

- [54] **ON-STREAM ANALYSIS**
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- [73] Assignee: **Gulf Research & Development Company**, Pittsburgh, Pa.
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- [52] U.S. Cl. .... **250/43.5 MR, 250/106 S, 250/106 T**
- [51] Int. Cl. .... **G01n 23/12**
- [58] Field of Search ..... **250/43, 43.5 FC, 43.5 MR, 250/106 R, 106 T, 106 S, 84.5**

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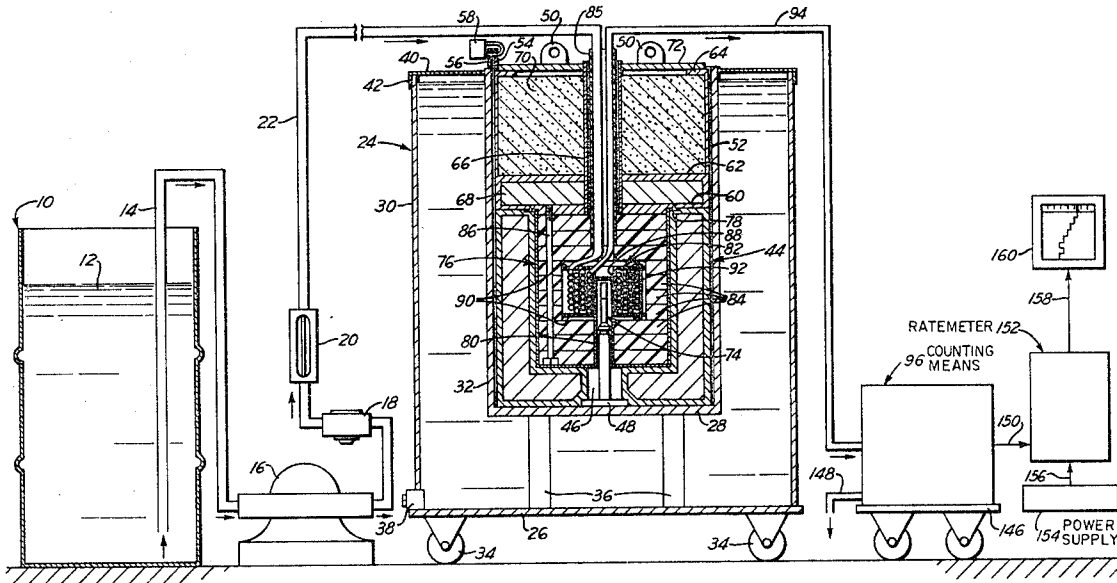
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[57] **ABSTRACT**

The preferred form of the invention comprises a relatively small Cf-252 radioactive source positioned within a coil irradiator, specifically for the detection of vanadium in hydrocarbon streams. The sample flow is from the outside towards the inside in the irradiator, and in the opposite direction in the detection means coil, so that decay counting efficiency is enhanced.

