

- [54] APPARATUS USING X-RAYS FOR MEASURING THE CONTENT OF AN ELEMENT HAVING A HIGHER MASS ABSORPTION COEFFICIENT THAN HYDROGEN AND CARBON IN HYDROCARBON COMPOUNDS
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- [30] Foreign Application Priority Data
- | | | |
|--------------|-------|--------------------------|
| Oct. 9, 1969 | Japan | 44/80950 |
| Oct. 8, 1969 | Japan | 44/96100 (utility model) |
| Oct. 9, 1969 | Japan | 44/80954 |

- [52] U.S. Cl. 250/358
[51] Int. Cl. G01n 23/12
[58] Field of Search..... 250/43.5 D, 43.5 MR, 250/106 S

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Primary Examiner—Archie R. Borchelt
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[57] ABSTRACT

In an apparatus for measuring the concentration of elements such as sulphur, chlorine, nickel or lead contained in hydrocarbon compounds there is provided a source of radioactive rays having an energy level of about 60 to 100 KeV, a target irradiated with the radioactive rays to emanate fluorescent X-rays having an energy level of about 23 to 24.5 KeV, and means to detect the fluorescent X-rays which are transmitted through the petroleum.

15 Claims, 19 Drawing Figures

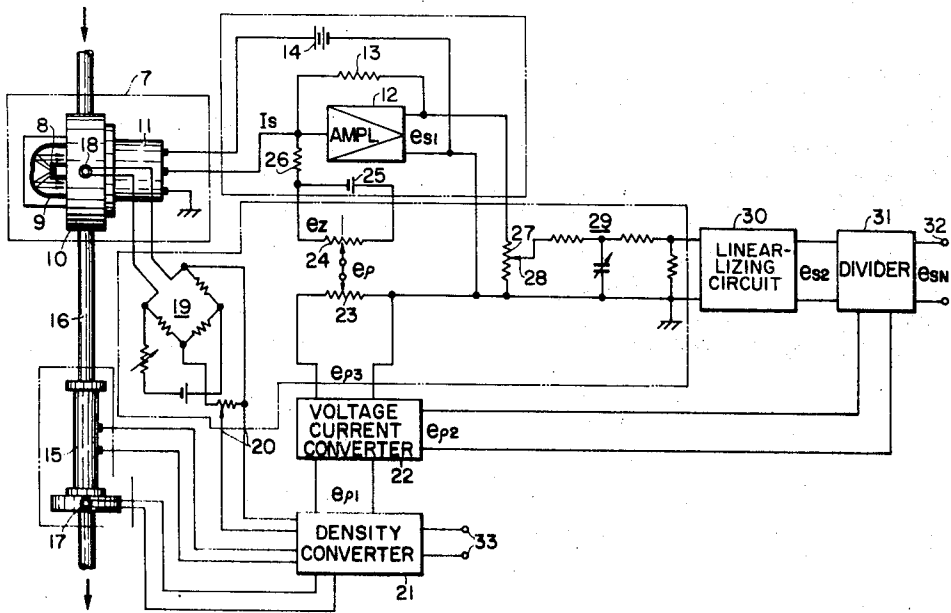


FIG. 1

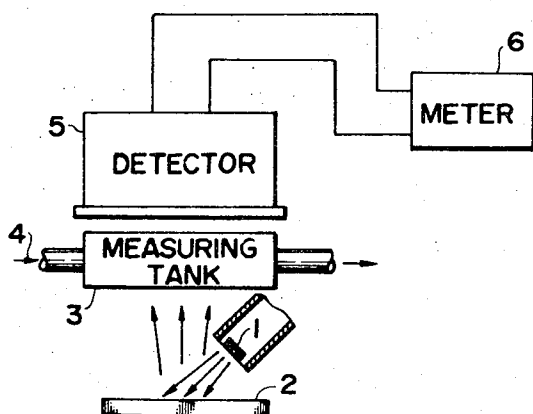


FIG. 2

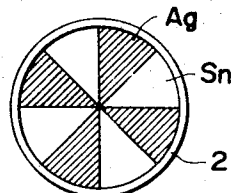


FIG. 3

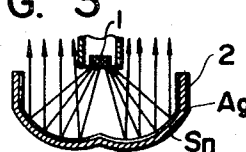
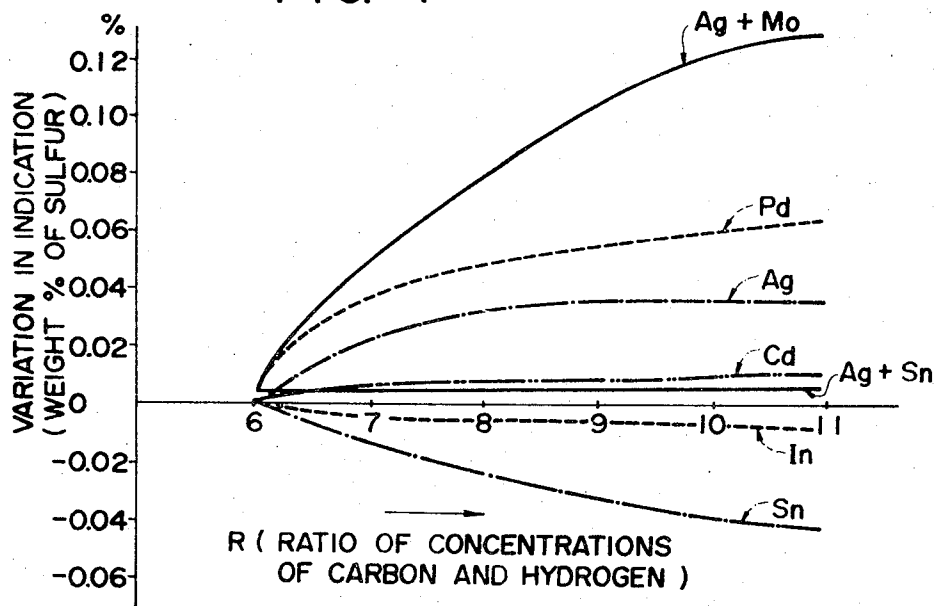


FIG. 4



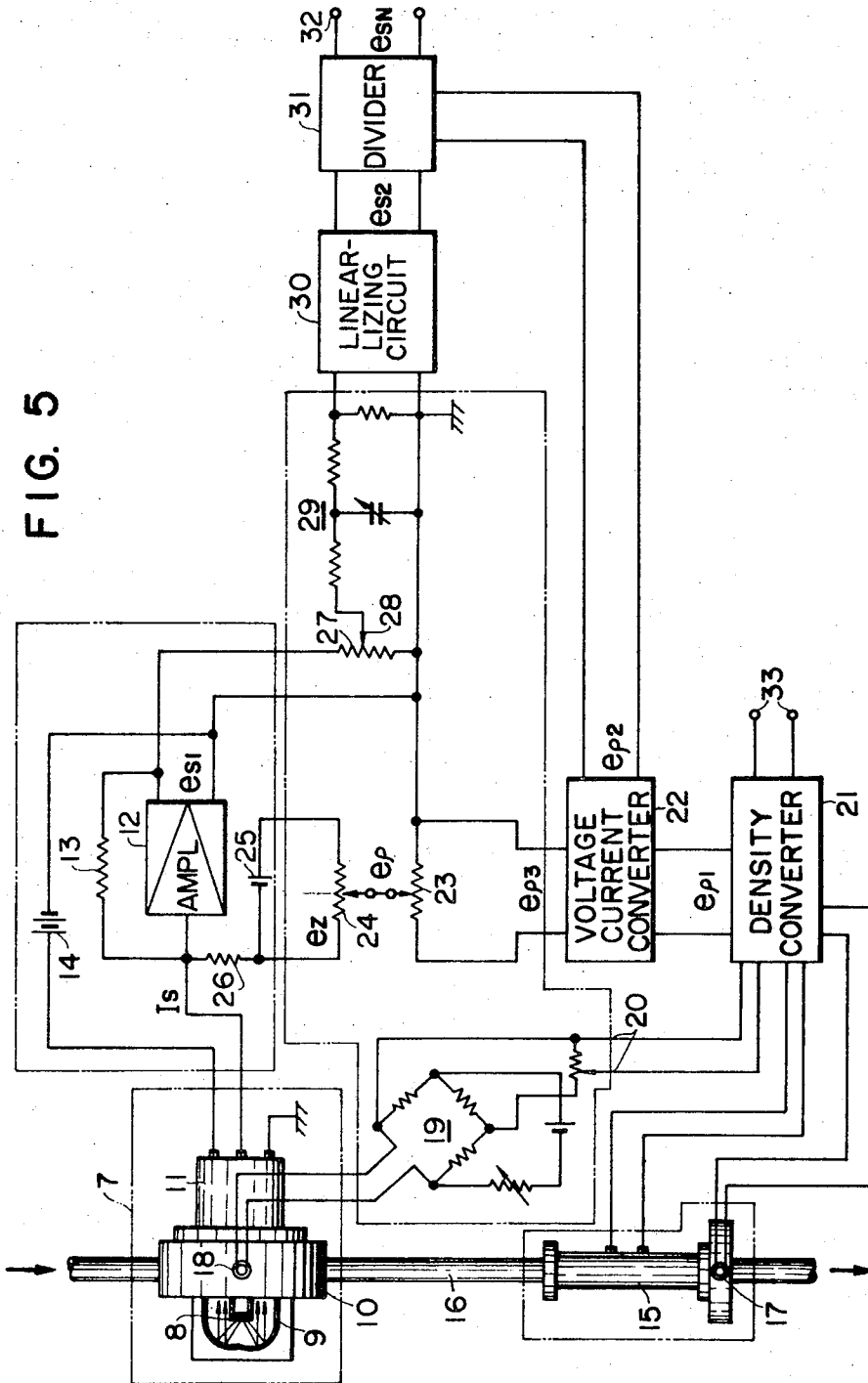
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FIG. 5



