

# THE REVIEW OF SCIENTIFIC INSTRUMENTS

VOLUME 22, NUMBER 4

APRIL, 1951

## Measurement of Low Level Radiocarbon\*

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(Received October 2, 1950)

Techniques are described for chemical purification and measurement of radiocarbon at natural levels ( $10^{-12}$  curie/g or less). The chemical cycle has the following steps: (1) conversion of the starting material to carbon dioxide, by combustion or hydrolysis, (2) precipitation as calcium carbonate, followed by evolution of the purified carbon dioxide, (3) reduction to elementary carbon with magnesium turnings, and (4) extraction with hydrochloric acid and water to remove magnesium and magnesium oxide. The over-all yield is about 85 percent, based on the carbon in the original sample.

The counting is done in a screen-wall counter, twenty-four inches long, with an eight-inch effective counting length. The sample (about 8.5 g) is mounted uniformly in an "infinitely thick" layer, on a split cylinder which can be shifted from "sample" to "background" position by sliding from end to end of the counter. An argon-ethylene filling is used. The background of the counter (about 400 cpm, unshielded) is reduced to 4.5 cpm by the use of an eight-inch thick iron shield and eleven anti-coincidence counters, eighteen inches long. The calibration of the counter on an absolute basis is described. Its efficiency for a 20 mg/cm<sup>2</sup> layer of carbon, over a 400 cm<sup>2</sup> area, is  $5.46 \pm 0.03$  percent.

### INTRODUCTION

IN the course of studies on natural radiocarbon,<sup>1-4</sup> techniques have been developed for chemical purification and measurement at levels of  $10^{-12}$  curie/g. The chemical processing has as its purpose the conversion of organic materials to a form which (1) has the highest possible specific activity, and (2) is radiochemically pure. Elementary carbon best satisfies the first requirement, while the second is achieved through the decontamination procedure described below.

The counting technique involves the use of the screen-wall counter,<sup>5,6</sup> whose design has been developed for greater ruggedness, ease of construction, and ease of sample changing. The necessary reduction in background has been accomplished by the use of a ring of shielding counters in anti-coincidence and by substituting iron for lead in the massive shield.

### CHEMICAL PROCESSING

The materials used in this work generally have been organic substances (wood, charcoal, antler, peat, dung, etc.) obtained by archeologists and geologists in the field. They have been exposed to surface and underground chemical agents for periods of thousands of years. It is necessary to remove intrusive materials, as well as constituents which may have undergone exchange reactions. The carbonate fraction is most vulnerable in this respect. For this reason, after being examined for gross physical intrusions, the samples are treated with dilute hydrochloric acid, until evolution of carbon dioxide is complete. Samples are filtered, washed, and dried and are then ready for the next step, which is combustion.

The apparatus in which the main part of the chemical procedure is conducted is shown in Fig. 1. The combustion of the sample is carried out in the Vycor tube (A). Oxygen is passed over the sample at a pressure slightly below one atmosphere, and the combustion gases are carried through hot copper oxide (furnace B) to complete the oxidation and then are dried and passed into two successive liquid nitrogen traps (C) in which the carbon dioxide is condensed. Enough material is burned to yield a final quantity of carbon of about 10 to 12 g. This amounts to about 24 liters of CO<sub>2</sub> gas.

\* Research supported in part by the Air Force, under Contract No. AF33(038)-6492 and the Viking Fund, Inc., New York.

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<sup>1</sup> Libby, Anderson, and Arnold, *Science* **109**, 227 (1949).

<sup>2</sup> E. C. Anderson and W. F. Libby, *Phys. Rev.* **81**, 64 (1951).

<sup>3</sup> J. R. Arnold and W. F. Libby, *Science* **110**, 678-80 (1949).

<sup>4</sup> W. F. Libby, "Sensitive radiation detection techniques," final report on Air Force Contract No. AF33(038)-6492.

<sup>5</sup> W. F. Libby, *Phys. Rev.* **46**, 196 (1934).

<sup>6</sup> W. F. Libby and D. D. Lee, *Phys. Rev.* **55**, 245 (1939).