**17 Claims, 7 Drawing Figures**





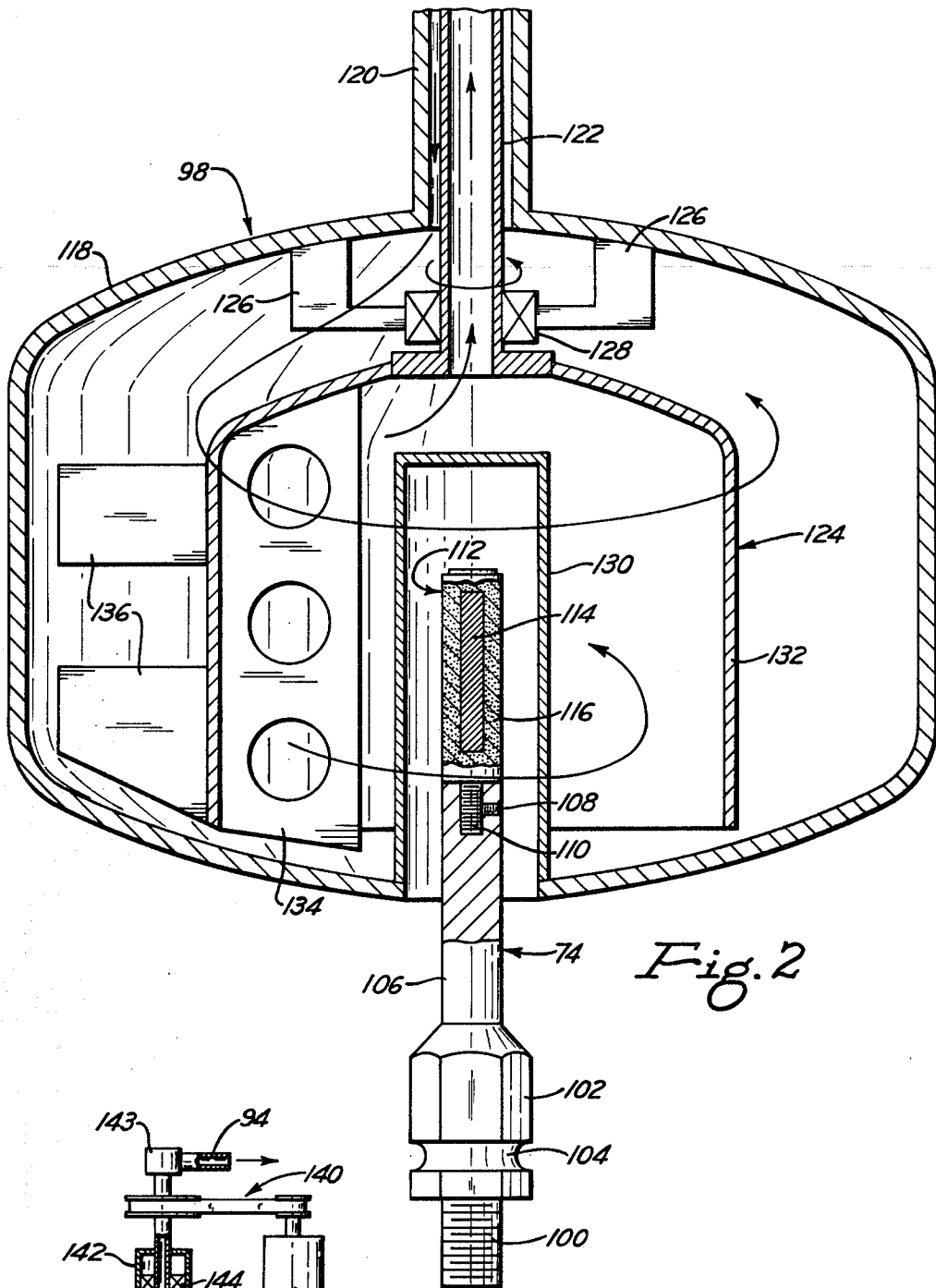


Fig. 2

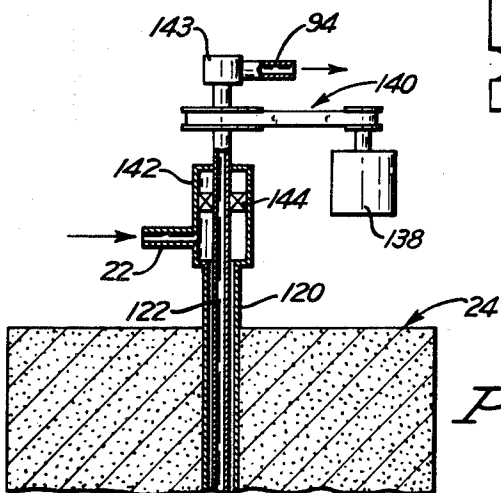
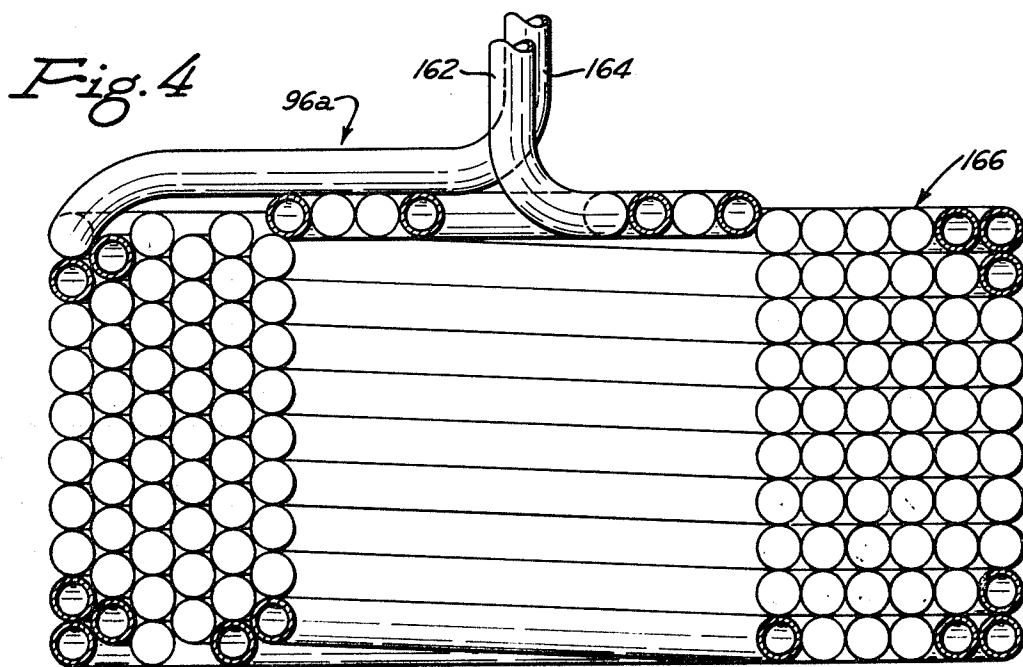
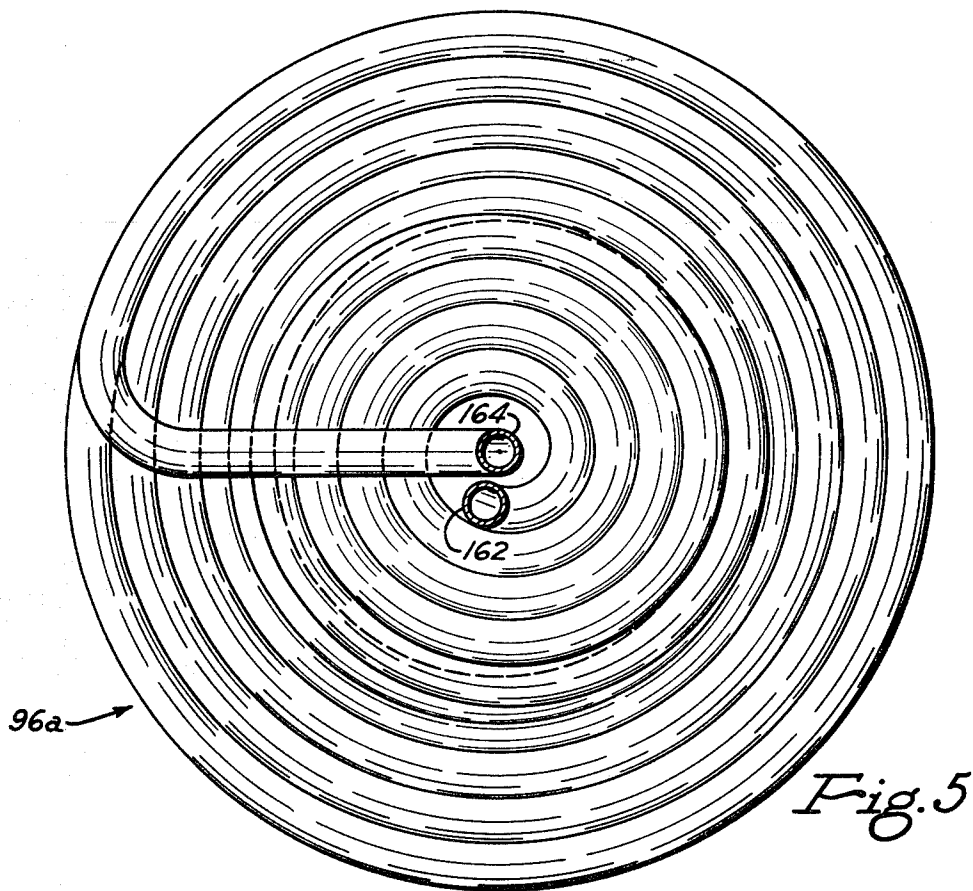