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FIG. 6

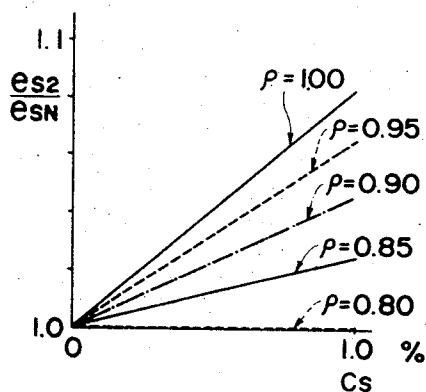


FIG. 7

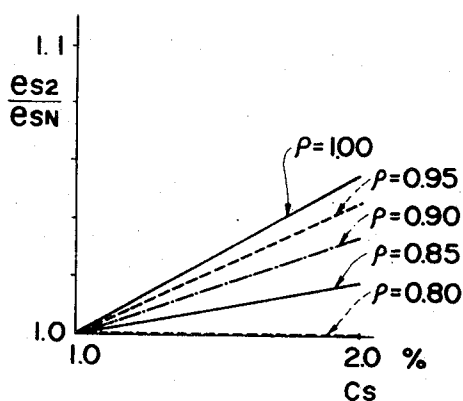


FIG. 8

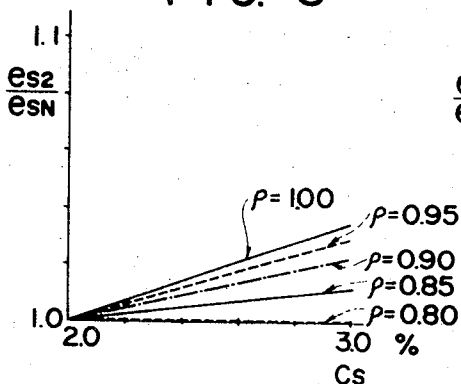


FIG. 9

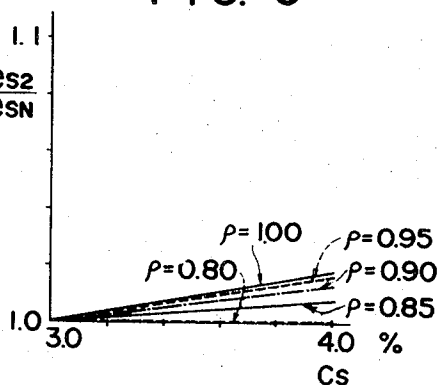
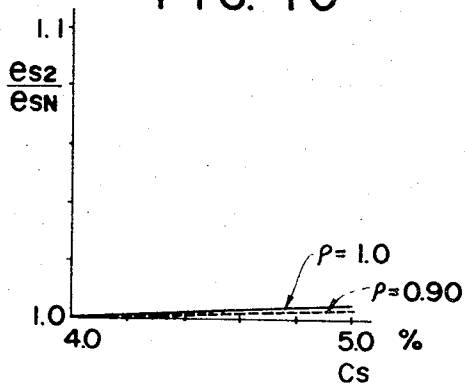


FIG. 10



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FIG. 11

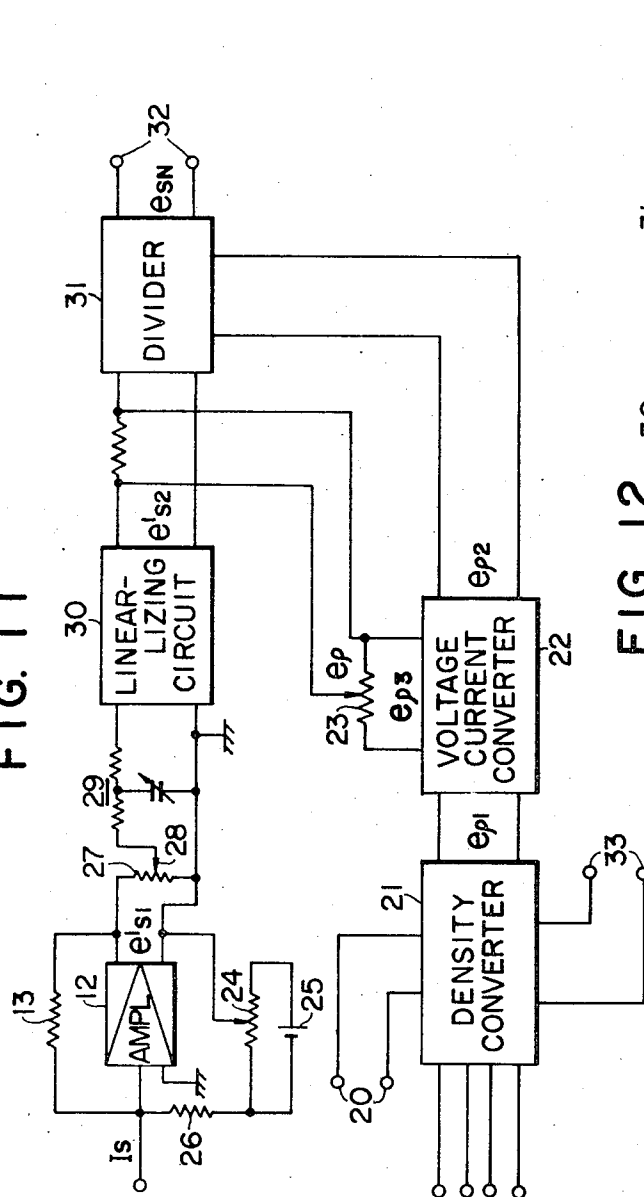
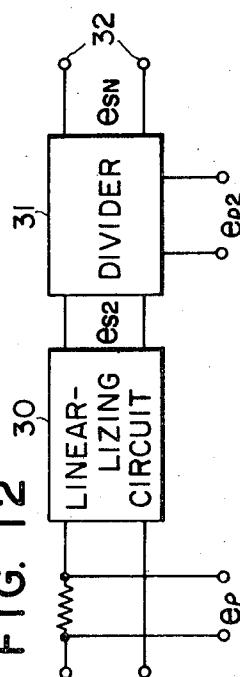


