

ARCHAEOLOGY AND CHEMISTRY

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THE subject of archaeology invites reminiscence. In the seven years that have passed since the liquid scintillation effect was discovered by Kallmann and Reynolds, a number of us have managed to grow old rather quickly. Our efforts in the prehistoric period of 1951-1953 were largely directed by a desire to develop this technique for use in archaeological dating by C^{14} . This effort has been only mildly successful, as we will show later.

Still, as one of the early workers in the field, I am made rather complacent by the fact that it has ramified in so many unexpected directions. This is actually a rather good case history of the unexpected applications which result from 'pure' research. I do not think that either the people at Los Alamos or the others who were working in the field at that time would have been much more successful in predicting all the applications represented at this conference.

It may be well to review briefly the factors which led us to choose the liquid scintillation method for development. The two most obvious characteristics of natural C^{14} are that there is very little of it per gram of ordinary carbon and that the sample size available for study is frequently very large. Often one has samples weighing many kilograms, and in some cases tons would be available if they could be used. The screen-wall counter method with which Libby *et al.* measured the first dates is limited in sensitivity by the self-absorption of the C^{14} beta-ray. One is effectively counting something of the order of 0.5 g of carbon in such a counter. Gas counter methods are limited by the low density inherent in this medium, although they possess some remarkable advantages in other respects. The scintillation counter method allows us to use samples of 10 g or more with very little difficulty, even without trespassing on the domain of the large detector people at Los Alamos. Since a large sample size is much more important for increasing sensitivity than a reduction in background, this method appeared to be very attractive.

I will not spend time here on a historical survey of the development of counters in various laboratories, since this has been covered in other papers and is not of great intrinsic interest in any case.

The great problem in using liquid scintillation techniques for C^{14} dating is the difficulty of preparing the sample in a suitable chemical form. This is in contrast to the situation for tracer applications. The scientist wishing to measure a carbon date is given material which may be wood, charcoal, shell,

or any other natural carbon-containing material. The sample probably contains a great deal of extraneous radioactivity. We must reduce all these things to a common and preferably a simple chemical form, and we must do this without sacrificing the possibility of placing large samples in a small detector. This means that nearly all the carbon atoms in the liquid scintillation solution should, if possible, originate with the sample.

The first step of purification is generally to convert the sample to carbon dioxide, since this is easy to do no matter what the source of the material. One then has the problem of converting this back into a suitable organic liquid, preferably itself a scintillation solvent like toluene. The best that any of us has been able to do in practice has been to convert the sample into a good diluent. Two schemes have actually been used for dating. Our own method has been to convert the carbon dioxide to acetylene following Suess, to polymerize the acetylene over ammoniacal cuprous chloride to divinyl acetylene (a rather dangerous substance), and finally to hydrogenate this material to hexane. The yield is about 40%, and the process takes about a week. Funt *et al.* have reduced the carbon dioxide catalytically to methanol, and converted this to the ester methyl borate. Both these materials are excellent diluents. The ester is somewhat easier to make, but results in a somewhat less concentrated sample. Hayes has proposed to study contemporary and near-contemporary materials by converting essential oils to *p*-cymene, which is a very good solvent. It is in this direction of bypassing the conversion to carbon dioxide in which hope for future progress lies.

So far, we have been discussing the large sample size (and therefore high counting rates) obtainable with this instrument. It remains to discuss the background. Backgrounds of liquid scintillation units tend to be rather higher than those of simple Geiger and proportional counters. Since the important parameter for low level counting is S^2/B , the background is not extremely important, but its effect is not negligible. Since our last paper on this subject, Mr. Julian Shedlovsky in our laboratory has made a study of the sources of background, which has showed us how to reduce the background rather considerably. Because this material is new, I will spend a good deal of time on it.