Fig. 3

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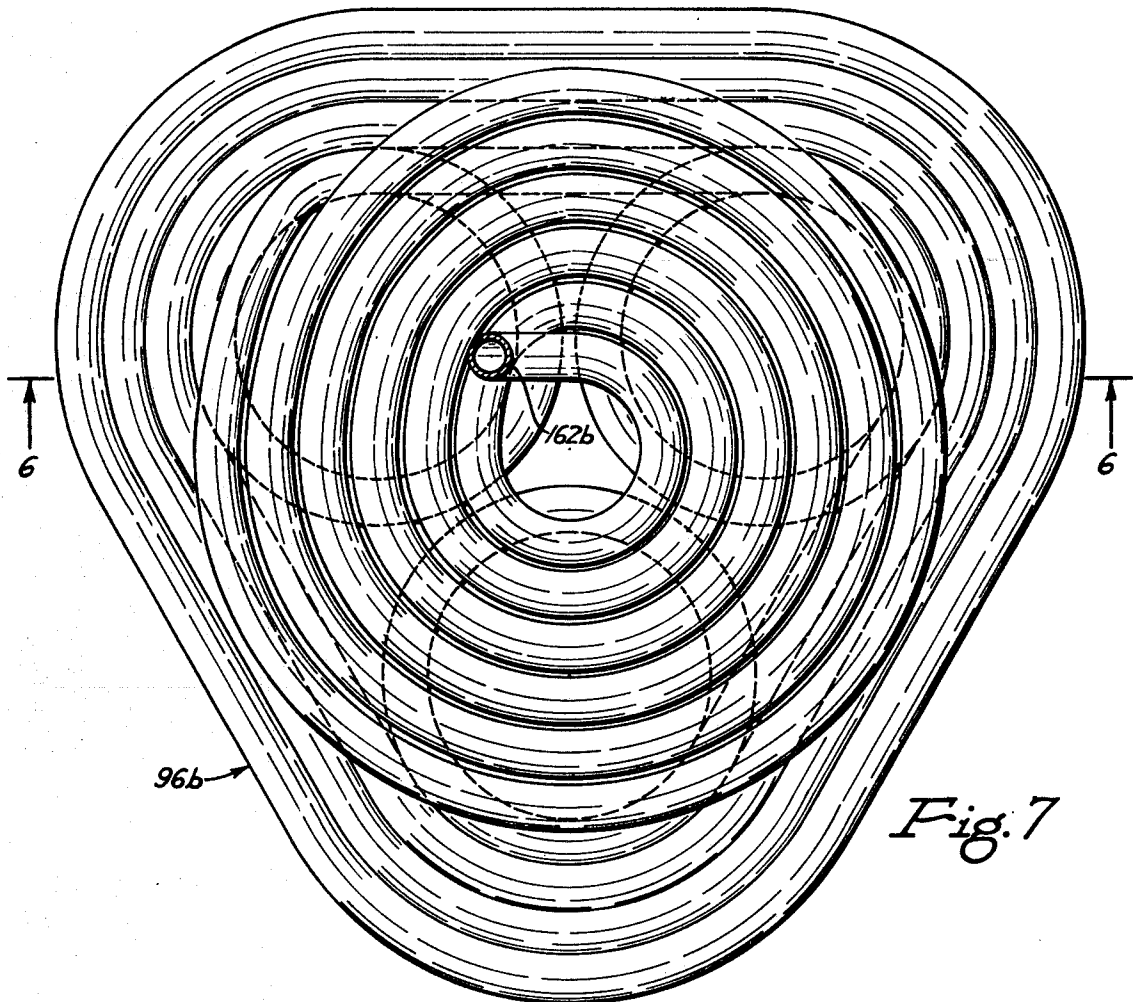