FIG. 12



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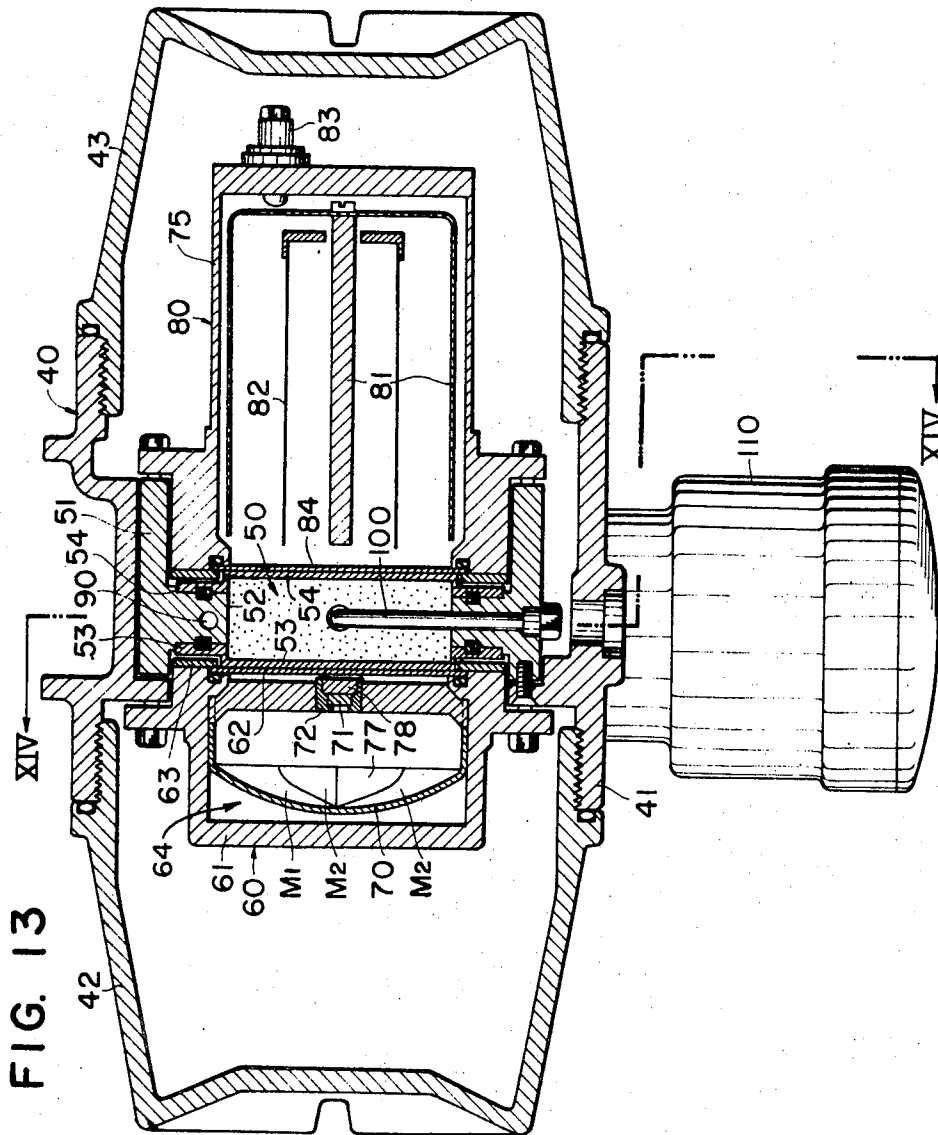


FIG. 13

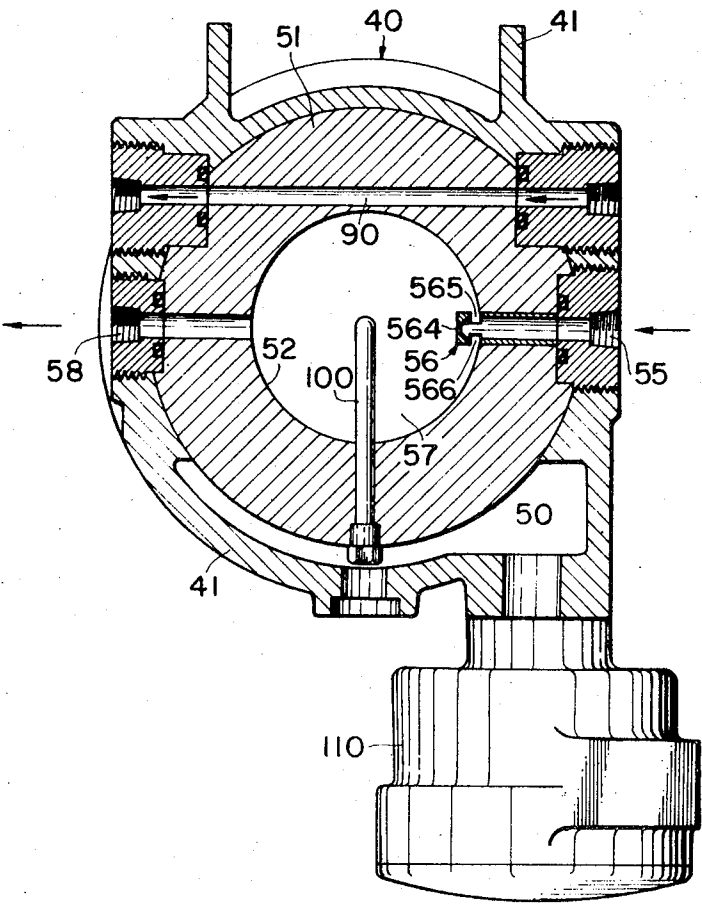
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FIG. 14



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FIG. 15

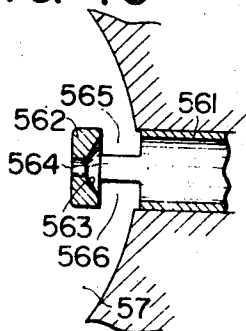


FIG. 16

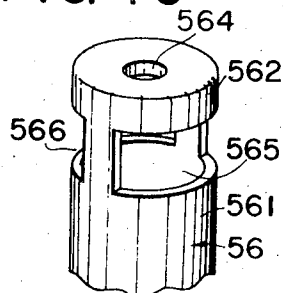


FIG. 17

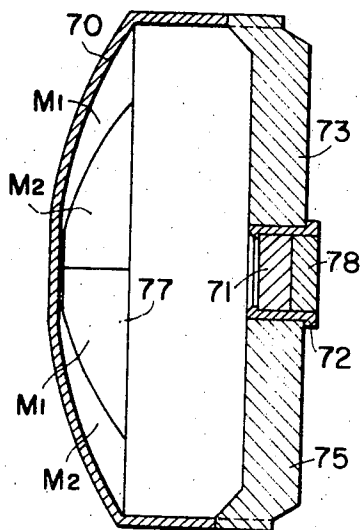


FIG. 18

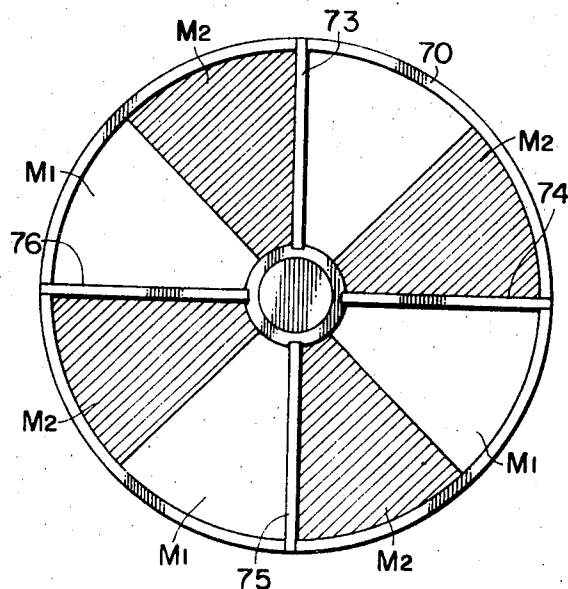
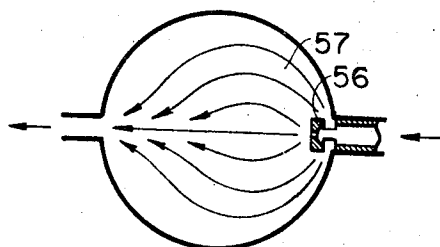


FIG. 19



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APPARATUS USING X-RAYS FOR MEASURING THE CONTENT OF AN ELEMENT HAVING A HIGHER MASS ABSORPTION COEFFICIENT THAN HYDROGEN AND CARBON IN HYDROCARBON COMPOUNDS

BACKGROUND OF THE INVENTION

This invention relates to apparatus for measuring concentrations of sulphur or another element for example, chloride, nickel or lead contained in hydrocarbon compounds such as crude oil or refined petroleum products by utilizing the absorption of radioactive rays.