There are several potential sources of background in this complex instrument. First, of course, are genuine ionizing events in the solution due to cosmic rays and local radioactivity. Most of these can be eliminated by pulse height selection, a feature which was introduced early into most instruments. The cosmic rays are actually rather unimportant because of the compactness of the detector and because they are likely to make rather large pulses. Local radioactivity may come from many sources. First, there is the shield. Because of some early bad experiences with lead, we have used a mercury shield, since mercury can be made very clean radioactively. Recently we have compared the count rate for a given arrangement in a mercury shield with

that in the lead shield of our Packard Tri-Carb unit. The figures were about 13 counts/min in the mercury shield and about 17 counts/min in the lead shield. This would be a negligible difference for most purposes, but because of our extreme requirements we have continued to use the mercury shield. Other materials in the counter region may also contribute volume contamination. All glass contains potassium, and the glass in the phototubes at least cannot be eliminated. There may be other radioactive materials in the neighborhood and, of course, in the cell containing the sample. Surface contamination may also be quite important. We find that a set of fingerprints on a cell can be detected without much difficulty. Over long periods of time air-borne contamination may build up on the counter and shield. These effects can be avoided only by scrupulous cleanliness.

The most important remaining source of background is Čerenkov radiation. This radiation is caused when a charged particle moves through a medium at a speed exceeding the speed of light in that medium. In glass, this would mean about 0.7 times the velocity of light in a vacuum. A particle moving faster than this critical speed generates a sort of optical shock wave, propagating in a forward direction along its path. This process is not a very efficient way of converting the energy of a charged particle into light, but it is just efficient enough to make pulses in the C^{14} or tritium region when particles of 1 or 2 MeV enter a suitable material. The solution itself is no problem, since this effect simply adds to the much larger scintillation effect. However, any transparent but nonfluorescent material is a copious source of Čerenkov pulses. This can be proved by introducing a plastic light pipe between the cell and the phototube. At first sight, this might be expected to reduce the background, since the glass of the tube is being removed from the neighborhood of the cell. Actually, the background rises considerably. One can also get quite a few counts from an empty plastic cell. Of course, Čerenkov radiation resulting from radioactivity can be reduced up to a point by the same precautions prescribed above. It can also be greatly reduced by minimizing the amount of clear material available to produce these pulses.

Phototubes with quartz faces have been examined in order to cut down further on Čerenkov effects. Unfortunately, these tubes are very expensive, and since tube selection is still necessary, the cost is prohibitive. We have purchased one pair of tubes, one of which was noisy, and the other very noisy. Despite this we have established with this one pair of tubes that there is an important reduction in the Čerenkov effect.

A third source of background, which Hayes has christened 'light-dark current', seems to be a very minor effect, if it exists at all, in modern equipment.

Accidental coincidences due to pile-up in the individual circuits become detectable at count rates of perhaps 5000 counts/min in each channel, and quite important at 50,000 counts/min with the usual circuit speeds. For C^{14} , this effect can be entirely neglected.

For this sort of work there is an exceptional premium on freedom from electrical noise and circuit disturbances, since counts of this type, being non-statistical, cause trouble out of proportion to their numbers. We have found the commercial unit quite satisfactory in this respect also.

Summarizing the above, we can best reduce the sources of background by removing local radioactivity from inside the shield, and by minimizing the volume of clear material seen by the phototubes. Our practice is to use a Lucite cell with a triethyl benzene solvent to achieve the former objective. To cut down clear material, we make our cell windows as thin as possible, and we paint the inside of the cell body with a reflecting paint. This reflector system is not ideal optically, but for C^{14} it pays us to accept this loss.

Presently, using a cell of 30 cm³ volume and all the tricks discussed above, we obtain a background of between 5 and 6 counts/min. This is perhaps a factor of 5 lower than what is customarily obtained. Some of these things are rather easy to do, and perhaps should be kept in mind even in less exacting applications.

It seems time to talk about the applications of the method. Because of the difficulty of chemical synthesis, perhaps 20 or 25 measurements have been reported, compared to several hundred for the screen-wall counter method, and a few thousand for gas counter methods. We ourselves have chosen to study samples where the full capacity of such a method is needed. In particular, we have been working on the Suess effect. This effect is a reduction in the specific radioactivity of living material in the twentieth century caused by the accelerated combustion of fossil fuels. The rate of fossil fuel burning has roughly doubled every 25 years for quite some time. Because coal and oil do not contain any C^{14} , the carbon dioxide which is produced dilutes the 'living' radioactive carbon dioxide. In Chicago, tree rings deposited by a living tree in 1950 will show as much as 5% less radioactivity than the rings of the same tree deposited in 1900, just in the opposite direction from what would be predicted from the radioactivity decay law. The effect is less pronounced in places far from industrial activity, but amounts to perhaps from 1 to 1.5% on a world-wide basis.

This effect, which is a minor nuisance in carbon dating work, opens up the possibility for some very interesting geochemical studies. Because we are injecting a non-radioactive tracer, we can study the mixing rates of carbon between the atmosphere and the various other reservoirs available to it. In particular, we have learned from these and other measurements that the average carbon dioxide molecule spends perhaps a decade in the atmosphere before being dissolved in the sea. C^{14} has also confirmed and expanded an older picture in which there is a very rapidly mixed upper layer of about 100 m depth in the ocean and a lower layer which mixes much more slowly. We have found that carbon in the lower layer takes perhaps a few hundred years to rise into the upper layer.

In order to do this work, it has been necessary to count for long periods of time to a counting precision of perhaps 0.3%. This point is worth stressing, since the precision possible with this and other modern counting methods is frequently underestimated. At higher levels, precise counting is, of course, a much easier job. There must be many problems in which a change of 1 or 2% in a count rate would be significant. It is now possible, though by no means trivially easy, to count much more precisely than this.

One other topic is worth mentioning, since it involves some new work. Our group has been interested in the possibility that Mn^{53} may exist in nature. In particular, we see reason why it might exist in the manganese nodules of the deep ocean. This isotope has a half-life of perhaps a million years. Its detection is a problem because it is a pure K-capture species. In this region of the periodic table, the X-ray energy is about 5 kV and to make matters worse, the fluorescence yield is only about 20%, that is, about 80% of the atoms decaying emit an electron rather than an X-ray. Here we have a similar set of problems to those we faced with C^{14} , though in some respects even worse. There are no easily prepared manganese-containing gases. The self-absorption of the X-ray prevents counting a very thick sample, for example, in a proportional counter. A liquid scintillation counter should detect both X-ray and electron though only with about the same efficiency as it has for tritium. The problem again is chemistry. Shedlovsky has succeeded in using a method borrowed from Los Alamos to dissolve high concentrations of this metal in solutions without intolerable quenching effects. He prepares the anhydrous salt of octoic acid (2-ethyl hexanoic acid). This salt is still somewhat pink, and the solutions are not water-white, but a solution containing 50% salt or 6% manganese by weight is still a fairly acceptable system. As others have already said, one trick or another of this type will serve to take almost any metal (except perhaps the alkali metals) into solution.

The second half of this talk is supposed to cover chemistry. I have not been able to learn just what I should discuss under this heading. With the exception of the applications to nuclear physics, practically everything that has been described at this conference is a chemical application of liquid scintillation counting. Anyone familiar with tracer methods should be able to see what can be done quite easily. Perhaps it is only worth repeating that nowadays nearly every carbon- or hydrogen-containing substance can be introduced reasonably effectively into a scintillation system. Of course, this is not to claim that the scintillation system is the best one for every application. We claim only that the instrument has become extremely versatile as the results of the efforts of many workers. I will content myself with describing a single experiment being done by Mr. Frederick Schatzman, whose equipment has recently been described in *Scientific American*. Schatzman has undertaken to repeat the work of Calvin and his co-workers, on the thermal decomposition of oxalic acid, using this technique with natural radiocarbon as a tracer.

His source material was oxalic acid produced by fermentation. The acid decomposed on heating in a dehydrating medium into equimolar quantities of carbon dioxide and carbon monoxide; because the isotopes are not identical in their chemical behavior, there is a difference in the isotopic composition of the two substances of several per cent. Schatzman has converted his carbon dioxide into a suitable form for counting by using a Grignard reagent, and his carbon monoxide similarly after oxidation over copper oxide. He has made preliminary measurements of the fractionation at two temperatures and finds good agreement with Calvin's original work. Here again, the precision of the tool is of importance.

The only thing that can be said with certainty about the future of liquid scintillation counting for carbon dating is that it awaits an elegant solution of the chemical synthesis problem. The only thing which need be said about the chemical uses of this technique is that they will continue to multiply perhaps even at an accelerating rate.