Fig. 7

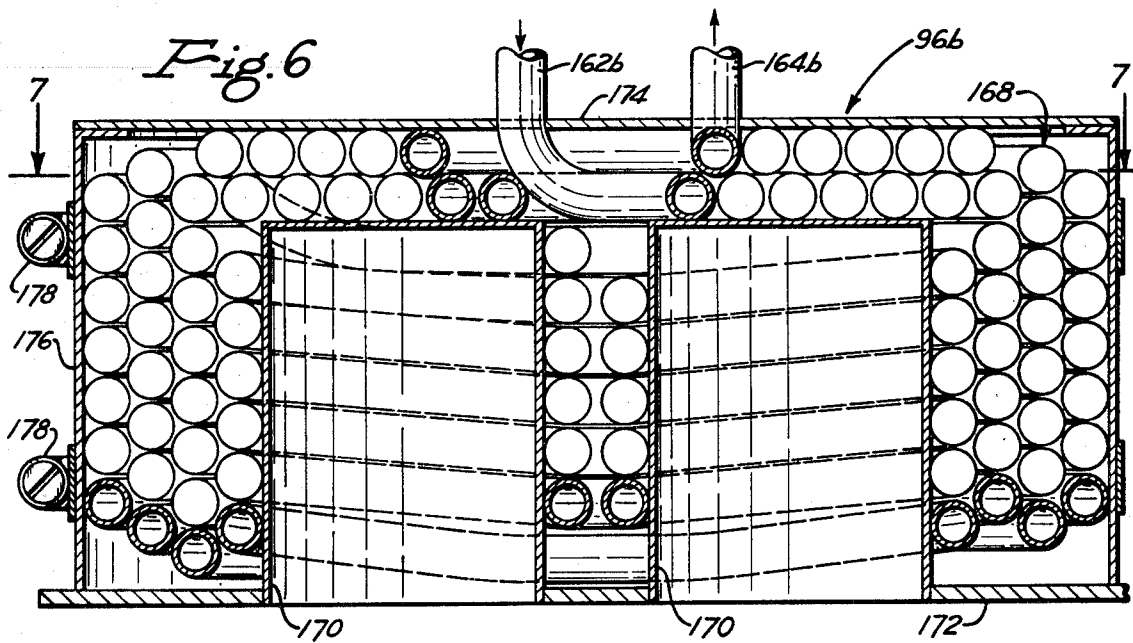


Fig. 6

## ON-STREAM ANALYSIS

The invention described herein was made in the course of, or under, Contract No. AT(38-1)-565 with the U. S. Atomic Energy Commission.

This invention pertains to the analysis of flowing streams to determine the quantitative content of a component therein. More particularly, the invention pertains to such analysis utilizing a radioactive source to create a detectable isotope of the component of interest. A specific form of the invention is directed towards making a quantitative determination of vanadium in hydrocarbon streams using a Californium-252 neutron source.

In its most general form, the apparatus of the invention is useful in handling any liquid sample stream which is to be exposed to a radioactive source in order to irradiate the sample liquid. The invention provides an improved apparatus which exposes the sample flow to the radioactive source in such a way that the exposure time is well controlled, uniformity of exposure is assured, and the sample flow is directed away from the source at the time when the sample is most radioactive. Means are provided to flow the sample, quickly, to improved counter means wherein, again, exposure time of the irradiated sample to the counting means is controlled, and the sample flow is brought to its closest proximity to the counting means when it is the most radioactive. These advantages are achieved by means of a coil having a relatively large number of turns of relatively thin tubular material. A separate coil is provided for the irradiator, and for the counting means. The sample flow is directed through the source coil from the outside towards the inside, and then through the counting means coil from the inside towards the outside. In this manner the sample flow is directed away from the source when it is most radioactive, and is then brought to its closest proximity with the counting means in the shortest possible time after leaving the irradiator.