Since sulphur contained in petroleum causes a number of public hazards, control of the concentration of sulphur has recently become the important object of public attention. In the measurement of the concentration of sulphur contained in hydrocarbon compounds, especially crude oil, heavy oil, light oil and other refined petroleum products by utilizing radioactive rays emanated from a target, major factors that cause errors in the measurement are considered to be the variation in the ratio of concentrations of carbon and hydrogen in the hydrocarbon compound and the variation in the density thereof. The former cause can be substantially eliminated by the suitable selection of the source of radioactive rays and the target whereas the latter cause can be compensated for by properly processing a signal representing the sulphur concentration and a signal representing the density of the hydrocarbon compound.

When measuring the concentration of sulphur in a hydrocarbon compound by measuring the quantity of radioactive rays transmitted, through a sample of the hydrocarbon compound, the following equation 1 is relied upon

$$I_s = I_o \exp - [(\mu_s - \mu_H + R\mu_C / 1 + R) C_s + \mu_H + R\mu_C / 1 + R] \rho t \quad (1)$$

where $R = C_c / C_H$ and

$$C_s + C_H + C_c = 1 \quad (2)$$

In the above equation I_s represents the electric output of the measuring apparatus produced by radioactive rays after they are transmitted through the sample, I_o the output of the measuring apparatus produced by the radioactive rays before transmission, μ_s the mass absorption coefficient of sulphur, μ_H that of hydrogen, μ_C that of carbon, C_s the concentration of sulphur, C_H that of hydrogen, C_c that of carbon, ρ the density of the sample, t the effective length of the sample and R the ratio of concentrations of carbon and hydrogen. In equation 1 since the values of μ_s , μ_H , μ_C and t are constant, if it were possible to make ρ constant the output I will be a function of C_s and R . In other words, the output I varies with the concentration of sulphur C_s and is influenced by the ratio C_c / C_H . For this reason, it will be clear that, in order to make output I free from the effect of the ratio R , conditions that $\mu_s \ll \mu_C$ and $\mu_s \ll \mu_H$ should be satisfied and that it is necessary to use radioactive rays satisfying a condition that $\mu_H = \mu_C$. A sulphur analyzing device has been proposed utilizing ^{241}Am as the source of the radioactive rays and silver as the target material so as to produce fluorescent X-rays of an energy level of 22,162 KeV which is inherent to silver.

However, with this device, it is difficult to completely eliminate the effect caused by the ratio of concentra-

tions of carbon and hydrogen so that it has been impossible to obtain a high degree of accuracy.

In a prior electrical measuring apparatus, to compensate for the density of the sample, after linearizing by means of a logarithmic amplifier, a sulphur concentration signal is divided by a density signal. However, the logarithmic amplifier is not only complicated and expensive, but also it is difficult to construct it to have high accuracies.

SUMMARY OF THE INVENTION

It is an object of this invention to provide improved apparatus for measuring the concentration of sulphur and the like contained in hydrocarbon compounds according to which the effect of the ratio of concentrations of carbon and hydrogen upon the accuracy of measurement can be greatly reduced.

Another object of this invention is to provide an improved apparatus for continuously measuring the concentration of sulphur and the like in hydrocarbon compounds wherein variation in the density of the sample can be automatically compensated for without the necessity of using an expensive logarithmic amplifier.

A further object of this invention is to provide a novel concentration measuring apparatus which utilizes radioactive rays for transmission through the sample, and which is free from fault, can be readily assembled and disassembled, has constant operating characteristics and can efficiently utilize the radioactive rays emanated from the source thereof.

Still another object of this invention is to provide an improved apparatus for measuring the concentration of sulphur and/or other elements contained in hydrocarbon compounds capable of preventing the sample to be measured from staying in a measuring tank and assuring uniform flow of the sample through the measuring tank. According to this invention there is provided a novel apparatus for measuring the concentration of an element contained in a hydrocarbon compound, typically petroleum and refined products thereof, said element having a higher mass absorption coefficient than the carbon and hydrogen and being typically sulphur, comprising a source of radioactive rays of an energy level of about 60 to 100 KeV, a target irradiated with the radioactive rays to emanate fluorescent X-rays having an energy level of about 23 to 24.5 KeV, and means to detect the fluorescent X-rays which are transmitted through the hydrocarbon compound.

It is a feature of this invention to construct the target as a composite body of a combination of two metals selected from the group consisting of silver, tin, indium and cadmium.

It is also a feature of this invention to construct the target from a single metal selected from the group consisting of indium and cadmium.

Another feature of this invention lies in a concentration measuring circuit comprising a concentration detector for measuring the concentration of an element contained in a hydrocarbon compound, an amplifier for measuring the concentration signal from the detector, a amplifier circuit for linearizing the output from the linearizing, a divider for dividing the output from the linearizing circuit with a signal related to the density signal of the hydrocarbon compound, means for converting the density signal into an exponential signal which is a function of the density and a reference concentration of the element and means for differentially

adding the exponential signal to a signal related to the concentration signal.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention can be better understood from the following detailed description taken in conjunction with the accompanying drawings in which:

FIG.1 is a diagrammatic representation of the measuring apparatus of this invention;

FIG.2 is a plan view of one embodiment of the target constructed according to this invention;

FIG.3 is a sectional view of a target and a source of radioactive rays.

FIG.4 shows a set of curves showing the relationship between the ratio of concentrations of carbon and hydrogen and indications in weight percent of sulphur for various types of targets;

FIG.5 is a block connection diagram of a measuring circuit employed in this invention;

FIGS. 6 to 10 inclusive are graphs showing the relationship between the concentration of sulphur and the input-output ratio of a divider, wherein the density is utilized as the parameter;

FIG.11 shows a block connection diagram of a modified embodiment of this invention;

FIG.12 is a partial connection diagram of another modification of the measuring circuit;

FIG.13 is a sectional view of a density signal generator utilized in this invention;

FIG.14 is a cross-sectional view of the density signal generator shown in FIG.13 taken along a line XIV—XIV;

FIG.15 is an enlarged sectional view of the diffuser 56 shown in FIG.14;

FIG.16 is an enlarged perspective view of the diffuser;

FIG.17 shows a sectional view of the source-target portion utilized in the concentration signal generator shown in FIG.13;

FIG.18 shows a plan-view of the source-target portion shown in FIG.17 and

FIG.19 shows the flow of liquid in a measuring tank utilizing a diffuser.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The measuring apparatus of this invention diagrammatically shown in FIG.1 comprises a source of primary radioactive rays or X-rays 1 having an energy level of 60 to 100 KeV, which may be ^{241}Am for example. The primary radioactive rays from source 1 impinge upon a metal target 2 to produce fluorescent X-rays inherent to the material comprising the target. Fluorescent X-rays transmit through a sample to be tested flowing through a measuring tank 3 by way of a pipe 4, and the transmitted X-rays are detected by a detector 5 in the form of an ionization chamber, for example. The output current from the detector 5 is amplified by an amplifier and is then supplied to a recording meter or a controlling device after being suitably combined with a density signal regarding the same sample for density compensation as described later in more detail.

As shown in FIG.2, the target 2 comprises a composite body of different metals, in this example, alternate sectors of silver (hatched portion) and tin. As shown in FIG.3, illustrating one example of a source of radioactive rays 1 and a target 2, the target 2 is generally in the

form of a cup with the center of the bottom slightly raised to form curved reflecting surfaces, and the source 1 is positioned above the center of the target.

When the primary radioactive rays are projected upon the target from a source of ^{241}Am , for example, the target emanates fluorescent X-rays due to its photoelectric effect. The energy of the fluorescent X-rays is inherent to the particular material comprising the target. Table 1 below shows specific energies of the fluorescent X-rays for typical elements.

TABLE 1

Metal		Specific Energy (KeV)
molybdenum	Mo	17.478
rutenium	Ru	19.278
paradium	Pd	21.175
silver	Ag	22.162
cadmium	Cd	23.172
indium	In	24.207
tin	Sn	25.270

Returning back to FIG.1, the fluorescent X-rays emanated from target 2 are absorbed by the sample 4 in measuring tank 3 according to equation 1 described above, and the fluorescent X-rays transmitted through the sample are received by detector 5 to produce an electric output corresponding to equation 1. The output current is amplified by an amplifier.