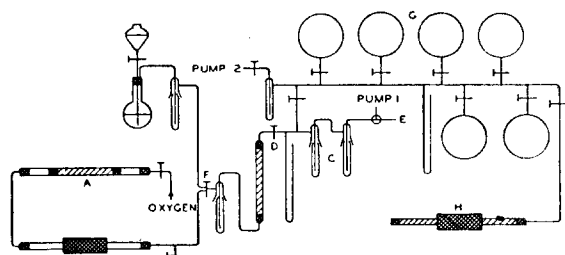


FIG. 1. The chemical preparation apparatus.

The material condensed in the trap system at the conclusion of the combustion consists not only of carbon dioxide, but also of oxides of nitrogen and sulfur, products of incomplete combustion, and part of any radon that may have been present in the original sample. It is necessary to do both a chemical and radiochemical purification before the carbon dioxide is ready for further treatment. A 1-liter flask, containing 500 cc of 6*N*  $\text{NH}_4\text{OH}$ , is attached to the pump stopcock at point E. After the traps have been pumped down at liquid nitrogen temperature, the Dewars are removed and the carbon dioxide is evolved. When the pressure reaches 60 cm, the trap system is connected to the flask. A rapid absorption of the gas takes place. The evolution of the gas is continued, and the flask is shaken to insure absorption until the traps are empty. The pressure at this point should be about 70 cm, and the solution should be quite hot.

A second solution, consisting of 180 g of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  in 180 cc of water, is heated nearly to boiling. The flask is removed from the line, and the hot calcium chloride solution is added slowly from a separatory funnel. Rapid precipitation of calcium carbonate takes place. It is essential that this step be carried out in such a way that the final temperature of the combined solution be higher than the  $70^\circ\text{C}$ . Otherwise a flocculent, poorly filterable precipitate results. The precipitate is filtered and washed free of ammonia on a Buechner funnel. It is then removed from the funnel and washed into a clean 1-liter flask. At this point, all of the oxides have been left behind in the form of soluble salts, and the radon has been eliminated.

The carbon dioxide is now recovered from the precipitate, using the same system employed in the combustion, by adding concentrated hydrochloric acid. The stopcock leading to the flask is opened, and acid is added from a separatory funnel at a rate sufficient to keep the pressure in the flask slightly below one atmosphere. This completes the chemical and radiochemical purification procedure.

The gas is now evolved into the system of 5-liter bulbs (G) and is ready for the reduction step. Reduction is carried out in an iron tube (H) which is filled with 85 g of magnesium turnings together with 1 g of cadmium powder or turnings as a catalyst. An 8-inch movable furnace, capable of reaching  $1000^\circ\text{C}$ , is placed around the tube. The ends of the tube are sealed with

rubber stoppers and de Khotinsky wax, and the reduction system is evacuated and tested for freedom from leaks.

Carbon dioxide is now admitted to the tube up to a pressure approaching one atmosphere, and external heat is applied with a torch at one end of the magnesium filling. When the melting point of magnesium ( $660^\circ\text{C}$ ) is reached, the reaction begins rather violently and produces sufficient heat to maintain itself, if gas is admitted at a moderate rate from the bulbs. Since the reaction (1)  $2\text{Mg} + \text{CO}_2 = 2\text{MgO} + \text{C}$  yields no gaseous products, no circulation is required. It is the practice to run in gas from one bulb until the pressure is reduced to about 20 cm, when the next bulb is cut in. In this way 5 or 6 bulbs of gas can be reacted smoothly, before the other end of the magnesium filling is reached. To complete the reduction, it is necessary to apply external heat using the furnace. The remaining gas is condensed in a trap and may either be expanded into a single bulb or reacted directly. When the reaction is complete, no more than 1 or 2 cm of pressure should remain in the manifold system, and the bulbs should be completely empty. The reduction tube is allowed to cool, and the carbon, magnesium oxide, and unreacted magnesium are removed from the tube using an iron rod.