The invention was developed in the environment of the petroleum industry, and more particularly with regard to the problem of determining the amount of vanadium in certain hydrocarbon streams. As is well known to those skilled in petroleum refining, it is important to know the amount of vanadium in certain hydrocarbon streams in order to cope with problems such as catalyst poisoning, corrosion, and the like. Just in the petroleum field, the invention could be used to determine the amount of other elements in other streams, for example, aluminum or chlorine. Generally, the invention can be used in virtually any on-stream analysis environment wherein an element of interest in the stream can be made into a radioisotope by neutron bombardment.

In recent times radioactive Californium 252 (Cf-252) has become available to a limited degree. This substance is a particularly strong and compact neutron source, a very small quantity of Cf-252 will permit the design of practical instruments, and also it has the advantage of a reasonably long half-life, on the order of about 2½ years. In the specific form of the invention which has been built and which is described herein, the apparatus described and the Cf-252 source were used to produce excellent data on amounts of vanadium in a water based vanadium solution, accura-

cies of about plus or minus 0.1 ppm of vanadium at about the 1 ppm level. Similar tests have been run with vanadium in oil, and at least equally good results were obtained.

The neutrons from the Cf-252 source are characterized by being of the fast moving variety. To change vanadium to its isotopic and detectable V-52 form, slow moving or thermal neutrons are preferred. Thus, the irradiator coil serves a dual function. In addition to uniformly exposing the sample stream to the radioactive source to avoid eddy currents, channeling, and the like, hydrogenous material in and around the coil serve to help moderate or thermalize the fast moving neutrons from the source. A coil made of polyethylene has been found to operate highly satisfactorily in the laboratory. However, in a commercial environment it may be desired to use the invention with sample streams which are at a pressure and/or temperature which could not be safely handled by a polyethylene coil. For such applications, an irradiator coil made of a metal which is a good neutron moderator would be desired. Beryllium is best suited for this application, but suffers from the disadvantage that it is an expensive material. During the course of developing the invention, an irradiator coil made of stainless steel was tried, and was found to be not as satisfactory as the polyethylene coil. Stainless steel absorbs neutrons and thus does not function particularly well as a moderator. A coil formed of aluminum was also tried, and was found to operate about as well as the polyethylene coil.

Another separate feature which was found to improve results was immersing the coil in paraffin. This was tried with several coils by simply putting the coil in liquid paraffin, and allowing the wax to solidify. In all cases tried the intimate presence of this hydrogenous material in the interstices between the turns of the coil was found to improve sensitivity. The hydrogenous material acts as an additional moderator to achieve the improved result. Since the invention was developed in a laboratory environment, these considerations may produce different results when applied in a commercial environment. For example, if the sample stream is hot, then it may be a problem to contain paraffin and keep it from smoking, and some other material, such as perhaps a paraffinic oil, may be usable as a bath around the coil irradiator.

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

FIG. 1 is a diagrammatic showing of the laboratory arrangement used in building the invention;

FIG. 2 is a somewhat diagrammatic representation of the source assembly and of a second embodiment of the irradiator;

FIG. 3 is a diagrammatic showing of the upper end of the irradiator embodiment of FIG. 2;

FIG. 4 is a cross-sectional elevational view of the preferred form of the counter coil;

FIG. 5 is a top plan view of the coil of FIG. 4;

FIG. 6 is a cross-sectional view taken on line 6-6 of FIG. 7; and

FIG. 7 is a cross-sectional view taken on line 7-7 of FIG. 6.

Referring now in detail to the drawing, there is shown in FIG. 1 the apparatus which was used in the laboratory in developing and testing the invention. As will be evident to those skilled in the art, certain parts shown in FIG. 1 would be used in any installation of the invention, and other parts do not form a material part of the invention. Such non-critical portions include a tank 10 containing a prepared solution 12 which contained various known quantities of vanadium. For example, a vanadium concentration of 31 ppm in water was prepared using vanadyl sulfate and was pumped at a constant rate of 135 cc/min. Using the specific form of the invention shown in the drawing and described below, tests have shown that the accuracy of vanadium concentration was independent of pumping rate in the range of about 80 to about 160 ml/min. This broad range greatly facilitates use, and was thought to have occurred because of a balance between several factors; saturation of the vanadium in the irradiator which is enhanced by a slow flow rate, decays of the V-52 enroute between the irradiator and the detector which is worsened by a slow flow rate, and concentration of V-52 in the sample stream which is enhanced by a slow flow rate. Thus, count rate or sensitivity is relatively independent of flow rate, which is quite significant in process applications.

A pipe 14 extends into the solution 12 and supplies the input side of a variable speed but constant displacement pump 16. The output of pump 16 flows through a constant flow regulator 18 and a flow meter 20. The devices 16 and 18 permit supplying a known and adjustable but constant flow via output pipe 22 to the irradiator assembly 24. In an on-stream application, conventional sampling means to make a slip-stream would be provided, and other means in lieu of 16, 18 and 20 could be provided to supply a constant volume of sample per unit time, all as is obvious to those skilled in the art.