Curves shown in FIG.4 were obtained by utilizing an experimental apparatus similar to that shown in FIGS. 1 to 3 and shown the relationship between indicated values of the outputs and varying ratio of concentrations of carbon and hydrogen for various materials of the target, wherein the concentration of the sulphur was maintained constant, and the values of the outputs were calculated in terms of the concentration (weight percent) of the sulphur. The measuring tank used in the experiment was made of bakelite and had a wall thickness of 6mm, an effective length of the liquid of 30mm and the surface density of the liquid was 1,975g/cm². A mixture of cyclohexane and tulvene was used and the ratio of the components was varied to provide liquid hydrocarbon mixtures of varying ratios of concentrations of carbon and hydrogen.

In FIG.4 a curve labelled with Ag + Mo shows the characteristics of a composite target consisting of silver and molybdenum sectors of an area ratio of 50 : 50, curves labelled with Pd, Ag, Cd, In and Sn show those of the targets of paradium, silver, cadmium, indium and tin, respectively, whereas a curve labelled with Ag + Sn shows the characteristics of a composite target consisting of silver and tin sectors of an area ratio of 50 : 50.

As can be clearly noted from FIG.4, in the cases of targets of Cd, Ag+Sn and In, the deviations of the indications are less than 0.01 percent whereas in the other cases the deviations are more than 0.02 percent. Especially, in the case of a composite target of Ag+Sn, the deviations of the indication are less than 0.005 percent. While in the illustrated example, the area ratio of silver to tin is 50 : 50, if the permissible range of the deviation were broadened to less than ± 0.01 percent, the area ratio of silver to tin could be increased to from 25 : 75 to 75 : 25. From table 1 and FIG.4 it can thus be concluded that, in order to bring the permissible error within a range of ± 0.01 percent (in terms of the weight percent of sulphur) the target is required to emanate fluorescent X-rays of the energy level ranging from 23 to 24.5 KeV.

In this example utilizing a composite target of silver and tin, as shown in FIG. 3, the body of the target is made of tin and 45° sectors of silver foils Ag are bonded to the inner surface of the cup-shaped body at a spacing of 45°, as shown in FIG. 2. The composite target may take many other forms, for example a sintered body or an alloy of silver and tin may also be used. Alternatively, a target having superposed layers of silver and tin may also be used wherein a thin film (about 10 to 100 microns thick) of silver or tin is applied on a substrate of tin or silver by suitable methods such as electroplating, vapour deposition, spraying, etc. Where the thickness of the film is selected to a suitable value it is possible to obtain a desired intensity of the energy of the fluorescent X-rays emanated therefrom.

Since the luminous efficiencies of silver and tin are nearly equal, the energy of the fluorescent X-rays per unit area of the composite target of silver and tin, is substantially equal to respective energies of silver and tin multiplied by respective areas of silver and tin and divided by the total area of silver and tin, where the layers of silver and tin are thick and have different areas; equal to about 23.7 KeV where the area ratio of silver to tin equals 50 : 50; whereas when a thin layer of one material totally covers the substrate of the other the energy is determined by the thickness of the thin layer.

In the case of the composite target of silver and tin described above, since the mass absorption coefficient μ_s of sulphur is larger than the composite mass absorption coefficient of carbon and hydrogen $\mu_H + R \mu_C / 1 + R$ by a factor of ten or more, sufficiently high sensitivity of measurement can be obtained.

Although in this example, the range of the measurement ranges from 0 to 5 percent (in terms of the weight percent of sulphur) and the density range ranges from 0.8 to 1.0 g/cm³, in order to use a broader range of the measurement or density it is necessary to modify the area ratio of silver to tin of the target by using a suitable mask or the like.

As can be readily noted from FIG. 4, targets made of a single metal, cadmium or indium manifest characteristics close to those of the composite target of silver and tin (see also table 1). Suitable combinations of cadmium and tin, cadmium and indium, and indium and silver can also be used to form composite targets producing energies of a similar level as those of the composite target of silver and tin. With targets of single metals it is impossible to adjust the energy level and composite targets are more advantageous in that it is possible to vary the energy levels within a definite range by varying the ratio of component metals.

Although in the embodiment described above, an ionization chamber was used as the detector, it may be substituted by another type of detector such as a scintillation counter. When compared with the scintillation counter, the ionization chamber is more advantageous in that it is possible to avoid errors due to miss-counting and to increase the sensitivity by increasing the intensity of the source of radioactive rays. Furthermore, it is possible to increase the accuracy of the measurement because it is possible to readily compensate for the temperature variation and to avoid the adverse effect of vibrations.

Thus, according to this invention, fluorescent X-rays having an energy level wherein the absorption coefficients of carbon and hydrogen are equal are produced by using a composite target of silver and tin, tin and in-

dium, cadmium and indium or cadmium and tin or a target of a single metal of cadmium or indium, thus providing apparatus for measuring at high accuracies the concentration of sulphur contained in hydrocarbons compounds without being affected by the ratio of the concentrations of carbon and hydrogen.

Although in the above described embodiment the concentration of sulphur was measured, it is to be understood that the novel apparatus can also measure the concentration of other elements having larger mass absorption coefficients than hydrogen and carbon, such as chlorine, nickel or lead.

FIG. 5 shows a block diagram of a measuring circuit utilized in this invention. The measuring circuit comprises a detector 7 for detecting the concentration of sulphur including a source of radioactive rays 8, for example ²⁴¹Am, a cup shaped composite target 9 of silver and tin, a measuring tank 10 and an ionization chamber 11. The measuring circuit further comprises an high input impedance amplifier 12 for amplifying the output current from ionization chamber 11 and provided with a feedback resistor 13, and a source of DC voltage 14 for the ionization chamber, one terminal of the source being grounded through one output terminal of the amplifier 12. There is also provided a density detector 15 connected in series with the sulphur concentration detector 7 via a conduit 16, which may be a vibration type density detector. Detector 15 is provided with a resistor 17 for measuring the temperature of the sample for correcting the density signal in accordance with the reference temperature. In the same manner, the measuring tank 10 is provided with a resistor 18 for measuring the temperature of the sample at the time of measuring the sulphur concentration thereof for correcting the density signal with the temperature prevailing in the concentration measuring tank. The temperature measuring resistor 18 is connected in one arm of a bridge circuit 19 which produces across its output terminals 20 a compensated density signal corresponding to the difference between the density of the sample at the temperature prevailing in the measuring tank and the measured density corrected to the density at the reference temperature. A density converter 21 is connected as shown to convert the output signal (a frequency signal) from the density detector 15 into a density signal at the reference density, and into a density signal at the temperature of the concentration measuring tank and to convert the density signal into a DC voltage signal $e \rho_1$ (for example a DC voltage of 0 - 10 mV for $\rho = 0.8 - 1.0 \text{ g/cm}^3$). The correction of the density by the temperature at which the sulphur concentration is detected can be made outside of the converter 21. For example a correction signal may applied to the output from the converter 21. To the output of converter 21 is connected a voltage-current converter provided with a function converting circuit 22 for converting the output signal $e \rho_1$ from the density converter 21 into a current or voltage signal having a higher level (for example a direct current of 10 - 50 mA or a DC voltage of 1 to 5V) proportional to the output signal $e \rho_1$ and into a DC signal $e \rho_3$ (for example 1 - 5V) in the form of an exponential function of the density and of the sulphur concentration (concentration at the reference temperature) in the same manner as the detected sulphur concentration signal. A variable potentiometer 23 is connected to the output of the voltage-current converter 22 to produce a density correction signal from the ex-

ponential voltage signal $\epsilon\rho_3$. The output of the potentiometer 23 is supplied to a potentiometer 24 for setting the reference concentration and the reference density of sulphur, the potentiometer 24 being connected across a DC source 25. A resistor 26 is connected between one input terminal of amplifier 12 and the junction between potentiometer 24 and DC source 25 to produce a density correcting signal (in the form of an output current) at the reference concentration of the sulphur, based on the sum of the exponential signal regarding the density at the measured temperature and the reference sulphur concentration adjusted by the potentiometer 23 for producing the density correction signal, and the signal regarding the reference concentration of sulphur provided by the potentiometer 24.

