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2,873,377

METHOD OF ANALYZING COMPOSITIONS

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Fig. 1.

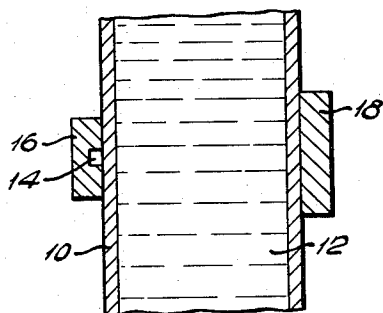


Fig. 2.

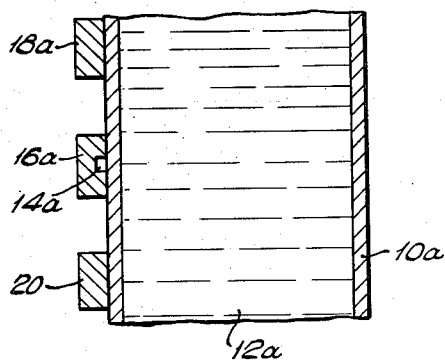


Fig. 3.

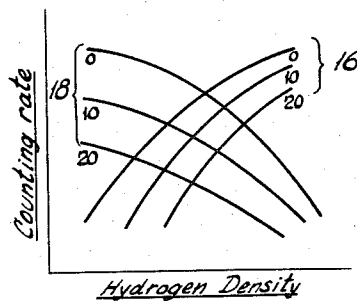
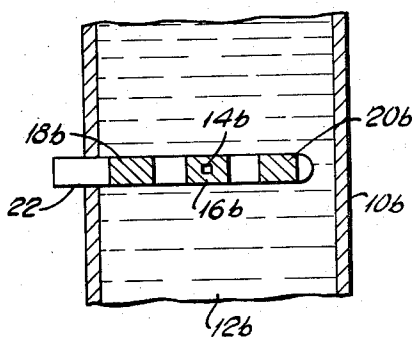


Fig. 4.

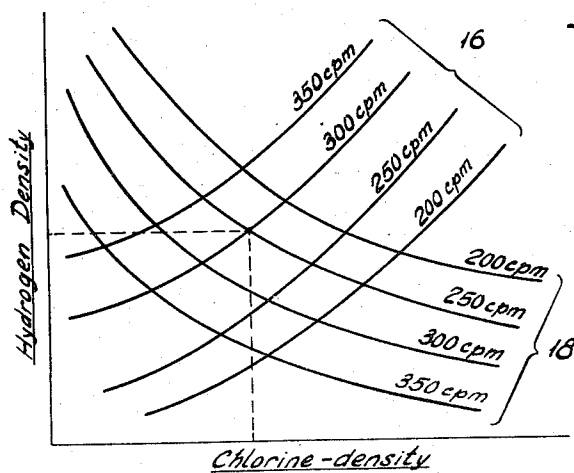


Fig. 5.

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## METHOD OF ANALYZING COMPOSITIONS

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16 Claims. (Cl. 250—43.5)

This invention relates to a method of analyzing compositions and more particularly to a method involving the use of radioactivity measurements for determining the proportions or concentrations of elements present in a chemical compound, mixture or the like. The principal object of the invention is the provision of a method of this type which is convenient and effective in situations where it is difficult, if not impossible, to have direct access to the material to be analyzed.

It is well known that there are frequently great difficulties in determining the relative proportions of various elements which are present in a composition under the conditions of high temperature, pressure and corrosion which exist in many chemical industrial processes. By way of example, this is very true in the oil refining industry where mixtures of oil, acid and the like are being treated under conditions of very high temperature and pressure, such as in hydrogenation for instance. Due to the high pressures involved the hot compositions are contained in or passed through vessels or pipes, the walls of which must be of considerable thickness and this factor renders it still more difficult to obtain easy access to the composition to be examined. There are many instances where the proportions of the elements in such a composition may vary during reaction and it is, of course, very important that such a change or variation in concentration be quickly determined.

In accordance with the invention, a method has been devised which will provide an indication almost instantaneously of a change in concentration of an element in a composition undergoing reaction. It is also contemplated that the method in addition to providing an indication of such a change, can be used to control the process continuously and automatically so as to maintain, as far as possible, the desired concentrations of the elements. As will be explained hereinafter, the actual geometrical arrangement of the apparatus will vary depending upon the particular problem, but in general the apparatus will comprise a source of fast neutrons such as a mixture of radium and beryllium or polonium and beryllium and one or more detectors of thermal neutrons. For the detectors one may use boron, tri-fluoride counters or a boron-carbide coated neutron counter of a suitable type such as is disclosed in the U. S. Letters Patent No. 2,443,731, granted June 22, 1948, to Gerhard Herzog and K. C. Crumrine. Usually two neutron detectors will be required, one in the immediate vicinity of the source and one at such a distance from the source that the neutrons will traverse material having the equivalent slowing down power of at least three inches of water.

For a better understanding of the invention, reference may be had to the accompanying drawing in which:

Figs. 1, 2, and 3 illustrate diagrammatically sections through a vessel, pipe or the like showing three slightly different arrangements of apparatus which can be used in carrying out the method, and

Figs. 4 and 5 are curves or rather families of curves

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which will serve to illustrate the method which will be described in detail hereinafter.

Referring to the drawing, in the somewhat diagrammatic illustration of Fig. 1 a portion of a vessel, pipe or the like 10 is shown as containing a fluid composition 12 or serving as a conduit for such a composition. The container 10 may be assumed to have an external diameter of the order of about one foot. A source of neutrons 14 is shown as positioned against or close to the outer surface of the container and this source may comprise, for example, a mixture of radium and beryllium or a mixture of polonium and beryllium. At least in the immediate vicinity of and shown as partly surrounding the source 14 is a detector 16 of thermal neutrons which may be of any suitable type such as a boron tri-fluoride counter or a counter of which the walls are coated with a thin layer of boron-carbide such as is disclosed in the aforementioned Herzog et al. Patent No. 2,443,731. Shown as disposed more or less opposite the source 14 is another thermal neutron detector 18 generally similar to the detector 16. The detectors 16 and 18 may be connected to suitable amplifying and indicating or recording apparatus, not shown.

Some of the fast neutrons from the source 14 will pass into the composition 12 within the container wherein they will be slowed down so that they will reach the detector 18 in the thermal neutron range. At the same time others of the fast neutrons will enter the composition 12 wherein they will be slowed down and scattered, some of them returning so as to be intercepted by the detector 16. The counting rates of the two counters or detectors 16 and 18 can be calibrated so that between them both the density of hydrogen and the density of some element with a high capture cross section for thermal neutrons can be determined. Sample calibration curves are indicated in Figs. 4 and 5 of the drawing.

In Fig. 4 the counting rates of the counters 16 and 18 are plotted as a function of the hydrogen density, the different sets of curves being obtained for different densities of chlorine, an element having a high capture cross section for thermal neutrons. The three curves indicated by the bracket 16 show the variations in counting rate as the hydrogen concentration or density varies, the counting rate being measured at the detector 16. Likewise, the three curves marked by the bracket 18 show the variations in counting rate at detector 18 for different densities of hydrogen within the composition 12. In each case, the composition measured contained different amounts of chlorine, these amounts or densities being indicated arbitrarily by the figures 0, 10, 20, etc. It will be seen that an increase in chlorine density decreases the counting rate of both counters and it will also be observed from the shapes of the curves that it is possible to keep the counting rate at detector 16 constant by simultaneously increasing both the hydrogen and chlorine densities. Similarly, the counting rate at detector 18 may be kept constant if one decreases the hydrogen density and at the same time increases the chlorine density. Since the counting rates at the two detectors can be kept constant by changing the concentrations of the two elements, the curves of Fig. 5 can be plotted, these curves showing hydrogen density as a function of chlorine density for several different counting rates at the two detectors 16 and 18.

It is to be understood that for a particular size or shape of container and for a particular geometrical arrangement of source and detector, fluids of known hydrogen and chloride concentrations can be placed in or passed through the container 10 in order to prepare the calibration curves of Figs. 4 and 5. Then with the same container and the same geometrical relationship of the source and detectors, the fluid composition containing the ele-

ments hydrogen and chlorine but in unknown quantities or concentrations are placed within or passed through the container and the counting rates of the two detectors 16 and 18 are observed. Then with reference to the curves of Fig. 5 the point of intersection of the two curves indicating the counting rates at the two detectors will give the densities both of the hydrogen and the chlorine in the composition in which their concentrations were previously not known. By way of example, the chart of Fig. 5 can be used in the following way to determine hydrogen and chlorine densities simultaneously. Assuming that detector 16 gives a counting rate of 300 counts per minute and that detector 18 gives a counting rate of 250 counts per minute, this will indicate only one possible hydrogen density and only one possible chlorine density as shown in Fig. 5 by the point where the 300 C. P. M. curve for detector 16 intersects the 250 C. P. M. curve for detector 18. This method of analysis is quite accurate provided that the other elements present in the composition are heavier than carbon and also have small capture cross sections for thermal neutrons or else that they are present with constant densities.

In the case of a fluid composition undergoing reaction or merely contained in or being passed through a container or conduit considerably greater than one or two feet in diameter, the apparatus can take the form illustrated in Fig. 2. In this embodiment the composition 12a is within a container 10a perhaps several feet or more in diameter. As in the case of Fig. 1, the neutron source 14a is shown as partially surrounded by a thermal neutron detector 16a on or close to the outer surface of the container 10a. In this case, however, the remote detector 18 of Fig. 1 is replaced by two thermal neutron detectors 18a and 20, these detectors being placed at the same side of the container as the detector 18a and separated from the source 14a by a distance such that some of the neutrons from the source will traverse a sufficient amount of the composition 12a to have the equivalent slowing down power of at least three inches of water. In making an analysis with the apparatus of Fig. 2 the operation and the use of the curves of Figs. 4 and 5 will be the same as has been described with reference to Fig. 1. Due, however, to the difference in size of the container and the different geometrical arrangement of the detectors and source, the curves of Figs. 4 and 5 will, of course, not be exactly the same as when the apparatus of Fig. 1 is used. Nevertheless, the curves will be generally similar and their use will be the same as that already described. It is also to be understood that there may be situations where both detectors 18a and 20 will not be needed, either one alone being sufficient.

In Fig. 3 another form of apparatus is illustrated for use with large containers. In this embodiment an elongated housing 22 is adapted to be inserted in a composition 12b within a container 10b as by insertion through the container wall or by being suspended from a cable or the like. Within the housing 22 is a neutron source 14b shown as surrounded by a thermal neutron detector 16b. Two other similar thermal neutron detectors 18b and 20b are also disposed within the housing 22 at opposite sides of the detector 16b and separated from the source 14b by a distance such that some of the neutrons from the source in reaching the detectors 18b and 20b will traverse an amount of the composition 12b having the equivalent slowing down power of at least three inches of water. Again, although it is preferable to use the two detectors 18b and 20b, one alone may suffice when space limitations arise. It is understood that the detector 16b will be connected to a suitable amplifying and indicating or recording device, not shown, and also that the two detectors 18b and 20b will both be connected to another suitable amplifying and indicating or recording device, not shown. The operation with the apparatus described in Fig. 3 will be substantially the same as those described in Fig. 2 and reference will be made to calibra-

tion curves similar to those in Figs. 4 and 5 both plotted from data obtained with a fluid or fluids of known hydrogen and chlorine concentrations which are present within the container 10b.

While in the previous explanation, reference has been made only to the use of this method for obtaining an indication of the densities of two elements in a composition, it is to be understood that with suitable additional apparatus the outputs of the thermal neutron detectors can be made to actuate inlet or outlet valves or the like so as to control the concentration of one or more elements within the composition.

In some situations where there is either none or a very small amount of hydrogen or other substance containing light atoms present, the neutron source may be surrounded by a moderating material such as paraffin, heavy water, carbon or the like and only one detector used and placed at such a distance from the source so that the absorption of the thermal neutrons can be observed, this absorption being dependent upon the concentration of an element such as boron or the like, such elements having a large thermal neutron capture cross section. In this case, shields of, say, cadmium may be used to reduce the number of thermal neutrons which might pass from the neutron source directly to the detector without passing through the substance being analyzed.

It would also be possible to use a gamma ray detector instead of a thermal neutron detector in the case where only the remote detector is required. The source-to-detector distance would of course be considerably greater than when a neutron counter is used and it would be necessary to have an efficient gamma ray shield such as several inches of tungsten or lead around the source if a gamma ray-emitting source such as a mixture of radium and beryllium is used.

One of the most obvious applications of this invention is in the halogenation process. Curves similar to those of Figs. 4 and 5 could be used for chlorine, bromine or iodine to determine the amount of hydrogen that has been replaced in the original organic molecule. The amount of fluorination could also be determined indirectly by observing the hydrogen density. The presence of the fluorine itself would have little effect on the counting rates because of its small capture cross section for thermal neutrons.

Another application is in the glass industry. The properties of certain glasses such as Pyrex depend critically upon the amount of boron which is present. With this invention, it is very easy to measure the amount of boron in the presence of the other glass atoms which are mainly oxygen and silicon and other elements of low capture cross section. One would therefore be able to obtain an accurate determination of the amount of boron present by simply observing the absorption of thermal neutrons by the hot glass mixture.

With the method described, one can also control hydrogenation progress. For instance, this method provides prompt means for determining the progress of the hydrogenation of vegetable oils.

Obviously many other modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. The method of determining changes in the concentrations of two elements in a material in a vessel, which comprises first bombarding with neutrons in said vessel a similar material containing known concentrations of said elements, simultaneously measuring the counting rates of thermal neutrons passing through different distances in said similar material, plotting a family of crossed curves showing the variation in density of each of said elements in said similar material as a function of the variations in density of another of said elements for

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predetermined different counting rates at each of said distances, repeating the aforementioned steps of bombarding with neutrons and measuring thermal neutrons with said first mentioned material in said vessel to obtain the counting rates at said two distances, and then referring to said curves to obtain the densities of said elements in the first mentioned material, the points of intersection of the curves for the counting rates subsequently obtained at said different distances with the first mentioned material constituting an indication of the densities of the two elements being measured.

2. The method described in claim 1 in which one of said measurements is made in the immediate vicinity of the source of neutrons.

3. The method described in claim 2 in which the other measurement is made at such a distance from the source of neutrons that the neutrons measured will have traversed material having the equivalent slowing down power of at least three inches of water.

4. The method described in claim 1 in which one of said elements is hydrogen and the other is an element having a high capture cross section for thermal neutrons.

5. The method described in claim 1 in which one of said elements is hydrogen and the other is chlorine.

6. The method described in claim 1 in which one of said elements is an element having a low capture cross section for thermal neutrons and the other is an element having a high capture cross section for thermal neutrons.

7. The method described in claim 6 in which the element having the high capture cross section is boron.

8. An apparatus for measuring the concentrations of two elements in a fluid composition contained in a vessel comprising an elongated housing adapted to be inserted in said composition within the vessel, a source of neutrons within said housing, a detector of thermal neutrons within said housing in the immediate vicinity of said source and at least one other similar thermal neutron detector in said housing and spaced from said source by a distance such that neutrons measured thereby will have traversed an amount of said composition having the equivalent slowing down power of at least three inches of water.

9. An apparatus as defined in claim 8 in which two of said similar thermal neutron detectors are disposed in said housing at opposite sides from the detector which is in the immediate vicinity of the source, each of said other detectors being spaced from the source as defined in claim 8.

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10. The method of determining the concentrations of elements in a material in a vessel which comprises irradiating with neutrons a plurality of samples of said material containing different known concentrations of said elements while measuring the counting rates of thermal neutrons detected after passing through different distances in said material and recording said counting rates of neutrons detected at the respective distances in correlation with the relative concentrations of said elements in order to provide calibration data, irradiating with neutrons an unknown sample to determine the concentrations of said materials contained therein while detecting and measuring the counting rates of thermal neutrons detected after passing through the said plurality of distances and comparing said counting rates at the respective distances with the calibration data to determine the concentrations of each of said elements in said sample.

11. The method described in claim 10 in which one of said measurements is made in the immediate vicinity of the source of neutrons.

12. The method described in claim 11 in which the other measurement is made at such a distance from the source of neutrons that the neutrons measured will have traversed material having the equivalent slowing down power of at least three inches of water.

13. The method described in claim 10 in which one of said elements is hydrogen and the other is an element having a high capture cross section for thermal neutrons.

14. The method described in claim 10 in which one of said elements is hydrogen and the other is chlorine.

15. The method described in claim 10 in which one of said elements is an element having a low capture cross section for thermal neutrons and the other is an element having a high capture cross section for thermal neutrons.

16. The method described in claim 15 in which the element having the high capture cross section is boron.

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