Generally, the irradiator assembly 24 comprises a U-shaped in cross-section outer water filled tank, a U-shaped in cross-section inner lead shield, a top structure on the inner lead shield, with both the inner shielding and its lid inside the "U" of the outer tank, and with the source and the irradiator proper inside the "U" of the inner shielding.

The outer tank comprises an outer bottom wall 26, an inner bottom wall 28, an outer cylindrical wall 30, and an inner cylindrical wall 32. Wheels 34 are mounted on bottom wall 26. A number of supports 36, four in the constructed embodiment, extend between the two horizontally disposed walls 26 and 28. A water drain 38 is disposed in the outer cylindrical wall 30. A lid 40 is positioned between the walls 30 and 32 and comprises a flange 42 that fits over the outside of outer cylindrical wall 30 and is held in place by a tight fit. The U-shaped cross-section water or oil filled tank as thus far described forms the outermost shielding.

The next layer of shielding is provided by a cup-shaped steel jacketed lead shielding assembly 44. Shielding 44 is provided with a central opening 46 in which is secured a source holder stanchion 48. The stanchion 48 is held in the position shown by means of four screws, not shown, which extend through the bottom flange of the stanchion into suitably formed openings in the steel jacketing of shielding assembly 44.

The shielding assembly 44 with its stanchion 48 normally remains in the well formed by walls 28 and 32, while the remainder of the irradiator assembly may be removed by means of the lifting hooks 50. The hooks 50 have been turned in the drawing, actually they are positioned so that the holes therein face each other so that a bar or the like can be inserted in the holes to facilitate lifting the inner portions of the irradiator assembly.

The inner irradiator assembly comprises an outer cylindrical wall 52 which snugly fits within the water tank inner wall 32, and extends from the top of the shielding assembly 44 to the vicinity of lid 40. Cylindrical wall 52 carries a hasp 54 which registers with a hasp 56 mounted on wall 32, by means of which hasps and a lock 58 the irradiator assembly may be secured to the water tank, as a normal safety precaution when operating with radioactive substances. The hooks 50 are affixed to the wall 52. The inner shielding is divided into two cells by means of a lower transverse wall 60, a middle transverse wall 62 and an upper perforated transverse wall 64. A central opening for access to the irradiator is provided by a tubular member 66 which is fixed in position as by welding to the walls 60 and 62. The chamber thus formed between the walls 60 and 62 and member 66 is filled with lead 68, and the upper large chamber may be filled with other shielding material 70 such as water, oil or paraffin. A lid 72 fits snugly over the tubular member 66 and rests on the upper transverse wall 64 to close off said upper chamber.

The irradiator itself as well as the radioactive source 74 is positioned within the well of shielding assembly 44. The irradiator coil and its final shielding is secured to the underside of lower transverse wall 60 by means of a liner 76 having a top flange secured to said wall 60 by means of a plurality of small screws 78. The liner 76 fits snugly within the well in shielding assembly 44, and is formed with an upwardly extending pocket 80 which fits closest over the stanchion 48 and the source 74, and which fits snugly within the center of the irradiator assembly 82. Seven slabs of polystyrene 84 are fitted within the liner 76 and define a chamber to receive the irradiator 82, as shown. As mentioned above, wax, paraffinic oil, or other hydrogenous material is preferred for slabs 84, because such material moderates the neutrons from the source. The environment of any specific application would have to be considered in choosing a material. Six threaded tie rods 86 screw into the underside of wall 60, and pass through suitably formed registering openings in the layers 84 to hold the layers together. A tubular member 85 snugly fits into the upper few layers 84, may be affixed thereto by any suitable means such as cementing, and nests snugly within the tubular member 66. Member 85 is preferably made of plastic. The two conduits serving the irradiator pass within tubular member 85.

The irradiator assembly 82 comprises an inner spool 88 which fits snugly over the outside of the pocket 80, and which is formed with upper and lower flanges 90. The flanges are held together by a plurality of straps 92 only one of which is shown in the drawing for the sake of clarity. The space between the spool 88, the straps 92 and the flanges 90 is filled with a large number of coils of tubing, the outer end of which is connected to

the supply pipe 22 and the inner end of which is connected to an output pipe 94. In the actual embodiment of the invention which has been built and successfully used, eight layers of coils of polyethylene tubing were provided in the irradiator assembly 82, but the tubing size has been exaggerated, and hence the number of layers reduced in the drawing for clarity. The tubing had an inside diameter of about  $\frac{1}{4}$  inch, and the coil had a capacity of about half a liter.

The output of the irradiator coil is delivered via output pipe 94. It is significant that the pipe or conduit 94 is of smaller diameter than the pipe or conduit 22 because, in this manner, at constant pumping speed or supply rate, the sample liquid will travel to the counting means 96 at an increased speed. In said successful embodiment, conduit 94 was  $\frac{1}{4}$  inch O.D., and conduit 22 was  $\frac{3}{8}$  inch O.D.