One output terminal of amplifier 12 is grounded through a potentiometer 28 for adjusting the range of the sulphur concentration. The movable arm 28 of potentiometer 27 is connected to one input of a linearizing circuit 30 with a voltage-current converter through a variable time constant circuit 29 for adjusting the statistic error of the source of the radioactive rays. The output e_{sz} of the voltage-current converter 30 is supplied to one pair of the inputs of a divider 31 and the other pair of the inputs thereof is connected to receive the first output $e\rho_2$ from the voltage-current converter 22 thus operating a divisional operation $e_{sz}/e\rho_2$ to produce an output e_{sz} across output terminals 32. Density converter 21 is provided with output terminals 33 for deriving a density signal corrected with the reference temperature.

The measuring apparatus operates as follows. When composite target 9 of silver and tin at an area ratio of 50:50 is irradiated with the primary radioactive rays from source 8 (^{241}Am) of the sulphur concentration detector 7 the target emanates fluorescent X-rays at an energy level of about 23.7 KeV which is never affected by the ratio of concentrations of carbon and hydrogen in petroleum but influenced only by the concentration of sulphur. Accordingly, when transmitted through the sample, for example petroleum, contained in the measuring tank, the fluorescent X-rays are absorbed by the petroleum, and the transmitted X-rays are detected by the ionization chamber 11, thus producing an output in accordance with equation (1). In this equation the term $\mu_H + R\mu_C / 1 + R$ corresponds to the mass absorption coefficient of the hydrocarbon compound. By substituting μ_{CH} for this term, equation (1) can be rewritten as

$$I_s = I_0 \exp - \rho t [(\mu_s - \mu_{CH})C_s + \mu_{CH}] \quad (4)$$

On the other hand, the density detector 15 operates to detect the density of the petroleum flowing through the concentration detector 7 to produce a frequency output proportional to the density. Since this frequency output is obtained at the temperature prevailing in the density detector it is necessary to correct it for the reference temperature condition. To this end the frequency output is corrected in the density converter 21 by the output from temperature measuring resistor 17. Further in order to correct the frequency output by the density prevailing in the sulphur concentration measuring tank, the output from the temperature measuring resistor 18 on the sulphur concentration detector 7 is converted into a correction voltage signal by the bridge circuit 19 and the output of this bridge circuit is applied to the density converter 21 to produce an output volt-

age $\epsilon\rho_1$ (for example, a voltage of 0 – 10 mV, at a density of $\rho = 0.8 - 1.0 \text{ g/cm}^3$) corresponding to the density signal at the temperature at which concentration of sulphur is detected.

The output voltage $\epsilon\rho_1$ is converted into a DC signal $\epsilon\rho_2$ (for example $\epsilon\rho_2 = 1 - 5 \text{ V}$ at a density of $\rho = 0.8 - 1.0 \text{ g/cm}^3$) and a signal $\epsilon\rho_3$ proportional to the exponential signal corresponding to the signal $\epsilon\rho_1$ and expressed by the following equation 5 by the action of the voltage-current converter 22 equipped with a function conversion circuit, not shown. This exponential signal $\epsilon\rho_3$ (about 1 – 5 V) is applied to potentiometer 23 for setting the density correction signal to produce an exponential output $\epsilon\rho$ given by equation 5

$$\epsilon\rho = R[I_0 e^{-\rho t \{(\mu_s - \mu_{CH})C_{sz} + \mu_{CH}\}} - I_0 e^{-0.8t \{(\mu_s - \mu_{CH})C_{sz} + \mu_{CH}\}}] \quad (5)$$

where C_{sz} represents the reference sulphur concentration (in percent) and R the resistance for voltage conversion.

DC source 25 and potentiometer 24 for setting a reference concentration of sulphur cooperate to generate a constant voltage expressed by the following equation 6.

$$e_z = RI_0 e^{-0.8t \{(\mu_s - \mu_{CH})C_{sz} + \mu_{CH}\}} \quad (6)$$

The voltage $\epsilon\rho$ generated by the potentiometer 23 for producing the density correction signal and the voltage e_z generated by the potentiometer 24 for setting the reference concentration of sulphur are added to each other to provide the following voltage signal.

$$\begin{aligned} \epsilon\rho + e_z &= R[I_0 e^{-\rho t \{(\mu_s - \mu_{CH})C_{sz} + \mu_{CH}\}} \\ &\quad - I_0 e^{-0.8t \{(\mu_s - \mu_{CH})C_{sz} + \mu_{CH}\}}] + RI_0 e^{-0.8t \{(\mu_s - \mu_{CH})C_{sz} + \mu_{CH}\}} \\ &= RI_0 e^{-\rho t \{(\mu_s - \mu_{CH})C_{sz} + \mu_{CH}\}} \end{aligned} \quad (7)$$

The voltage signal given by equation 7 is caused to flow through resistor 26 to generate a current signal representing the reference concentration of the sulphur as shown by the following equation 8.

$$\frac{\epsilon\rho + e_z}{R} = I_0 e^{-\rho t \{(\mu_s - \mu_{CH})C_{sz} + \mu_{CH}\}} \quad (8)$$

Subtracting the sulphur concentration signal I_s given by equation (4) from the reference concentration current signal of sulphur given by equation (8), we obtain

$$\begin{aligned} \Delta I_s &= I_s - I_0 e^{-\rho t \{(\mu_s - \mu_{CH})C_{sz} + \mu_{CH}\}} \\ &= I_0 e^{-\rho t \{(\mu_s - \mu_{CH})C_{sz} + \mu_{CH}\}} \\ &\quad - I_0 e^{-\rho t \{(\mu_s - \mu_{CH})C_{sz} + \mu_{CH}\}} \end{aligned} \quad (9)$$

This difference signal ΔI_s is amplified by the high input impedance amplifier 12 to provide an output signal e_{s1} proportional to the product of ΔI_s and the resistance of feedback resistor 13. This output signal e_{s1} is

adjusted by the potentiometer 27 and the output voltage from its adjustable terminal 28 is supplied to the a linearizing circuit 30 with a voltage-current converter, not shown, via time constant circuit 29 for adjusting the statistical error, thus producing a linearized output signal e_{s2} .

Since the signal e_{s1} corresponds to the difference between the concentration signal and the reference concentration signal of sulphur, the range of signal e_{s1} is narrow and hence the curvature of the characteristic Δ Is with respect to the concentration of sulphur is small so that it is possible to readily linearize the signal e_{s1} by using a simple linearizing circuit including a diode in the feedback circuit for amplifier.

FIGS. 6 to 10 inclusive show the relationship between the concentration of sulphur and the ratio of e_{s2}/e_{sN} (where e_{sN} equals e_{s2} at a density $\rho=0.8\text{g/cm}^3$) for various ranges of sulphur concentration 0 - 1 percent, 2 - 3 percent, 3 - 4 percent and 4 - 5 percent, wherein the density is used as the parameter.

From these figures, an approximate value of e_{s2} can be shown by the following equation 10

$$e_{s2} = K_o [1+K(\rho-0.8)](C_s-C_{s2}) \quad (10)$$

where K_o and K are constants.

By the action of divider 31, the linear output e_{p2} regarding density provided by the voltage-current converter 22 equipped with a function circuit is converted into a signal $1+K(\rho-0.8)$ and the signal e_{s2} given by equation (10) is then divided by signal $1+K(\rho-0.8)$ as shown by the following equation (11), thereby giving an output e_{sN} representing the concentration of sulphur at the reference density ($\rho=0.8\text{g/cm}^3$)

$$e_{sN} = \frac{e_{s2}}{1+K(\rho-0.8)} \quad (11)$$

$$= \frac{K_o[1+K(\rho-0.8)](C_s-C_{s2})}{1+K(\rho-0.8)} \quad (11')$$

$$= K_o(C_s-C_{s2})$$

By modifying equation (11), we obtain

$$(e_{s2}/e_{sN}) = 1 + K(\rho-0.8) \quad (12)$$

The lefthand term (e_{s2}/e_{sN}) of this equation corresponds to the ordinate in FIGS. 6 to 10, so that it is possible to determine the value of K from these figures and equation (12). Thus, for example, in the case of a range of sulphur of 0 to 1 percent, from FIG. 6, it can be shown that e_{s2}/e_{sN} equals 1.08 at $\rho=1.0\text{g/cm}^3$ and $C_s=1.0$ percent. Accordingly by substituting this value in equation 12, we can obtain $K=0.4$ for equation (11).