The material is placed in a 3-liter beaker. Concentrated hydrochloric acid is added, cautiously, until violent evolution of gas has stopped, and then more added to a total of about 800 cc. The mixture is allowed to stand overnight. It is then brought to a boil on a large hot plate. One liter of water is added, and it is again boiled for 15 minutes. The supernate is then removed by filtration, using a sintered glass filter stick operating directly into a water aspirator, and 1500 cc of water added. The solution is again boiled for fifteen minutes and filtered. The water addition, boiling, and filtration cycle is repeated twice more, after which the carbon is washed into a small beaker and the water removed using the filter stick. After the open beaker has been heated on the hot plate on "low" heat for 4 hours, the carbon is thoroughly dry. It is then returned to the 3-liter beaker, 300 cc of concentrated hydrochloric acid are added, and the mixture is allowed to stand for several hours. The solution is brought to a boil, 1500 cc of water are added, and the whole boiled and filtered. The water-washing cycle is repeated three times more, and finally the carbon is dried as before. It is now ready for mounting and measurement.

This extraction procedure serves to remove over 98 percent of the magnesium oxide and magnesium originally present. However, the remaining magnesium oxide is sufficient to constitute an appreciable correction in the measurement. This correction is determined by ashing about 200 mg of the sample in a small porcelain crucible.

Sometimes a sample of carbon still contains more than 10 percent ash at this point. These recalcitrant

samples are treated by heating in a Vycor test tube to a dull red heat (with glass wool in the test tube mouth to protect the carbon from oxidation) for several hours. The usual extraction procedure after the first drying is then followed. At this point, the ash content is found to have dropped to a few percent.

The over-all yield of the chemical processing sequence, described above, based on the organic carbon content of the original material is in the neighborhood of 85 percent. A large part of the losses can be accounted for as mechanical loss in handling. It follows, therefore, that effects due to isotopic fractionation in the course of the various reactions are negligibly small. One of the great problems in producing a final product free from intrusive radioactivity is, of course, the purity of the reagents used. We have controlled this difficulty by buying our reagents in very large batches from single sources.†

#### MOUNTING PROCEDURE

The carbon sample is mounted on one-half of a split cylinder, the other half of which remains bare, as a blank for comparisons (see below for details of counter construction). The effective area of the sample is 400 cm<sup>2</sup>; 8.5 g of material are taken, providing a slight excess over the 20 mg/cm<sup>2</sup> required for an infinitely thick layer.

The sample is first ground carefully in an agate mortar and pestle, and the proper amount of carbon weighed into a 150-cc beaker. Water is added (about 50–55 cc), until the well-stirred slurry has reached just the proper consistency. This can be judged by the rate of flow on tipping the beaker; a second or two should be required for the carbon to reach the lip. The carbon is then pushed rapidly onto a “shovel” and transferred to the cylinder, using a long glass rod and a 4-inch spatula. The carbon is then spread as smoothly as possible on the inside of the cylinder, using the glass rod, making sure that the ends are well covered. Finally the cylinder is spun rapidly by hand, first a few turns in one direction, then a few in the other, until a smooth shiny uniform layer is achieved.

At this point, a hair dryer is turned on, and the hot stream of air directed over the inside of the cylinder, while rotating it slowly by hand. After about 5 minutes, enough water is removed to “set” the sample; at this point, it resembles a heavy coat of flat black paint and will no longer flow.

The operations described must be carried out rapidly and with as little contact of the hands with cylinder or sample as possible. Some practice is necessary for good results. Thin cotton gloves and Kleenex can be used to advantage in various stages. After setting, the two

† The sources are as follows: hydrochloric acid and ammonia, Baker and Adamson; calcium chloride dihydrate, analytical reagent, Mallinckrodt Chemical Company; magnesium turnings, Merck and Company; iron tubes, Central Steel and Wire Company.