The function of counting means 96 is to bring the now irradiated sample liquid in conduit 94 into proximity with means to measure the radioactivity of the component of interest in the sample liquid. Two forms of such counting means are shown in FIGS. 4 through 7 inclusive, and are described further below.

Referring now to FIG. 2 there is shown an alternate form 98 of the irradiator which was developed in the course of developing the preferred irradiator shown in FIG. 1. The source assembly 74 shown in FIG. 2 is the same as that of FIG. 1, and comprises a mounting stud portion 100, and a hexagonal section 102 formed with a groove 104. The source may be moved by means of a socket which fits on hex section 102, and which has one or more spring loaded detent pins to fit in groove 104, along with suitable extension means on the socket. Extending from hexagonal portion 102 is a capsule holder arm 106 provided with suitable openings to receive a locking set screw 108 which cooperates with a threaded stud 110 formed on the capsule assembly 112. Assembly 112 comprises the source proper 114, which source was supplied by the Atomic Energy Commission of the United States government in the successfully constructed embodiment of the invention. Source 114 comprised 500 milligrams of Cf-252 encapsulated in stainless steel. As further protection and for the purpose of facilitating handling, source 114 is itself encapsulated as at 116. Secondary encapsulation 116 is made of stainless steel.

The second embodiment of the irradiator 98 comprises an outer shell 118 which is secured, by means not shown, to a neck 120. A conduit 122 is nested within neck 120 and carries an inner shell assembly 124 at its lower end. A pair of struts 126 are secured to the inside of inner shell 118 and support a bearing 128 in which is rotatably mounted the conduit 122. Outer shell 118 has a pocket 130, similar to pocket 80 in liner 76, and which receives said pocket 80 and the source therein. Inner shell 124 comprises a skirt portion 132 which surrounds pocket 130 and which carries inner mixing fins 134 and outer mixing fins 136, only a few of which are shown in the drawing.

Irradiator 98 was found to operate reasonably well, but the coil type of FIG. 1 is preferred because the coil avoids eddy currents, channeling, and the like in the sample flow, to thereby assure uniform exposure of the sample to the source. In tests run in developing the invention, better sensitivity was achieved with the coil

than with the FIG. 2 embodiment. Precision of measurements was theoretical with the coil, and poor when using the FIG. 2 embodiment in the non-mixing mode. Rotation of the inner can to cause mixing gave theoretical precision to the measurements, but this did not improve sensitivity. Other tests also showed that better sensitivity was achieved when the flow in the irradiator coil was from the outside to the inside, than when the flow was in the opposite direction.

Referring now to FIG. 3 there is presented a diagrammatic showing of the means to turn the inner shell assembly 124 to mix the sample liquid, while at the same time supplying sample liquid down the annulus between the neck 120 and the conduit 122, and then up the conduit 122. To this end, a motor 138 is provided and is connected by any suitable transmission means 140 to the conduit 122 extending above the overall assembly 24. The neck 120 is formed with an enlarged portion or chamber 142 carrying a bearing 144 between itself and the rotating conduit 122. Line 22 feeds into chamber 142. A rotating union 143 is provided at the junction of conduits 122 and 94.

Referring back to FIG. 1, the remaining apparatus on the right hand side serves to analyze the irradiated stream in output pipe 94 so as to determine the quantity of the now radioactive component of interest in the sample stream. Two embodiments of the counting means 96 are provided and described below in regard to FIGS. 4 and 5, and FIGS. 6 and 7. To complete the description of FIG. 1, the counting means are mounted on a wheeled cart 146 and include a drain pipe 148, which may return the sample liquid to the original process stream, or otherwise dispose of the sample. The detection means in the counting means 96 supply a signal on a line 150 to a ratemeter or the like 152 which is powered from a high voltage power supply 154 via a line 156. The output of the ratemeter is present on a line 158 and passes to display means such as the recorder 160. As will be evident to those skilled in the art, the signals from the counting means on line 150 could be handled by many different arrangements of apparatus equivalent to the means 152 through 160 inclusive. Another system would use the same detector signal would go to a P.A.D. (Pre-amplifier Amplifier Discriminator), then to a scaler. The scaler could be interfaced to a desk top digital computer which is programmed for Vanadium analysis, and the vanadium content of the flowing stream would be printed out on a printer. This system could be programmed to print a value out every few minutes to approximate continuous stream monitoring.

Referring now to FIGS. 4 and 5, there is shown a preferred form 96a of the counting means. In this form a single a scintillation counter is provided, and the general approach is similar to that which was used in regard to the coil irradiator, i.e., a large number of turns of continuous tubing is provided so as to uniformly expose the scintillation counter to the irradiated sample material. Further, the flow is from positions closest to the counting means outwardly to positions furthest from the counting means so that the counter "sees" the most radioactive material as soon as possible after it leaves the irradiator. As is known, radioactive analysis is based on a statistical counting of radioactive decays per unit time, and each decay not

counted detracts from the overall accuracy. Thus, this form 96a comprises one continuous coil of tubing, copper in the particular embodiment which was built, having ends 162 and 164 connected to the lines 94 and 148 of FIG. 1 in such a way as to flow the sample material from the inside towards the outside of the turns 166. The embodiment 96a is fabricated by winding the copper tubing around a mandril or other form, and then spot welding or soldering the turns 166 to each other at random positions to hold the turns together. It is thought that aluminum would also serve as well as if not better than copper. As will be clear to those skilled in electronics, it may be desirable in this form 96a to use an analog stabilizer to avoid gain shifts due to environmental changes and the like.