FIGS. 6 to 10 also show that the ratio e_{s2}/e_{sN} approaches to unity and hence K approaches to zero as the concentration range of sulphur C_s increases. This means that the error of measurement caused by density is reduced.

FIG. 11 shows a modified measuring circuit of this invention, wherein component parts identical to those shown in FIG. 5 are designated by the same reference numerals. The circuit shown in FIG. 11 is different from that shown in FIG. 5 in the following points. The reference concentration signal of sulphur at the reference

density is subtracted from the detected concentration signal of sulphur on the input circuit to the high input impedance amplifier 12, and the difference signal is amplified and linearized by the linearizing circuit 30 to provide an output e'_{s2} . An output e_p which is obtained by properly adjusting the exponential output e_{p3} from the function converting circuit 22 with a voltage current converter equipped with a function conversion circuit, not shown, is subtracted from the output voltage e'_{s2} and the difference signal thus obtained is divided by the signal e_{p2} related to the density signal. Even when the linearizing circuit 30 has a wide operating range, the same result can be obtained.

FIG. 12 shows a partial diagram of a modification of the circuit shown in FIG. 12. In this modification, instead of differentially adding the adjusted voltage e_p of the exponential output e_{p3} from the voltage-current converter 22 to the output e'_{s2} from the linearizing circuit 30, the voltage e_p is added differentially to the input of the linearizing circuit 30. Alternatively, the voltage e_p may be added to the output of potentiometer 27 (in FIG. 11) for adjusting the range.

When the linearized signal related to the density is applied to the divider as in this embodiment, where the range of the density is narrow, for example from 0.8 to 1.0g/cm^3 , or a difference of 0.2g/cm^3 , the exponential density characteristic is close to a straight line so that the curvature of the characteristic is only 2 percent of that of the wider range of density. Accordingly, such characteristic can be considered straight and even when the linearized signal is applied to potentiometer 23 for setting the density correction signal and to the divider 31, the resulted error is negligibly small.

Although in the foregoing embodiment, for the density range of 0.8 to 1.0g/cm^3 , a reference density of 0.8g/cm^3 was selected, as long as the density is included in the range described above, any reference density may be used. It should also be understood that the density range is not limited to from 0.8 to 1.0g/cm^3 but may be higher or lower than this range.

Further, in the above described example the span of sulphur concentration was assumed to be 1 percent the span may be lower or higher than this value.

In the above embodiments, a vibration type density meter was used as the density detector because it has high accuracy and is suitable for continuous measurement. But, any well known density detector can be used.

The above described measuring circuit comprises an amplifier for amplifying the concentration signal of sulphur and the like in hydrocarbon compounds, a linearizing circuit to linearize the output from the amplifier, a divider circuit to divide the output from the linearizing circuit by a signal related to the density signal of the hydrocarbon compound, a circuit for converting the density signal into an exponential function of the density and the reference concentration like the concentration signal of sulphur and the like and means for differentially applying the exponential function and the sulphur concentration signal to the input of the amplifier or to the input of the divider so that it is possible to provide a novel concentration measuring apparatus which can measure at high accuracies the concentration of the sulphur or other impurities in hydrocarbon compounds and can provide required density compensation without the necessity of utilizing a logarithmic amplifier.

FIGS. 13 and 14 show the details of a signal generator utilized in this invention, which comprises a casing 40 including a main body 41 and lids 42 and 43 removably secured to the opposite ends of the main body. A frame 51 is contained in the main body 41. A central opening 52 in frame 51 cooperates with covers 53 and 54 on the opposite ends thereof to define a measuring tank 50.

As shown in FIG. 14, the frame 51 is formed with an inlet port 55 for the sample liquid, a diffuser 56 positioned at the entrance of the chamber 57 in the measuring tank 50 and an outlet port 58. As shown by the enlarged views shown in FIGS. 15 and 16, the diffuser 56 comprises a cylinder 561, a tapered opening 563 and a through opening provided in the bottom wall 562 of the cylinder 561 which are coaxial with the axis of cylinder 561. A pair of rectangular windows of equal size 565 and 566 are formed on the periphery of the cylinder 561. As shown in FIGS. 14 and 15 the diffuser is mounted near the entrance of chamber 57 in measuring tank 50 with its windows 565 and 566 directed to the inner periphery of the chamber 57. The diffuser may be modified to have different constructions. For example circular windows may be substituted for rectangular windows and the bottom plate 562 may be a hollow hemisphere. It is only necessary to uniformly diffuse the fluid and cause it to flow towards the outlet port without undue stagnancy. The frame 51 is made of corrosion resistant metal such as stainless steel, whereas covers 53 and 54 are made of a material which transmits the fluorescent X-rays with a low attenuation coefficient and is not deformed or deteriorated by heat or petroleum, polyethylene for example.

A source assembly 60 is mounted to the left of the measuring tank 50. The source assembly comprises a frame 61 having a window 62, a ring 63 for securing window 62 to frame 61 and a source-target portion 64. The window 62 constitutes a lid for hermetically sealing the interior of the source assembly 60 and is brought into intimate contact with cover 53 to reinforce the same when the source is secured in the tank 50. Advantageously, the window 62 is made of a metal having an extremely low absorption coefficient of radioactive rays such as beryllium. The source target portion 64 comprises an inner frame 70 of a cup shaped as shown in FIGS. 17 and 18 and comprises a holder 72 for holding radioactive substance 71, four radial vanes 73 to 76 for supporting the holder 72 and a target 77 on the inner bottom wall. The radioactive substance 71 is held in holder 72 by means of a threaded plug 78 at nearly the focus of the spherical composite target 77 constituted by a metal M_1 constituting the inner frame 70 itself and 45° metal foils M_2 bonded to the inner bottom surface at a spacing of 45° . As the radioactive substance, ^{241}Am is preferred whereas metals M_1 and M_2 of the target are tin and silver respectively.

A detector 80 in the form of an ionization chamber is secured to the right of the measuring tank 50. Detector 80 comprises potential electrode 81, a collector electrode 82, and output terminal 83 and a window 84 of the same material as the window 62 of the source 60. The interior of detector 80 is sealed with a gas such as xenon for increasing the ionization current. The measuring tank 50 is heated by steam flowing through a conduit 90. The tank is also provided with a resistor 100 for measuring the temperature of the sample for performing temperature compensation and a terminal

box 110. Suitable O-rings (indicated in cross section) are used to prevent leakage.

To assemble the signal generator, first window covers 53 and 54 are secured on the opposite ends of the tank frame 51 and then the temperature measuring resistor 100 is secured. The frame 51 is then inserted in the main body 41 to complete the measuring tank 50. The inside frame 70 with the radioactive substance 71 secured in holder 72 is housed in the source 60 and then window 62 is applied. The source assembly 60 is secured to the lefthand side of the measuring tank, as shown in FIG. 13, by screws. Xenon gas is sealed in the detector 82 with electrode 81 and collector electrode 80 and the detector assembly is secured to the righthand side of the measuring tank 50. Finally after completing necessary pipings and wirings, end covers 42 and 43 are mounted to complete the assembling operation.

In operation, the liquid to be measured is admitted into the chamber 57 in the measuring tank 50 through inlet port 55. Diffuser 56 located at the entrance of chamber 57 diffuses the flow in three directions. One small flow enters straightforwardly into the chamber through opening 564 in the bottom plate 562 whereas other two flows are directed along the circumferential surface of chamber 57. Consequently, the liquid flows uniformly through chamber 57 as shown by arrows in FIG. 19, so that there is no stagnancy.

Even when the liquid is viscous, such as heavy oil, it is heated by the steam flowing through the passage 90 to decrease its viscosity. Radioactive rays emitted by substance 71 travel towards the left as viewed in FIG. 13 to impinge upon target 77 which emanates fluorescent X-rays in the opposite direction, the energy level of X-rays being determined by the area ratio of silver to tin of the composite target. The X-rays are absorbed and hence attenuated by the concentrations of carbon, hydrogen, sulphur, etc, contained in the liquid to be measured, petroleum for example, and finally arrive at the detector 80. However, as has been pointed out hereinabove, since the mass absorption coefficients of carbon and hydrogen for the fluorescent X-rays are equal, the value of the ionization current generated in the detector varies in dependence upon the concentration of sulphur thus enabling measurement of the concentration of sulphur contained in the petroleum.