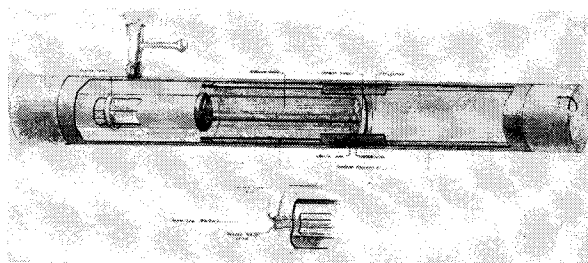


FIG. 2. The screen-wall counter.

halves of the cylinder are joined together and inserted into the counter through the free end. The end cap is put on, and the counter sealed with de Khotinsky wax. This wax is made up in the laboratory from shellac and pine tar.<sup>7</sup> The counter is attached to a vacuum system, and the remaining water is pumped off. Drying in an air furnace has been found to introduce variable amounts of contamination. It is then ready for filling.

After each run, the sample is removed from the cylinder with a spatula. The final cleaning of the cylinder, before mounting a new sample, is done with Kleenex or cheesecloth, or by rinsing with distilled water. The cylinders are periodically cleaned with nitric acid of sufficient strength to remove a macroscopic amount of metal from the surface.

#### SCREEN-WALL COUNTER

The screen-wall counter is a device in which (1) absorptive material between sample and counter is eliminated, (2) a large sample area is used, and (3) sample and background counts can be compared directly by sliding the sample cylinder from end to end. The counter, presently in use, is illustrated in Fig. 2. (Detailed blueprints are obtainable from the authors.) The intermediate screen or grid, whose potential can be adjusted separately, serves to define the operating characteristics of the counter, so that a change in the surface of the wall (sample), so long as it remains conducting, will have no effect.

The counter is constructed of lead-free brass and Lucite. It is 24 inches long; the sample cylinder is 16 inches long. The grid assembly is supported at one end and can be removed by sliding off the end cap. The grid itself is maintained in position by three  $\frac{3}{16}$ -inch brass support rods, which are threaded at one end through a brass collar and at the other through a Lucite disk, so that the effective counter length is just 8 inches. The present design uses 33 grid wires; an earlier design using 9 wires showed an annoying amount of interpenetration of fields, although its operation was generally satisfactory. Both copper and iron wires have been used; we now use copper-covered iron wire (Dumet). The

<sup>7</sup> *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, Ohio), twenty-fourth edition, p. 2430.

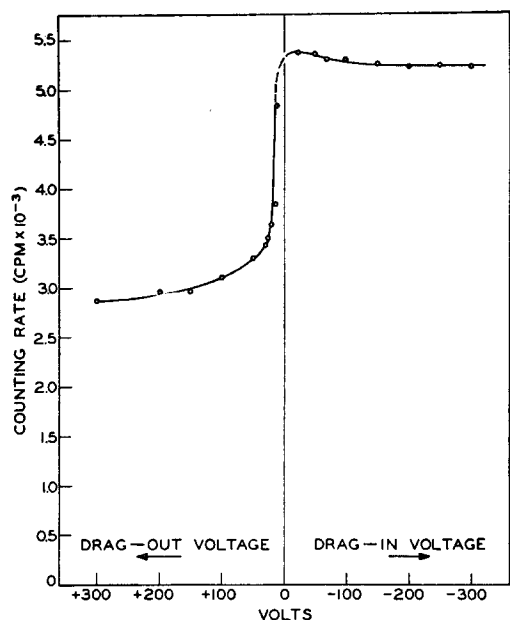


FIG. 3. Counting rate vs drag voltage for the screen-wall counter (external standard).

center wire is 0.010 inch in diameter, the grid wires 0.012 inch. After assembling the grid support, the wires are prepared by cutting a suitable length, cleaning with alcohol, and heating one end in a gas-oxygen flame to form a ball. The wires are then threaded through the Lucite disk and tightened with screws set in the brass collar. The center wire is prepared in the same way; threaded through the Lucite disk and the Lucite tube support, brought out through a glass tube and brass cap, kinked and soldered in place. The grid lead is brought out in the same way.

In operation, the voltage between the grid and center wire is adjusted to the middle of the plateau range. The sample cylinder is normally biased somewhat negatively (about 100 volts) with respect to the screen allowing electrons to be pulled into the counter space, so that the counter volume reaches out to the sample cylinder. This condition is known as "drag-in." The counter can also be operated with a "drag-out" voltage, so that the effective counter volume is defined by the grid. Figure 3 illustrates the two conditions. The counting rate of an external gamma-ray standard is given as a function of cylinder-grid voltage. Small amounts of air and some other impurities may have the effect of reducing the "drag-in" counting rate, while the plateau characteristics remain satisfactory.

The counter can be operated with any standard filling, but because of the large surface area per gram of our carbon samples, we have chosen ethylene which is less strongly adsorbed than ethyl alcohol. A filling of 0.5-cm ethylene and 9.5-cm argon gives a starting potential of about 1200 volts, with entirely satisfactory plateau characteristics while being adsorbed on the

carbon to the extent of a few tenths percent by weight. The ethylene is tank gas from the Matheson Company, purified by repeated freezing and pumping on a vacuum line. The argon is commercial tank gas, not further purified.

Two sorts of difficulties occur with this instrument. The first is that dust particles from the sample may collect on the wires, resulting in poor counter operation. A thorough cleaning is then necessary; gentle flaming may be a satisfactory technique for this purpose. Secondly, counters which have been in vigorous discharge for some time show spurious counts for some time afterward, even after repeated pumping and refilling. A particularly virulent form of this disease is caused by accidental reverse application of the potential between screen and center wire. The spurious counts may disappear slowly over a period of days or even weeks; the only quick cure is to rebuild the instrument with new Lucite insulators.

With the precautions described above, the counter has proved suitable for continuous use on a routine basis.

#### REDUCTION OF BACKGROUND COUNT

When prepared as described above, a sample of carbon from contemporary living material shows an effect in our counters of 6.7 counts per minute. It is necessary to reduce the background count (about 400 cpm, unshielded) to about the same quantity, before accurate measurements can be made. The reduction is accomplished by proper shielding and by the use of anti-coincidence counters.

The unshielded background has three main sources: (1) local gamma-radiation from the laboratory walls, etc., (2) soft component of the cosmic radiation, (3) hard component (mesons). Since anti-coincidence counters will not eliminate counts due to gamma-rays, (because of the low efficiency of the Geiger tube for such radiation) shielding must be massive enough to remove them. Two inches of lead are sufficient for this purpose, but, unfortunately, the laboratory lead bricks themselves have been found to contribute about thirty cpm of gamma-impurities. Various other materials were considered; iron was chosen as the best compromise between price, radiochemical purity, and high atomic number. A shield was constructed of hot-rolled steel plate, 8 inches thick. An additional 2 inches of lead had no effect on the background in this shield.

A diagram of the shield with the counters in place is shown in Fig. 4. In a later model, the jack-raised door has been replaced by a split door, in which one half counterweights the other, and which can be operated by hand.

The remaining background is presumably due chiefly to the meson component, since the shielded background rate of 100 cpm is in almost quantitative agreement with

various reported measurements of the cosmic-ray meson flux at sea level in this latitude. By arranging a ring of eleven ordinary counters around the screen-wall counter, and in anti-coincidence with it, these counts can be largely eliminated. The anti-coincidence counters are cosmic-ray counters available commercially, 2 inches in diameter, with an 18 inch effective counting length. The arrangement is shown in Fig. 5.

The background is reduced in this way to about 4.5 counts per minute. After the anti-coincidence counter pulses are amplified and inverted, they are put through a mixing stage with the screen-wall counter pulses, and the remaining uncanceled counts fed directly to a mechanical register. At these low counting rates, no scaling circuit is needed. The circuits are shown in Fig. 6.

The causes of the residual background require further investigation. A certain fraction must be due to mesons which come into the screen wall from the ends without firing the anti-coincidence counters. These could be eliminated by "skirts" of small counters at each end.

TABLE I. Efficiency of screen-wall counter along its length.

Position	Efficiency (percent)	Background increase due to sample (percent of net count)
1	$5.11 \pm 0.10$	—
2	$5.94 \pm 0.10$	—
3	$5.74 \pm 0.10$	—
4	$5.88 \pm 0.10$	—
5	$5.69 \pm 0.10$	—
6		
7	$5.98 \pm 0.10$	5.2
8	$4.39 \pm 0.10$	20.9
Average	$5.57 \pm 0.05$	
Correction for effect on background	-0.19	
	$5.38 \pm 0.05$	

Remaining impurities in shield and counter materials may cause some counts. It is worth noticing that sample cylinders of copper and stainless steel show the same background, within a few tenths of a count per minute, as lead-free brass. Ordinary shop brass, Armco iron, and particularly aluminum showed higher backgrounds. The fact that three materials give the same effect would indicate that the effect due to the counter materials themselves is small. Radioactive substances in the air may produce a very small effect; replacing the air in the shield by carbon dioxide gave no measurable decrease in background. Thermionic emission of counter walls has also been suggested; this component would show a large temperature effect and sensitivity to surface treatment, neither of which is seen.

Some fluctuations of background count, outside statistics, have been observed. These do not normally exceed 0.25 cpm, but in extreme cases fluctuations of as much as 1 cpm occur over 24 or 48 hours. To minimize these fluctuations, it is necessary to alternate between sample and background positions every few hours.

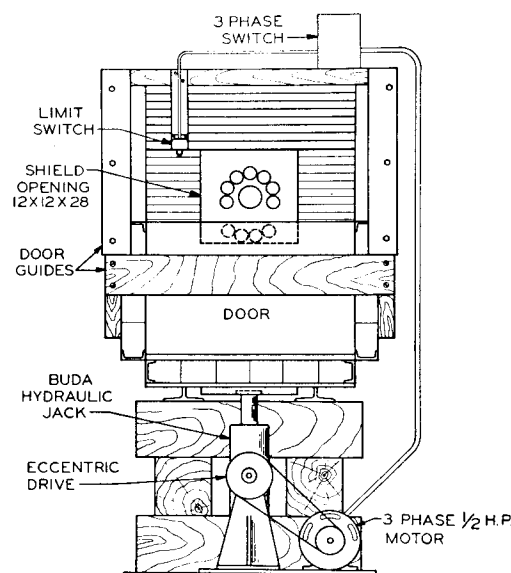


FIG. 4. Front end of the shield, showing the door not quite fully lowered, and the counters in place.

The usual counting run lasts 48 hours, with alternation between the sample and background positions occurring as frequently as convenient but not less than three or four times. This suffices to measure samples of low activity to a statistical counting error of 0.1 counts per minute. The agreement of duplicate runs indicates an actual scatter, certainly, not much greater than this.

The absolute efficiency of the counter for  $C^{14}$  radiation from solid carbon was determined to be  $5.46 \pm 0.03$  percent, for a 20 mg per  $cm^2$  layer of carbon over a 400  $cm^2$  area. For this calibration, four samples of  $CO_2$  were used which had been absolutely assayed in a gas counter.<sup>8</sup> These were diluted with inert  $CO_2$ , converted to C and counted in the usual way. In order to determine the variation of efficiency with position in the counter, a "ring standard," 1 inch in length, was prepared and counted at 1-inch intervals along the active volume, beginning with the support end. The results are shown in Table I.

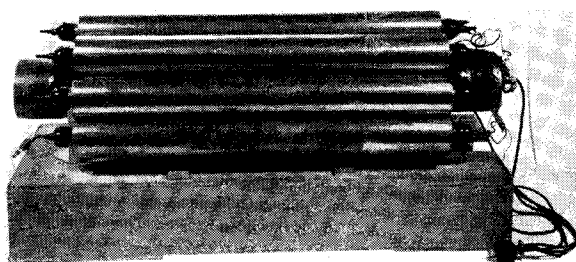


FIG. 5. Side view of the counter assembly.

<sup>8</sup> Engelkemeir, Hamill, Inghram, and Libby, *Phys. Rev.* **75**, 1825 (1949). We are indebted to Mrs. Engelkemeir for these samples.