The embodiment 96b of FIGS. 6 and 7 differs from the form 96a in that this form accepts three small scintillation counters as opposed to the one larger scintillation counter of FIGS. 4 and 5. The turns 168 were made of copper tubing, but the same comments regarding the metal in the preferred form are applicable here. The ends of the single continuous tubing of FIGS. 6 and 7, labelled 162b and 164b, are connected into the remaining apparatus in the same way as the ends of the preferred embodiment. The turns are formed about three cups members 170, each of which snugly receives one of the scintillation counters. A base member 172, a top member 174, and a side member 176 are provided, along with tensioning straps 178 to tightly hold the assembly together. In the form of this embodiment constructed, coupling were used because shorter lengths of tubing were more easily handled.

This embodiment 96b happened to be developed first. Sodium iodide counters were used. The single counter embodiment is preferred because it is more efficient, less expensive, and is compatible with a spectrum analyzer.

Another advantage of the present invention is that accuracy can be increased by making the measurement over a longer period of time. Because accuracy is primarily governed by statistical laws operating on the counts collected, the accuracy is increased approximately with the square root of the number of counts collected. Thus, for example, counting for 25 minutes would produce an answer approximately 5 times better than that obtained by counting for 1 minute.

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. A method of determining the content of a component in a stream of other material comprising the steps of exposing the stream to a radioactive source which will change the component into a detectable form, flowing said stream around said source starting from positions located furthest from said source, and ending at positions located closest to said source, and detecting the amount of said detectable form of said component in said stream by the step of flowing said stream through multi-turn coil means surrounding detecting means starting from positions located closest to said detecting means and ending at positions located furthest from said detecting means.

2. The method of claim 1, wherein said step of flowing said stream around said source comprises the step of flowing said stream through a multi-turn coil of conduit surrounding said source.

3. The method of claim 1, wherein said step of flowing said stream around said source comprises the steps of flowing said stream from an outer chamber to an inner chamber nested within said outer chamber, and mixing said stream as it passes through each of said chambers.

4. The method of claim 1, and exposing said stream to said source at a constant volume per unit time.

5. The method of claim 1, and flowing said stream away from said source at a speed greater than the speed at which said stream is flowed to said source.

6. Apparatus for determining the content of a component in a stream of other material comprising a radioactive source for changing said component into a detectable form, irradiator means for causing said stream to flow around said source starting from positions located furthest from said source and ending at positions located closest to said source, means for detecting the amount of said detectable form of said component in said stream, said detection means comprising means to expose said stream containing the detectable form of said component to counter means, and said means for exposing said stream to said counter means comprising a multiturn coil of conduit surrounding said counter means, whereby said stream is flowed around said counter means starting from positions located closest to said counter means and ending at positions furthest from said counter means.

7. The combination of claim 6, wherein said radioactive source comprises Cf-252.

8. The combination of claim 6, wherein said stream consists of a hydrocarbon material and said component consists of vanadium.

9. The combination of claim 8, wherein said radioactive source comprises Cf-252.

10. The combination of claim 6, and conduit means for flowing said stream to and from said irradiator means, and wherein the conduit means in which said stream is flowed to said irradiator means is larger than the conduit means in which said stream is flowed away from said irradiator means, whereby said stream is flowed away from said source at a speed greater than the speed at which said stream is flowed to said source.

11. The combination of claim 6, said irradiator means comprising a continuous multi-turn coil of conduit surrounding said source.

12. The combination of claim 11, wherein said coil is completely immersed in a hydrogenous material.

13. The combination of claim 12, and wherein said irradiator assembly comprises an inner spool on which said coil is wound, a pair of end flanges on the ends of said spool, and strap means at the outer ends of said flanges to hold said coil on said spool between said flanges.

14. The combination of claim 13, wherein said coil consists of aluminum and said hydrogenous material consists of paraffin.

15. The combination of claim 6, wherein said irradiator means comprises a pair of nested shells, means to turn the inner shell within the outer shell of said pair of shells, mixing vanes on the inside and the outside sur-

faces of said inner shell, means to flow said stream to the space between said shells, means to flow said stream away from said irradiator means from said inside shell, and means to position said radioactive source within said inner shell.

16. The combination of claim 6, said detection means comprising ratemeter means for counting the radioactive decays of said detectable form of said component determined by said counter means, and display

means driven by said ratemeter means.

17. The combination of claim 6, and supply means for pumping said stream from a sampling location to said irradiator means, said supply means comprising a variable speed constant displacement pump, whereby a known and adjustable but constant volume flow per unit time is supplied to said irradiator means.

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