The novel signal generator has following advantages:

More particularly, the measuring tank, source of radioactive rays and detector 80 are constructed as independent sealed units. Consequently these units can be readily assembled and disassembled. Further the invasion of outside corrosive gas such as hydrogen sulphide or sulphurous acid into the signal generator can be prevented thus preventing deterioration of its characteristics due to corrosion. The diffuser mounted at the liquid inlet opening of the measuring tank assures uniform and constant flow of the admitted liquid whereby it is possible to always measure fresh liquid. As the target is in the form of a hemisphere and as the radioactive substance 71 is located at substantially the focus of the curved target radioactive rays emanated from substance 71 are efficiently utilized.

Further, when assembled, windows 62 and 54 are brought into firm contact with covers 53 and 54 of the measuring tank 50 so that the windows 62 and 84 act to reinforce covers 53 and 54. Intimate contact of these windows and covers prevents deposition of mois-

ture or dirt so that transmission of the radioactive rays will not be interfered with. Heating of the measuring tank 50 by steam permits smooth flow of the liquid to be measured. When the temperature of the liquid is regulated at a constant temperature by means of the temperature measuring resistor, errors due to temperature variation can be effectively eliminated.

While the invention has been shown and described in terms of preferred embodiments thereof, it will be clear that many changes and modifications can be made without departing from the true spirit and scope of the invention as defined in the appended claims.

What is claimed is

1. Apparatus for measuring the concentration of an element contained in a hydrocarbon compound, said element having a higher mass absorption coefficient than the carbon and hydrogen in said hydrocarbon compound, comprising a source of radioactive rays having an energy level of about 60 to 100 KeV, a target irradiated with said radioactive rays to emanate toward said hydrocarbon compound fluorescent X-rays having an energy level of about 23 to 24.5 KeV, and means to detect said fluorescent X-rays which are transmitted through said hydrocarbon compound.
2. The apparatus according to claim 1 wherein said hydrocarbon compound is petroleum or its refined product and said element is selected from the group consisting of sulphur, chlorine, nichel and lead contained in said hydrocarbon compound.
3. Apparatus for measuring the concentration of an element contained in a hydrocarbon compound comprising concentration detector means including a source of radioactive rays of an energy level of about 60 to 100 KeV, a target irradiated with said radioactive rays to emanate toward said hydrocarbon compound fluorescent X-rays of an energy level of about 23 to 24.5 KeV, and a detector for detecting said fluorescent X-rays which are transmitted through said hydrocarbon compound; a density detector for detecting the density of said hydrocarbon compound; a measuring circuit for amplifying the concentration signal from said detector; a linearizing circuit to linearize the output from said measuring circuit; a divider for dividing the output from said linearizing circuit with a signal related to the density signal from said density detector, means for converting said density signal into an exponential signal which is a function of the density and a reference concentration of said element and means for differentially adding said exponential signal to said concentration signal to reference said concentration signal with respect to said reference concentration.
4. The apparatus according to claim 1 wherein said target is a composite target and comprises a combination of two metals selected from the group consisting of silver, tin, lidium and cadmium.
5. The apparatus according to claim 1 wherein said target comprises a signal metal selected from the group consisting of indium and cadmium.
6. The apparatus according to claim 3 wherein said detector comprises an ionization chamber.
7. A concentration measuring circuit for use in apparatus for measuring the concentration of an element in a hydrocarbon compound by using the absorption of fluorescent X-rays by said hydrocarbon compound,

comprising a concentration detector for measuring the concentration of said element, an amplifier for amplifying the concentration signal from said detector, a linearizing circuit for linearizing the output from said amplifying circuit, a divider for dividing the output from said linearizing circuit with a signal related to the density signal of said hydrocarbon compound, means for converting said density signal into an exponential signal which is a function of the density and a reference concentration of said element and means for differentially adding a signal related to said exponential signal to a signal related to said concentration signal to reference said concentration signal with respect to said reference concentration.

8. The concentration measuring circuit according to claim 7 wherein said exponential signal is applied to the input of said amplifier.

9. The concentration measuring circuit according to claim 7 wherein said exponential signal is applied to the input of said divider.

10. The concentration measuring circuit according to claim 7 wherein said exponential signal is added to the input of said linearizing circuit.

11. The concentration measuring circuit according to claim 7 wherein said differentially adding means applies the sum of a density correction signal derived from said exponential signal and a second exponential signal regarding a reference density and a reference concentration of said element to the input of said amplifier differentially with said concentration signal.

12. The concentration measuring circuit according to claim 7 wherein said differentially adding means applies an exponential signal which is a function of a reference concentration and a reference density of said element, and a detected concentration signal differentially to the input of said amplifier, and a second exponential signal which is a function of said reference concentration and density of said element differentially to the output from said amplifier.

13. A signal generator for use in apparatus for measuring the concentration of an element contained in a hydrocarbon compound comprising a source of radioactive rays including a curved target and a radioactive substance located at substantially the focus of said target; a detector including an ionization chamber having a potential electrode and a collector electrode; a measuring tank through which said hydrocarbon is continuously passed and having covers at the opposite ends of said tank, said covers being of a material leaving a low absorption coefficient for said radioactive rays, both said source and said detector being of a sealed construction and having a window of a material having a low absorption coefficient for said radioactive rays, said windows being in intimate contact with said covers to reinforce them; and a diffuser at the inlet port of said measuring tank to cause said hydrocarbon compound to flow uniformly through said tank.

14. The signal generator according to claim 13 including means for detecting the temperature of said hydrocarbon compound within said measuring tank.

15. The signal generator according to claim 13 including a conduit adapted to have steam flow therein to heat said measuring tank.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,746,874

Dated July 17, 1973

Inventor(s) Shuichi Ohata, Tadashi Kamino, Tsutomu Hirayama, Yoji Takeuchi, Kaisuke Muraki, Takeshi Ishiguro, Hiroaki Kamano

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

In "[75] Inventors:" correct the spelling of the name "Isutomu" to read -- Tsutomu --.

Column 1, line 58, " μ s < μ c" should be -- μ s > μ c --.

line 59, " μ s < μ_H " should be -- μ s > μ_H --.

Column 2, lines 4, 61, 63

Column 7, line 19

Column 9, lines 3, 5, 12 and 13

Column 10, lines 4, 12, 18, 20, 23, 31, 51, 52 and 53

Column 13, lines 42 and 44

Column 14, lines 4, 6 and 23

Correct the spelling of the words "linearlize", "linearlized" and "linearlizing" as the case may be to read:

-- linearize --

-- linearized --

-- linearizing --

Column 2, line 30, correct "therof" to -- thereof --.

line 60, correct "measuing" to -- measuring --.

(continued on page 2.)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Page - 2

Patent No. 3,746,874

Dated July 17, 1973

Inventor(s) Shuichi Ohata, Tadashi Kamino, Tsutomu Hirayama, Yoji Takeuchi, Kaisuke Muraki, Takeshi Ishiguro, Hiroaki Kamano

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

Column 2, line 62, "linearlizing" should be -- amplifier --.

Column 4, line 28, "show" should be -- shown --.

Column 4, line 29, "shown" should be -- show --.

Column 4, line 37, "bakelite" should be -- BAKELITE --.

Column 5, line 23, delete "area".

Column 5, line 58, "incres" should be -- increase --.

Column 6, line 19, "an" should be -- a --.

Column 7, line 48, "rewitten" should be -- rewritten --.

Column 7, line 50, " $\mu s - \mu_{CH}$ " should be -- ($\mu s - \mu c$) --.

Column 8, line 10, "equipted" should be -- equipped --.

Column 9, line 30, "equipted" should be -- equipped --.

Column 10, line 8, "equipted" should be -- equipped --.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,746,874 Dated July 17, 1973

Inventor(s) Shuichi Ohata et al. Page - 3

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

Column 12, line 13, "detector 82" should be -- detector 80 --.

Column 12, line 14, the numeral "80" should be -- 82 --.

Column 12, line 31, "viscosty" should be -- viscosity

Column 12, line 66, the numeral "84" should be -- 54 --.

Column 13, line 28, "nichel" should be -- nickel --

Column 13, line 59, "claim 3" should be -- claim 1 --.

Signed and sealed this 27th day of August 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents