of the sample cells in the radioactive ray permeating direction shall be respectively d and d'.)

4 is a standard absorbent. With the sample cells **3** and **3'** empty, the standard absorbent is positioned in the radioactive ray permeating path and a standard indication is set in a recorder **21**. A K_3 setting circuit **17** is adjusted and coupled to the recorder so that a correction can be made for the respective half-life periods of the ray sources. An aluminum plate is used as the standard absorbent, for example.

In the Geiger Mueller tubes, each radioactive ray is converted to a pulse-shaped electric signal. The radio-active ray detector outputs are fed to impedance converters **8** and **9**. By this means, electric signals of high output impedances from the Geiger Mueller tubes **6** and **7** can be transmitted over a long distance. **10** and **11** are so-called logarithmic counting rate meters from which the outputs are direct currents which are proportional to the logarithmic values of the numbers per unit time of pulse-shaped electric signals from the impedance converters **8** and **9**, respectively. That is to say, the outputs of meters **10** and **11** correspond to the factors log I and log I' in the Formula 1. **12** and **13** are direct current amplifiers which can well amplify the output signals of the logarithmic counting rate meters **10** and **11**, respectively. The outputs of amplifiers **12** and **13**, for example, direct currents i_1 and i_2. The total conversion constants of a the logarithmic counting rate meter **10** and direct current amplifier **12** and b the logarithmic counting rate meter **11** and direct current amplifier **13**, are made exactly the same.

The above-described direct currents i_1 and i_2 are fed respectively to electric resistors **15** (of a resistance r_1) and **14** (of a resistance r_2) so that direct current voltages e_2 and e_1 may be respectively generated at both ends. Here, the ratio of r_2/r_1 is made proportional to K_1 in the Formula 1. The direct current voltages e_1 and e_2 are connected together by conductor **20** so that their polarities may be reverse to each other. If e_3 is obtained, it will be direct current voltage proportional to ($K_1 \log I' - \log I$) in the Formula 1.

16 is a circuit for generating a direct current voltage e_4 proportional to K_2R in the Formula 1. The proportion constant between e_4 and K_2R is made exactly the same as the proportion constant between e_3 and ($K_1 \log I' - \log I$). The K_2R setting circuit **16** can be made manually variable in response to C/H of the petroleum fraction flowing to the sample cells. **17** is a circuit for generating a direct current voltage e_5 proportional to K_3 and the proportion constant is the same as in the case of e_4. As shown in FIGURE 1, the K_2R setting circuit **16** and K_3 setting circuit **17** are connected in series so that the polarities of the generated voltages e_4 and e_5 may be in the same direction as of e_3 according to the Formula 1. The voltage e_6 is equal to the sum of e_3, e_4 and e_5 and is proportional to the numerator of the Formula 1.

As K_4 in the Formula 1 is a constant, e_6 will be pro-

portional to S in percent (sulfur in percent). Therefore, S in percent can be measured by directly reading e_6 in a direct current ammeter. **19** and **19'** are output terminals. If the recorder **21** is connected to them, continuous measurement will become possible.

Therefore, as understood also from the drawing, the apparatus according to the present invention has numerous advantages, such as, it includes no division circuit, only two simple amplifiers are used, the formation construction of the circuit is simple and the number of parts is small. Therefore, the maintenance of the apparatus is easy and the errors of the apparatus are small.

Further, stability of the apparatus can be easily obtained and manufacture of the apparatus at a low cost is possible. Therefore, it is possible to satisfy all of the features of precision, stability and maintenance required in industrially usable measuring devices.

Further, the correction for the damping of the ray source is also very simple. The K_3 setting circuit **17** may be adjusted so that the output permeating through the standard absorbent, for example, the aluminum plate, may be of a predetermined value (by setting in advance the standard indication when the standard absorbent is inserted into the recorder). The same method can be used to correct not only the damping of the ray source but also the displacement of the position of the ray source, the variation of the detector output and the displacement of the position of the detector.

Since the various circuit elements for the K_2R, K_3 and K_4 circuits and logarithmic converting operations are well known to persons acquainted with analog computing circuits and since such elements are not part of this invention, they will not be further described herein.

It has been found acceptable to use, as the impedance converters **8** and **9**, Type PC–8 impedance converters manufactured by Hokushin Electric Works, Ltd. of Kobe, Japan. The log counting rate meters **10** and **11** may be Type RM–4 rate meters made by the same manufacturer.

Referring to FIGURE 2, the sample cell **3'** has a beta ray source **21** associated therewith for directing beta rays through the cell toward the detector **6'**. A metal foil **22** of 20 to 80 mg./cm.^{2} thickness is positioned between the beta ray source and the cell **3'** in order to minimize the effect of variations in the *C/H* ratio in the petroleum product.

With the apparatus of the present invention, there can be obtained excellent results such that the accuracy of measurement of percent S is 0.06% S for a light oil of 0.25 to 1.0% S, and 0.08% S for a heavy oil of 1.0 to 3.8% S.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A system for continuously and automatically measuring the sulfur content of petroleum products passing through a pipe, comprising:

an X-ray sample cell and a beta ray sample cell provided in association with the pipe;

an X-ray source and an X-ray detector on opposite sides of the X-ray sample cell;

a beta ray source and a beta ray detector on opposite sides of the beta ray sample cell;

a metal foil positioned between said beta ray source and said beta ray sample cell;

an operation circuit which is constructed so as to operate in accordance with the following formula:

$$\text{Percent } S = \frac{K_1 \log I' - \log I - K_2 R - K_3}{K_4}$$

wherein percent S is the sulfur content of the sample, I and I' are the X-ray and beta ray transmission intensities of the sample respectively, R is the carbon/hydrogen ratio of the sample and K_1, K_2, K_3 and K_4 are constants, said circuit being connected to said detectors for receiving separate signals therefrom indicating the transmission intensities of the sample by X-rays and beta rays, respectively, said circuit being operative to provide an output signal indicative of the sulfur content of the sample and means responsive to said output signal for continuously and automatically indicating the sulfur content calculated with said operation circuit.

2. A system according to claim **1**, wherein said X-ray source is a member selected from the group consisting of ^{55}Fe, ^{3}H and ^{147}Pm.

3. A system according to claim **1**, wherein said beta ray source is a member selected from the group consisting of ^{90}Sr and ^{144}Ce.

4. A system according to claim **1**, wherein said metal foil is a member selected from the group consisting of tin, aluminum and cadmium foils.

5. A method according to claim **1**, wherein the thickness of said metal foil is 20 to 80 mg./cm.^{2}.

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