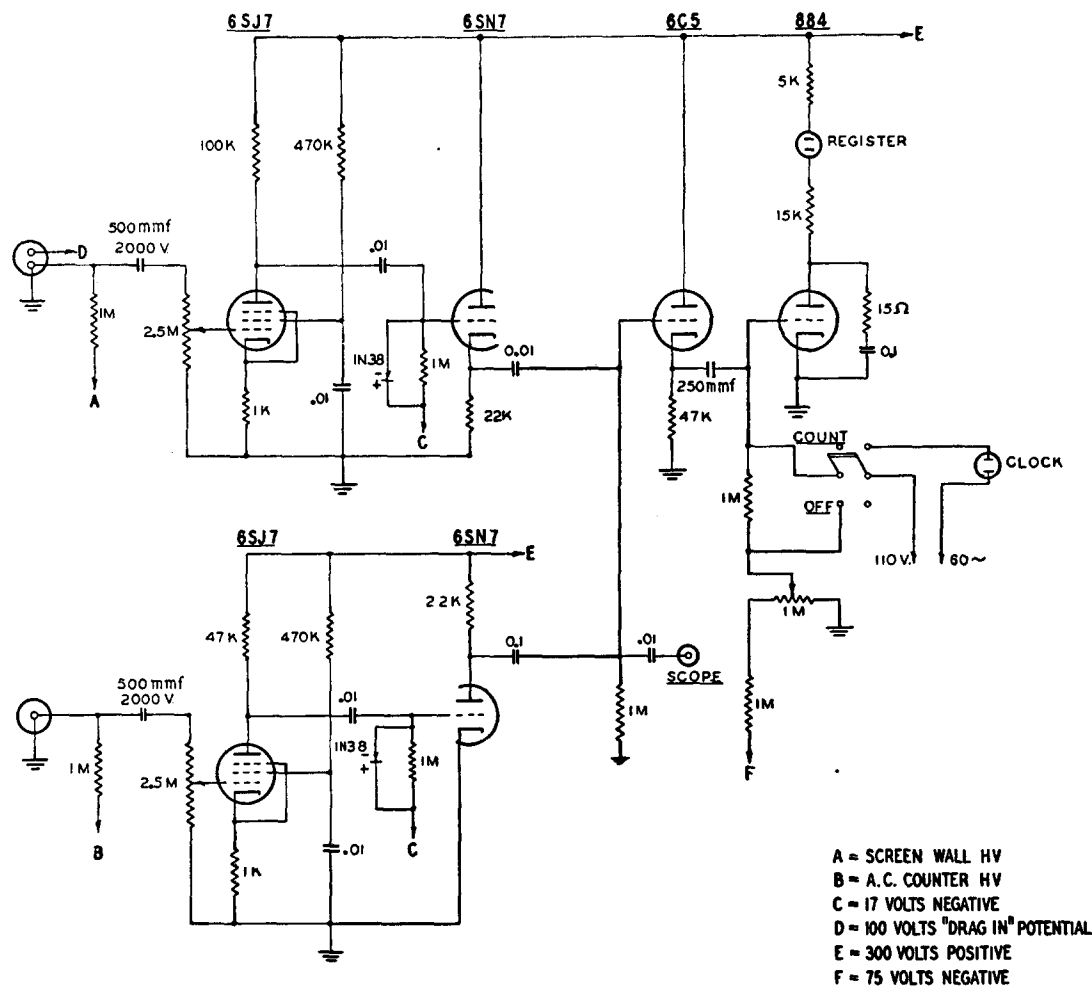


FIG. 6. The anti-coincidence circuit.

It will be seen that the counter retains high efficiency even quite near the ends, with an essentially constant efficiency in the middle 6 inches. The effect of counts "firing in," when the sample cylinder is in the back-ground position, is small.

#### ACKNOWLEDGMENTS

The authors wish to acknowledge the contributions of Mr. Robert Schuch to the design of the counting equipment, and the assistance of Mr. Robert Merrill in developing the chemical procedure.