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B. M. Tolbert

March 5, 1956

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ABSTRACT

A practical review is presented on ionization-chamber assay of radioactive gases. The subjects covered include: ion chamber theory, samples and sample preparation, combustion of organic compounds to CO_2, design and construction of ion chambers, measurement of ion chamber currents and approximate calibration data, and detailed procedures for carbon-14 and tritium assay.

IONIZATION CHAMBER ASSAY OF RADIOACTIVE GASES

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INTRODUCTION

The basic idea of an ionization chamber for the detection of radio-activity involves two very simple concepts: The first is that when radiation goes through and interacts with some material such as a gas it produces electrons and positively charged nuclei. The second concept is that if these electrons and positively charged nuclei are generated in a gas within a closed metal chamber, the electrons may be collected on a positively charged probe. These collected electrons can act as an electrical current, which may be measured and may be related to the amount of radiation passing through the chamber. This ionization chamber is really nothing more than a metal can -- if one desires, such a chamber can easily be made from a tin can with an insulated probe placed inside (see Fig. 1). The detection of the electrical current from the ionization chamber can be accomplished by any one of several methods, such as the vibrating-reed electrometer, the electroscope, or sensitive dc amplifiers.

This manual gives a brief review of the principles of ionization chambers, then discusses the various types of information needed for practical ionization-chamber assay of radioactive gases. The subjects covered include the types of samples that may be analyzed and how they can be prepared; descriptions of various standard types of ionization chambers and the special problems that are associated with them; methods for measuring the ionization-chamber currents, with special emphasis on the use of the vibrating-reed electrometer; and finally, some typical experimental setups with specific examples of the calibration and calculation procedures. (For general material, see References 1,2,3,3a.)
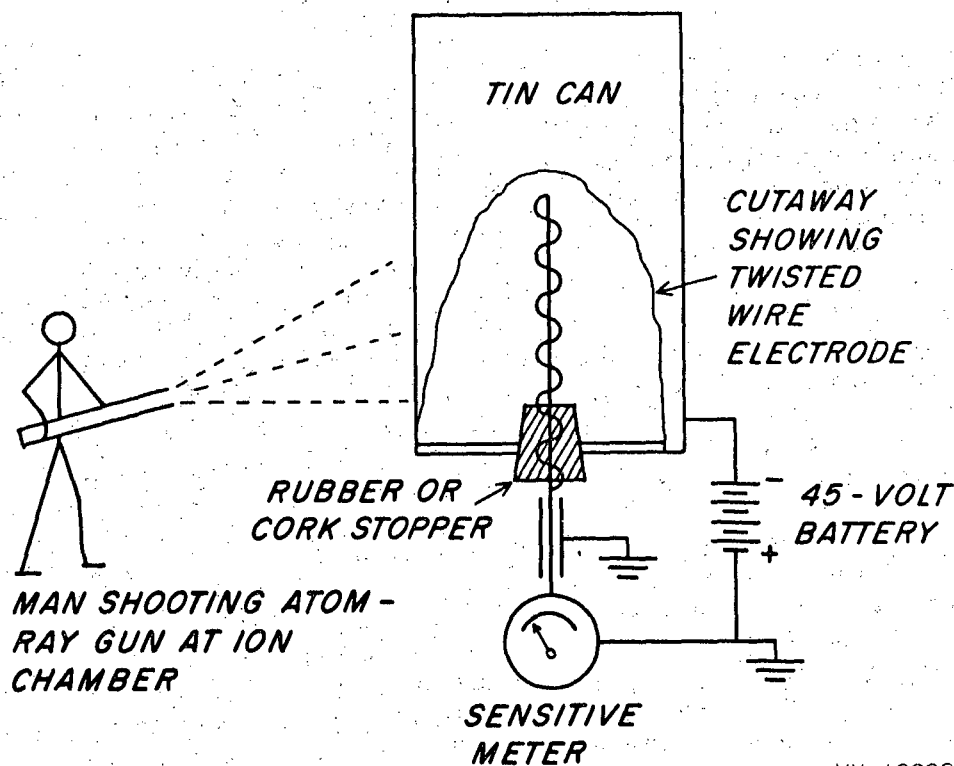
Fig. 1. Simple ion chamber. This may be used for home civil
defense work. (Note: For a one-pint tin can and a 50-μamp
meter, a radiation field of 1 r/hr will give 0.5% of full scale
deflection, 10 r/hr will give 5% deflection and 100 r/hr will
give 50% deflection).

Theory

When radiation interacts with air, there is usually approximately one ion pair produced per 32.5 electron volts (ev) of absorbed energy. Other gases have similar values for the ionization as a function of energy absorbed. One can easily estimate the approximate number of electrons that will be produced, for instance, by a C^{14} beta particle which has an average energy of 45,000 ev. In a gas such as air, this energy would produce about 1500 electrons. For a tritium beta particle, which has much less energy, some 150 electrons would be produced. These radiation-produced electrons, collected in an ionization chamber, produce the current that is detected by the measuring system. One can easily see that, because the number of electrons is directly proportional to the amount of radiation in the chamber, the amount of current produced by the ionization chamber and measured by the electrical measuring system is directly proportional to the amount of radioactivity in the ionization chamber.

The collection of the electrons in an ionization chamber is a relatively simple matter. The electrons, which are very mobile, move toward and collect on any positively charged surface. This collection area is usually a small polished rod somewhere near the center of the chamber. In practice, the wall of the chamber is given a negative charge (from a battery) of between 90 and 300 volts, and the center electrode is kept fairly close to zero or ground potential. The electrons inside the chamber see this only as a voltage differential, and are readily collected on the center electrode. It is necessary to have sufficient voltage on the ionization chamber to collect all the electrons, and especially to collect them before they can recombine with any of the positive ions. Yet it is also important not to have too much voltage, since if the electrons are accelerated rapidly as they move toward the center electrode they can interact with other molecules of the gas and produce secondary electrons, which would give false readings (too high). The range of voltage over which the electrons are adequately collected is usually very wide. Thus, a 250-cc ionization chamber usually gives satisfactory electron collection from about 15 volts up to 1000 volts or more. It is desirable to collect the electrons, rather than the positive ions, because the latter are quite slow-moving and do not clearly show sudden changes in ionization rate.

There are many devices for measuring the current flow derived from the collected electrons. Some of the early instruments for this purpose were the goldleaf electroscope, the Lauritsen electroscope, and many different sensitive direct-current amplifiers. Although sensitive dc amplifiers are commonly used in fixed and portable instruments for measuring high-level radiation fields, they have not been particularly important for routine assay of radioactive gases in the experimental laboratory. *

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* Keithley Instruments are currently presenting some dc electrometers of superior design. They may prove useful.

Far and away the best and most sensitive device for the measurement of these currents is the vibrating-reed electrometers,[4] which is made by several manufacturers.* (See Fig. 2.) Such an instrument converts the very small direct current from the ionization chamber into an alternating current. This alternating current is then amplified, in a standard electronic tube circuit with enough feedback so that the system is electrically stable over long periods of time. The vibrating-reed electrometer is capable of detecting as small a current as 10^{-17} ampere, which corresponds to only 63 electrons per second.

It is also desirable -- for reasons to be explained later -- to record the reading of the vibrating-reed electrometer on some kind of recording potentiometer. This potentiometer chart is an automatic written record of the amount of radioactivity being measured in the ion chamber.

SAMPLES AND SAMPLE PREPARATION

Although ionization chambers have a wide range of applicability and may be used with almost any type of radiation, this review is limited to a discussion of the measurement of radioactive gases. In this field, the ionization chamber, together with the vibrating-reed electrometer, is particularly suited to the measurement of such radioactivity as that from C^{14}, S^{35}, T, krypton, and other elements that are soft beta-emitters and can be incorporated in gases. Typical examples of such gases are $C^{14}O_2$, $C^{14}O$, $C^{14}H_4$, H_2S^{35}, $S^{35}O_2$, T_2 (or HT), CH_3T, radioactive Kr, etc. These particular radioactive isotopes are mentioned because their low-energy beta particles are not very satisfactorily detected by most of the common methods of radiation measurement. The radiation from these elements in the form of gases in an ionization chamber can be precisely measured with excellent sensitivity.

The special areas of applicability of the ionization chamber-vibrating-reed electrometer are to be found whenever one is in need of very precise radioactivity determinations, or of very sensitive radioactivity determinations, or of continuous indications of radioactivity in a gas flow system.

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* a. Vibrating Reed Electrometer, Applied Physics Corp., Pasadena, California.
  b. Dynamic Capacitor Electrometer, Curtiss-Wright Corp., Carlstadt, New Jersey.
  c. Beckman Model VL Micro-Microammeter, Beckman Instruments, Inc., Fullerton, California.
  d. Brown Recording Electrometer, Minneapolis-Honeywell Regulator Co., Philadelphia, Pennsylvania.
  e. The Vibron Electrometer, Model 93, Electronics Instruments, Ltd., Richmond, Surrey, England.
  f. A-C operated pH indicator No. 7664, Leeds and Northrup Co., Philadelphia, Pennsylvania.
  g. Electrometer Type 1086, Etalco Ltd., Beeston, Nottingham, England.
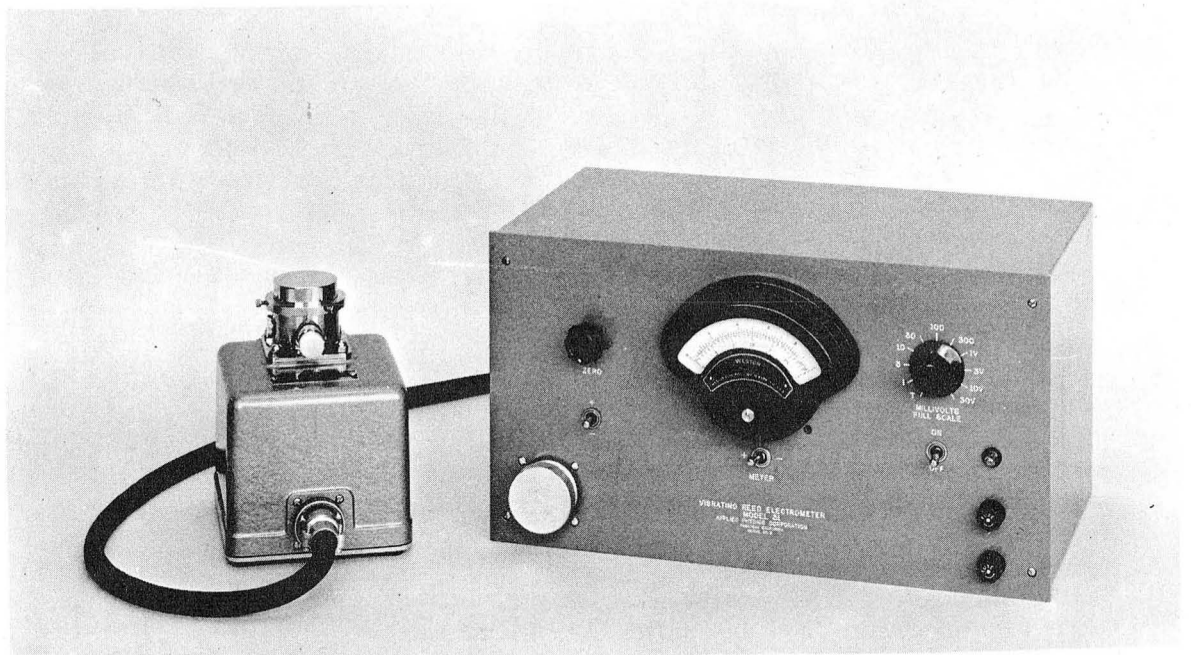
ZN-1563

Fig. 2. A vibrating-reed electrometer (Applied Physics Corpora-
tion, Model 31).

Since a gas can be introduced into an ionization chamber in a manner that is reproducible to about 0.1%, since the performance of an ionization chamber can itself be made reproducible to a few hundredths of a percent, and since the vibrating-reed electrometer–recorder combination can be standardized to better than 0.2%, such an instrumental combination can be made to give analytical results within 0.2% precision or better. This type of reproducibility, of course, is just not possible with any type of solid sample; and Geiger-Mueller tubes and proportional counters show day-to-day variation much larger than these limits.

Very sensitive radioactivity determinations are possible with an ionization chamber–vibrating-reed electrometer combination, because the size of the ionization chamber can be increased to the point where it is possible to introduce sufficient sample into the measuring device so that extremely small specific activities may be detected. Since the ionization chamber is not dependent upon any special gas filling containing quench materials, any inert gases such as helium, or any specific proportional gases such as methane, it is possible to flow "on stream" substances through an ionization chamber and continuously measure their radioactivity. Thus, one may detect the radioactivity in the breath of a human or monitor the tritium or krypton in the air of an atomic power plant, or study a radioactive C^{14} tagging process in a continuous pilot-plant operation.

The applicability of this method to various isotopes depends on (a) convertibility of the radioactive material one starts with into some gas to be introduced into the ionization chamber, (b) freedom from contamination of the chamber by the gas (i. e.; it is not adsorbed by or does not react chemically with the chamber walls), and (c) sufficient sample with sufficient radioactivity in it to produce an adequate electrical signal. As an example of the limitations of this method, the measurement of tritium as tritium water does not work very well without special precautions because the radioactive water exchanges with the water that is adsorbed on the walls of almost any metal or material, and thus produces a semipermanent contamination. Also, isotopes with very low-energy radiation do not produce many electrons per radiation particle, and thus not much current. This low sensitivity makes it necessary in tritium measurements to use fairly large amounts of radioactivity; the instrument is still sufficiently sensitive, however, that one can study body-water radioactivity levels in humans.

The preparation of samples for use in ionization chambers can be reviewed in only a limited manner, since many preparation problems are rather specialized. However, we can briefly describe what is necessary here. If a radioactive sample is already in the gaseous form very little preparation is needed to introduce it into an ionization chamber and measure its radioactivity. For example, in the combustion of organic compounds in an analytical train, the CO_2 produced may be collected directly into an evacuated ionization chamber. As another example -- already mentioned -- the $C^{14}O_2$ in the breath of an animal or of a human may be directly measured by merely passing the expired air through an ionization chamber. The krypton and other radioactive elements that are to be found in pile gases may be easily measured by means of a small ionization chamber sampler.

If solid or liquid organic compounds are to be analyzed for C^{14}, it is usually necessary that they be combusted to CO_2. True, if the liquid is volatile enough it may be swept through the chamber by use of a carrier gas such as methane, but this may well lead to contamination, and a batchwise combustion process will probably be found most expedient.

There are at least four fundamental methods for the combustion of organic compounds to CO_2, and many variations on each one of these procedures.[5] These methods, with their more important variations, are as follows:

1. The burning of organic compounds over hot copper oxide.
   a. This combustion may be done by flushing the sample through a furnace-heated tube. (See the procedures of Anderson and Bothner-by[6,7] that are used at Brookhaven National Laboratory.)
   b. The sample may be combusted in small closed tubes. (See the procedures of Wilzbach and Sykes[8] that were developed at the Argonne National Laboratory.)
2. Oxidation of the sample to CO_2 by means of the Van Slyke-Folch oxidizing mixture.[9]
   a. This procedure is of special applicability to biological samples. (See the methods used at the Radiation Laboratory, University of California.[10])
   b. Precision assay of organic chemical samples may be made. (See the procedures of Collins and Neville at the Oak Ridge National Laboratory.[11,12])
3. The peroxide bomb fusion method; and
4. The persulfate liquid oxidation procedure; both of these have limitations and are not very important today.[13]

The assay of organic compounds for tritium is a considerably more difficult problem than for C^{14}. Foremost as a difficulty here is the low energy of the tritium beta particle; it is only about one-tenth the energy of the C^{14} beta particle. Another problem is that large errors are easily introduced by the isotope effect that is produced by the large mass difference between hydrogen and tritium. Thus, in the reaction of water with the Grignard reagent (methyl magnesium iodide) to give methane as an ion-chamber assay gas, the specific activity of the methane from the reaction run at 0° C is about 20% less than from that run at 100° C. In order to avoid isotope effects all analytical reactions should go to completion, and the combined products be allowed to mix. Probably the best procedure for the conversion of an organic compound to a hydrogen-containing gas is that of Wilzbach, Van Dyken, Kaplan, and Brown,[14,15] in which the organic compound is sealed in a tube, together with a small amount of zinc, nickel oxide, and water. After three hours' heating at 670° C all the hydrogen has been converted into a mixture of hydrogen and methane, which may then be directly introduced into the chamber for assay. Otherwise the solid or liquid organic samples that are to be analyzed for tritium by the ionization chamber–vibrating-reed electrometer technique must first be oxidized to water and the water then converted into some suitable gas.[16,17,18]

Tritium water itself may be easily converted into a gas suitable for ionization-chamber measurements by several methods:

1. It may be passed over a bed of hot zinc or magnesium[19] or treated with sodium[20] to produce hydrogen. These procedures, although satisfactory, tend to exhibit "memory" effects (because of activity that remains in the apparatus), and isotope effects, and are relatively slow.
2. A second (and preferable) method involves the treatment of the water with lithium aluminum hydride in some nonvolatile etheric solvent such as diethyl carbitol.[21,22] Lithium aluminum hydride in such a solvent reacts rapidly -- or even violently -- on contact with water, to produce hydrogen gas and lithium aluminum oxide. If water is added slowly and in small quantities to a few ml of lithium aluminum hydride solution in diethyl carbitol, a controlled production of hydrogen can easily be attained (see Fig. 3).
3. The third procedure involves the addition of water to methyl magnesium bromide.[23] The interaction of water with this Grignard reagent produces methane and MgBrOH. The methane is suitable for detection in an ionization chamber, and the procedure is satisfactory except for a relatively large isotope effect.
4. A fourth procedure uses the production of acetylene when calcium carbide is treated with water.[24]
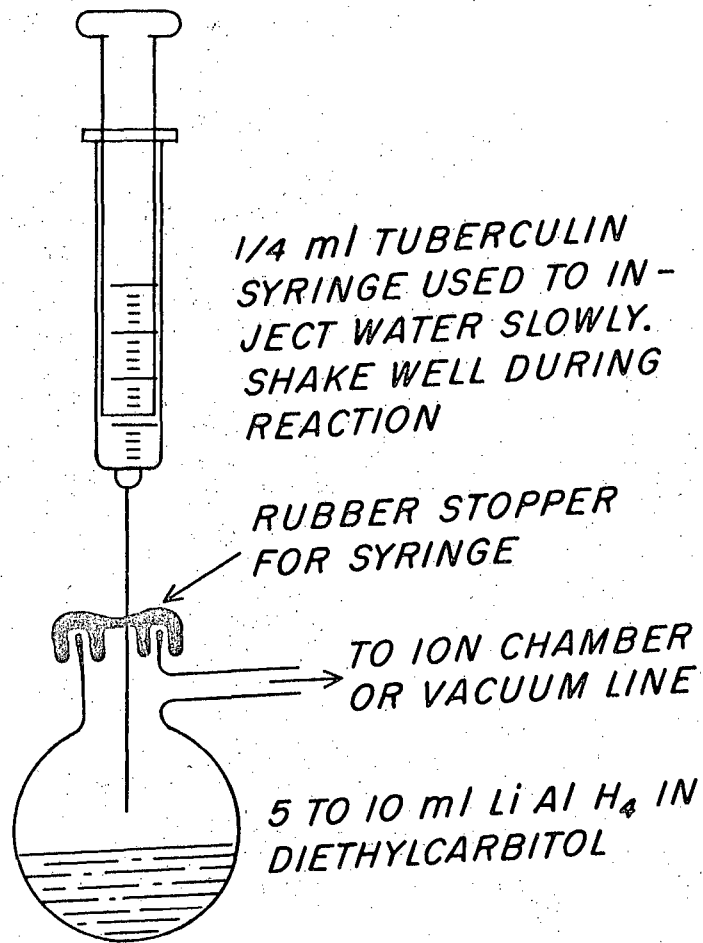
Volatile sulfur compounds can easily be produced for assay of sulfides and sulfites by the treatment of these substances with acids. Thus, sodium sulfide can be converted to hydrogen sulfide and swept into an ionization chamber and the radioactivity detected. If the ionization chamber is carefully constructed of materials that are inert chemically to these gases and are pretreated with inactive gases of the same type so that all potential reactive groups are combined (probably into stable sulfides), it is possible to reduce the problem of chamber contamination to a minimum.

IONIZATION CHAMBERS

Although the basic make-up of an ionization chamber is exceedingly simple -- a metal can and insulated probe -- there is in practice a large variety of ionization chambers. There are high-pressure ionization chambers, micro-thimble-size ionization chambers, routine radiation-survey ionization chambers, cyclotron and atomic pile control ion chambers, and x-ray-monitoring ion chambers, to mention but a few of the more common types of specialized units.

Let us illustrate some of the specialized features of an ionization chamber through an examination of the so-called Borkowski chamber, which is shown in Fig. 4. This ionization chamber, originally designed at the Oak Ridge National Laboratories, is very commonly used today for measuring the radiation of radioactive gases. The "can" around the outside (Fig. 4, a) is provided with a negative voltage of 90 to 200 volts, and should be made with a very smooth inside surface so as to reduce contamination problems. The central probe (Fig. 4, b) goes through the long axis of the chamber and through a small sapphire insulator in the base* and protrudes

---

* The original Borkowski ion chambers were made with polystyrene insulators. Later models used Teflon, but the Applied Physics chamber using sapphire seems the best.

1/4 ml TUBERCULIN SYRINGE USED TO INJECT WATER SLOWLY. SHAKE WELL DURING REACTION

RUBBER STOPPER FOR SYRINGE

TO ION CHAMBER OR VACUUM LINE

5 TO 10 ml Li Al H$_4$ IN DIETHYLCARBITOL

MU-12389

Fig. 3. Simple apparatus for the generation of H$_2$ from H$_2$O in tritium analysis.
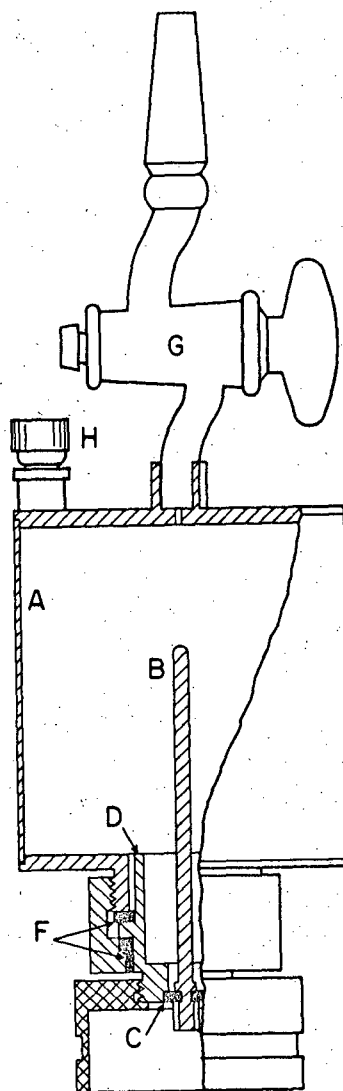
MU-12390

Fig. 4. Borkowski ionization chamber. The chamber body, a,
    may be made in almost any desired size. The various parts
    are: central probe, b; sapphire insulator, c; grounding shield,
    d; grounding dust cap, e; chamber insulator, f; stopcock, g;
    collection potential binding post, h.

for making a contact with the vibrating-reed electrometer to which the chamber is attached (usually after it has been filled with a radioactive gas). The metal shell that surrounds this protruding probe and extends up around the probe insulator and well into the ionization chamber is insulated from both the chamber proper and the probe and is nominally maintained at ground potential. This is done because it is undesirable to have a large collection-voltage differential across the small insulator that holds a central probe or to have the insulator "see" any of the high-potential area in the collection field of the ion chamber proper. A simple stopcock and standard taper joint are provided (Fig. 4, g) for the connection of the ionization chamber to a vacuum line and for the introduction of radioactive gases.

A chamber such as the one described above may be easily and quickly disassembled without destroying its calibration; it may be cleaned, preferably by mechanical scrubbing rather than chemical methods; and except for the center probe and the center-probe insulator may be, in general, quite roughly handled. As in all ionization chambers, this center probe with its insulator, although appearing to be very rugged, is one of the most delicate parts of the unit. It must be especially cleaned and should never be physically stressed. Sapphire insulators can be cleaned in distilled water with detergent added. They should then be thoroughly rinsed in distilled water and dried. Teflon insulators may be cleaned in chromic acid—sulfuric acid cleaning solution, then washed many times in distilled water and dried. Any insulator, once cleaned, should not be touched with the hands.

Another type of ionization chamber in use today is the Tolbert-Cary instrument. This unit is represented in Fig. 5, and differs from the Borkowski ionization chamber in its mode of closure -- which gives a somewhat greater ease of opening and cleaning -- and in its smaller dead volume. This type of ionization chamber has been constructed in a large range of sizes, from 10 cc up to 20 liters. Again, as in the ionization chamber previously described, the metal can is maintained at a negative potential of from 90 to several hundred volts. This metal can is insulated from the grounded shield by means of an inner-outer standard-taper sleeve adaptor. The probe assembly may be removed in a few seconds' time for cleaning of the chamber, or for installation of the probe on a different-sized ionization chamber.

In the construction of ionization chambers there are three important areas to which one should give major consideration. These are the electrical characteristics of the center probe insulator, the radiation level and contamination resistance of the ionization chamber wall itself, and the efficiency of the chamber. The solution of the problems dealing with the first of these, the electrical characteristics of the probe insulator, is far more of an art than a science. The electrical characteristics of insulators are related to solid-state physics and to surface charge phenomena, and are incompletely understood. Insulators have been made of glass, quartz, polystryene, Teflon, sapphire, and many other materials. The most satisfactory materials for these insulators are sapphire, Teflon (polytetrafluoroethylene--trademarked, patented duPont product) and Kel-F (polytrifluoromonochloroethylene--trademarked, patented M. W. Kellogg Co. product). Insulators made from these substances all have excellent resistance (greater than 10^{18} ohms) and show relatively small hysteresis, charge soak-in, and piezoelectric characteristics as compared with other material.

VALVE AND
BALL CONNECTOR
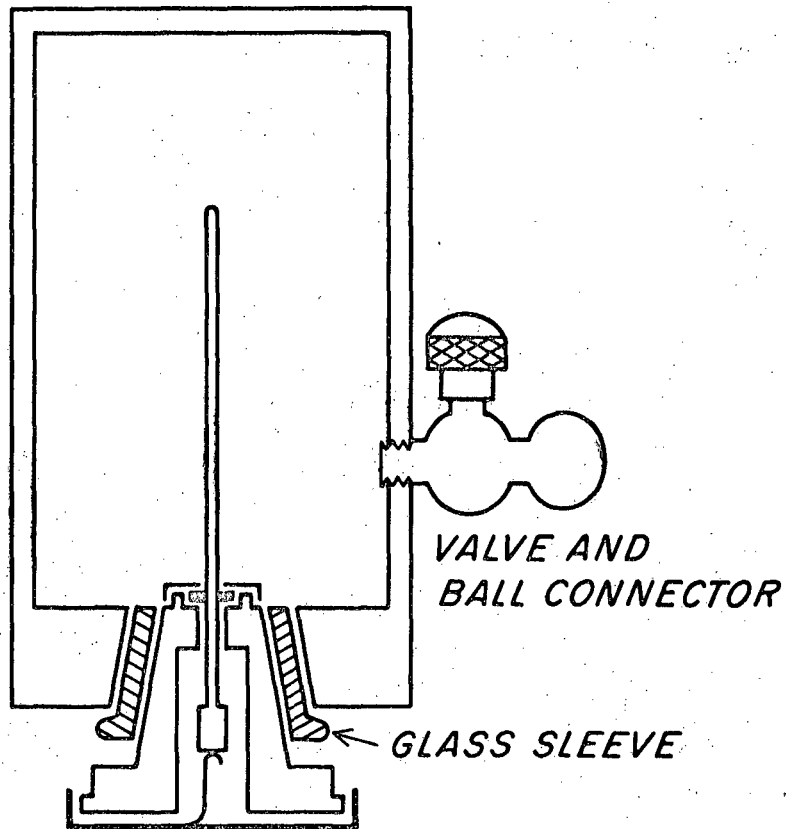
GLASS SLEEVE

MU-12391

Fig. 5. Tolbert-Cary ionization chamber of 100 cc capacity. The
    "can" is fitted with a 1/8-inch Hoke sylphon-type needle valve
    and a ball for an 18/9 $ socket. The insulation glass sleeve is
    24/40 to 29/42 $ sleeve adaptor, cut off to 1 inch effective
    length.

If carefully handled, insulators made from these materials (sapphire, Teflon, Kel-F) give good service. When installed on an ionization chamber they come to a background current reading in a few minutes' to half an hour's time. Although a probe going through a sapphire insulator should not be pushed, plucked or twanged, these devices can stand normal handling, and after resting for a period of hours or days they return to a standard reference hysteresis-current state. Although the experimenter may easily build his own insulator assemblies, he will generally find it cheaper in terms of time, money, and performance to buy some standardized unit containing a tested probe assembly.

The characteristic background radiation level of the ionization chamber is dependent upon radiation from the chamber walls and the cosmic-ray contribution. Cosmic-ray effects are proportional to volume. Shielding is helpful, but usually may be omitted because the cosmic-ray level is quite constant. The greatest reduction in background is made by careful selection of the chamber wall material. An ionization chamber should be constructed of materials with as low a background as possible, in terms of both alpha contamination and beta-gamma contamination.

Of the various types of radioactive contamination to be considered -- alpha, beta, gamma, and cosmic ray -- the most bothersome are alpha rays, because the heavy particles produce many ion pairs and a great deal of current. Furthermore, the alpha particles usually are not sufficiently frequent to provide a good statistical randomization of events, so that they produce large statistical deviations in ionization chamber current readings. Beta particles are at least a thousand times less bothersome than are alpha particles, and gamma rays and cosmic rays produce a relatively small number of electrons in passing through the volume of the ionization chamber. This is particularly convenient, since it is not always easy to shield an experimental setup from cosmic rays.

Although we do not normally think of pure metals, purchased commercially, as contaminated, we know that nearly everything has a certain natural background radioactivity. In particular, almost any element that is closely related to the lathanide or actinide series (i.e., rare earths), or to the radium-containing alkaline earths, will probably show appreciable contamination. Thus one avoids metals containing any lead, calcium, or magnesium. Glass, even when coated with thin metallic films, exhibits a high natural radioactivity level.

The types of materials that have proved most satisfactory for ionization chamber construction are, in general, pure metals of the transition-element series. Thus, pure iron, pure copper, and stainless steel all have very low natural radioactivity levels. Brass is a fair material, provided there is no lead used in its manufacture. (Many brasses, however, have a small percent of lead in them to make them machine easily, and must be strictly avoided.) Stainless steel has a rather low natural radiation level and an excellent chemical resistance to contamination. In general, in the construction of ionization chambers it is advisable to make a test chamber from the material to be used in order to learn something about the radioactivity characteristics of the substance.

The efficiency of an ionization chamber is a function of the filling gas and of the shape and size of the chamber in comparison with the mean range of the radiation being measured. Thus, the chamber should be large enough that most of the energy from the radiation is absorbed by the gas rather than being absorbed in the walls of the chamber itself. Although there are many theoretical and experimental papers on optimum shape and size of ionization chambers,[25, 26] for practical work with carbon, tritium, and sulfur such considerations are not critical, and as long as the chamber is of a convenient size and enough radiation can be introduced into it to give a sufficiently precise reading, satisfactory results can be obtained. (See Fig. 6.) An indication of the relative efficiencies of the various types of gases is given by Tables I and II. Thus, we see that methane is a very excellent gas with which to fill ionization chambers, but the entire variation from hydrogen -- one of the less efficient gases -- to argon -- one of the more efficient -- is only about 40%.

ELECTROMETERS AND RECORDERS

Although sensitive dc amplifiers have been much improved in recent years,[27, 28] the vibrating-reed electrometer is still the most stable, accurate, sensitive, and convenient current-measuring device for use with ionization chambers. Such an electrometer is not very complex compared with many other instruments, but it has a number of critical parts, and repair work should not be undertaken lightly by an amateur. The essentials of the input circuit are discussed below, since such information is often necessary in working with ion chamber—electrometer combinations.

The electrical current or potential from the ionization chamber is fed into a circuit as shown in Fig. 7. The condenser C_v consists of a fixed metal piece and a vibrating metal plate near it. The plate, or reed, vibrating at about 450 cps, modulates the potential being measured, and this modulated signal is passed through a condenser and a resistor to the first stage of the electronic tube amplification circuit. Since an electronic tube "sees" only alternating current, it takes the alternating current produced by the modulating reed and amplifies it in a very stable 100% inverse feedback electrical circuit. The signal, after being rectified, has then sufficient strength to drive an ordinary recorder or meter. In order to be satisfactory this electrometer must be very carefully and precisely built of exceedingly high-quality materials.

The recorder used with the vibrating-reed electrometer may be almost any standard instrument as long as it has a linear scale, sufficient precision for the work to be done, and a satisfactory response time. Typical recorders that perform well with the vibrating-reed electrometer are the Leeds and Northrup Speedomax recorders, Minneapolis-Honeywell Brown recorders, and the Varian Associates' seven-inch rectilinear recorder.

There are two fundamental methods of using an electrometer-recorder combination to measure the current from an ionization chamber. They are called the "rate-of-charge" method and the "high-resistance-leak" method. The circuit differences for these two methods are given in Fig. 8.

STAINLESS STEEL

'O' RING SEAL

GLASS SLEEVE BUSHING

SAPPHIRE INSULATED
PROBE BASE

-270v
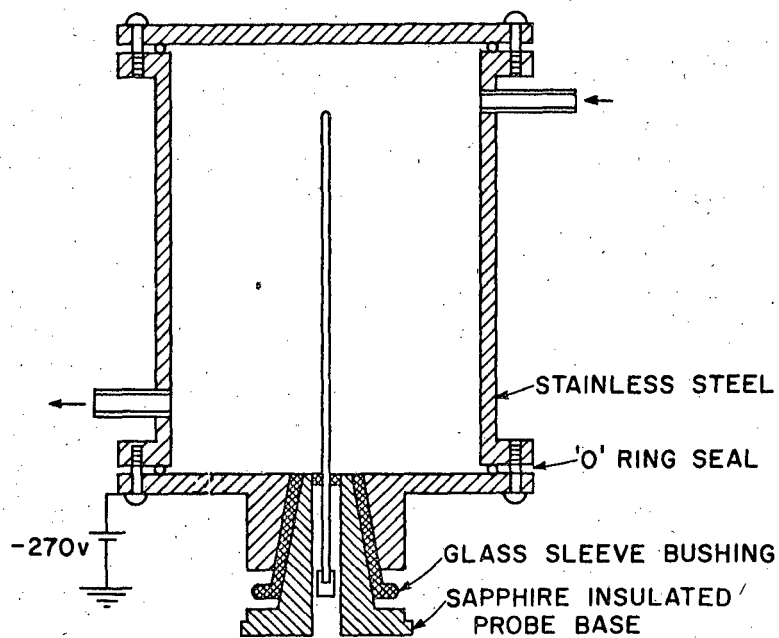
MU-9186

Fig. 6. One-liter ionization chamber. The chamber is 5.25 in.
by 4 in. in diameter. It has a very low and stable back-
ground and a good efficiency.

Table I

Ionization collected by tritium radiation in several gases[a]		
Gas	Relative Ionization	Ion pairs per disintegration[b]
Hydrogen	0.685	132
Nitrogen	0.82	158
Air	0.83[c]	160[c]
Helium	0.84	162
Carbon dioxide	0.84	162
Oxygen	0.85[c]	164[c]
Methane	1.00	193
Argon	1.06	205
Propane	1.13	218

a   From Wilzbach, Van Dyken, and Kaplan, Anal. Chem. 26, 881 (1954).

b   Based on a value of 27.0 electron volts per ion pair in argon and 5.69 kev for the average energy of tritium radiation.

c   These values estimated from report ANL-5143, Oct. 1953.

Table II

Gas	ev per ion pair	Gas	ev per ion pair
Helium	42.7	CO_2	34.5
Neon	36.8	Air	35.5
Argon	26.4	O_2	32.5
Krypton	24.1	N_2	36.6
Xenon	21.9	CH_4	29.2
Hydrogen	36.3, 37.0	C_2H_2	27.2
		C_2H_6	26.6
		C_2H_5	28.0

Ion pair yield in pure gases by alpha particles[a]

a After W. P. Jesse, Argonne National Laboratory.
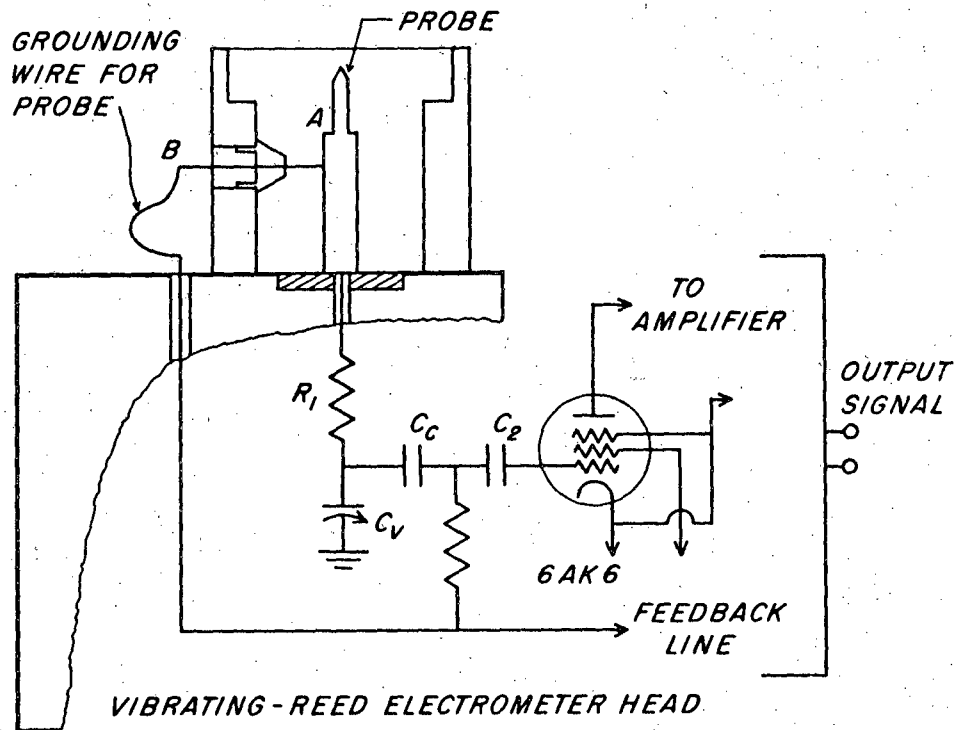
MU-12392

Fig. 7. Schematic diagram of part of a vibrating-reed electro-
meter circuit. C_v, the vibrating capacitor, is about 25μμf;
C_c, 10 μμf. Only C_c is important in charge collection.
The effect of C_v is canceled out by the feedback circuit. The
resistor for the high-resistance-leak circuit is connected
between A and B.
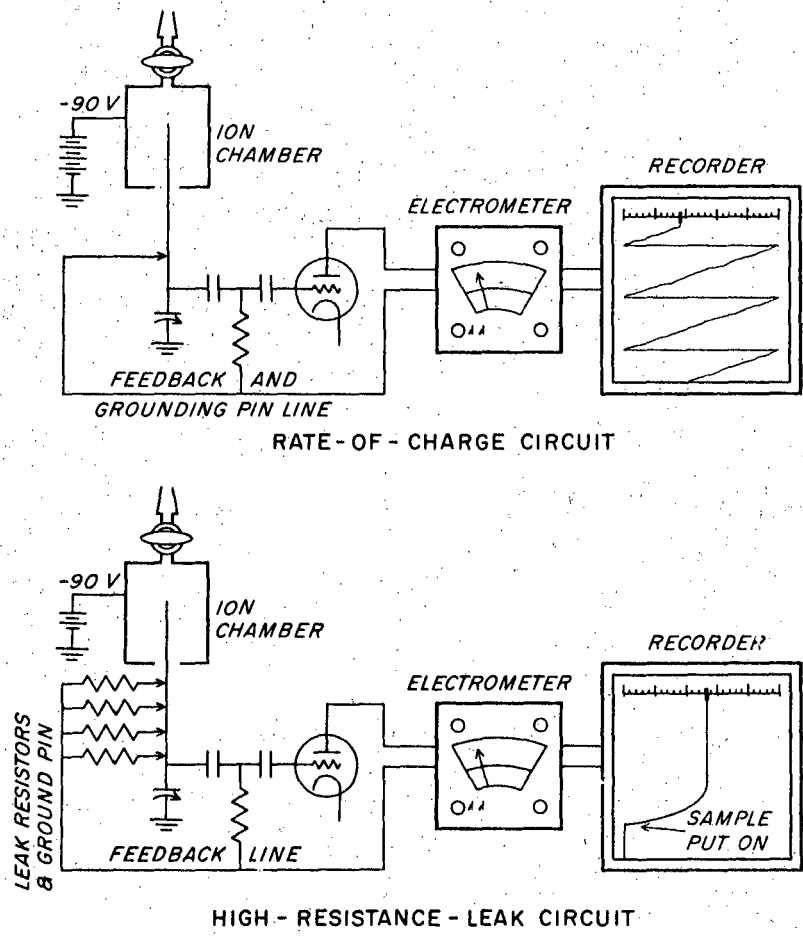
Fig. 8. Circuits for measuring current from an ionization chamber.

In the rate-of-charge method the ionization chamber probe is connected to the input terminal of the vibrating-reed electrometer. As can be seen, this probe has no conducting connection with any other parts of the circuit except through the two condensers, C_V and C_C. Therefore, as electrons are collected on the probe the potential of this center electrode increases in direct proportion to the number of electrons being collected, which, as a rate of increase with time, is directly proportional to the amount of radioactivity that is present in the chamber. If one examines the potentiometer record, one finds a steady increase with time in the output potential of the electrometer. The rate of increase of this potential, or the slope of the lines so obtained by the recorder, can be measured and directly related to the radioactivity in the chamber.

If the radioactivity level is very low, and the rate of charge very small, one often finds short pulses in the recorder chart. These short pulses are derived from α particles. (See Fig. 9.) They may be subtracted from the over-all rate of charge to give a more reliable answer. (This correction is an important reason for using a recording potentiometer.) These α pulses are usually due to α-radioactive materials in the chamber walls, but they may be due to radon gas. This α-radioactive gas is bothersome and quite common. Many rocks, sands, and soils contain traces of uranium from which the daughter products radium and eventually radon are produced. Barium and calcium salts often contain appreciable amounts of radium, and hence radon is given off. Fortunately, the halflife of radon is short, 3.8 days, and it soon decays away, but it gives off several α particles in quick succession before it reaches a long-lived isotope.

A low-background 250-cc ion chamber filled with aged air (i.e., radon-free) shows less than 3 to 4 α's/10 min. An average 250-cc stainless steel ion chamber may show 4 to 5 α's/10 min.

In the high-resistance-leak method for measuring ionization chamber current a high resistance is connected between the center electrode of the ionization chamber and the feedback circuit (see Fig. 8). This resistance draws off the current being produced in the ionization chamber so that an equilibrium voltage is reached at the collection electrode which is a function of the amount of current being produced and of the resistance itself. In this case, the potentiometer record appears first as a curved line and then as a straight line -- or nearly straight line -- at the equilibrium voltage. By taking the average value of this potential one obtains a figure that is directly proportional to the radioactivity in the chamber.

These two methods have rather definite and different areas of applicability. The rate-of-charge method is the more sensitive procedure for measuring very small currents. Since the capacity of the electrometer head is about 10 micromicrofarads, production of a very small number of electrons in the ionization chamber can give rise to an appreciable charge in the system. The rate-of-charge method also shows the sudden and sharp shifts in the current output that are the result of production of alphas in the ionization chamber. These alpha pulses can be subtracted to give a more accurate rate than is otherwise possible. The rate-of-charge method, furthermore, is not dependent upon any resistors, and for very precise work seems to achieve somewhat more accuracy than can be obtained by the addition of a resistor to the input circuit. Only very well-made vibra-
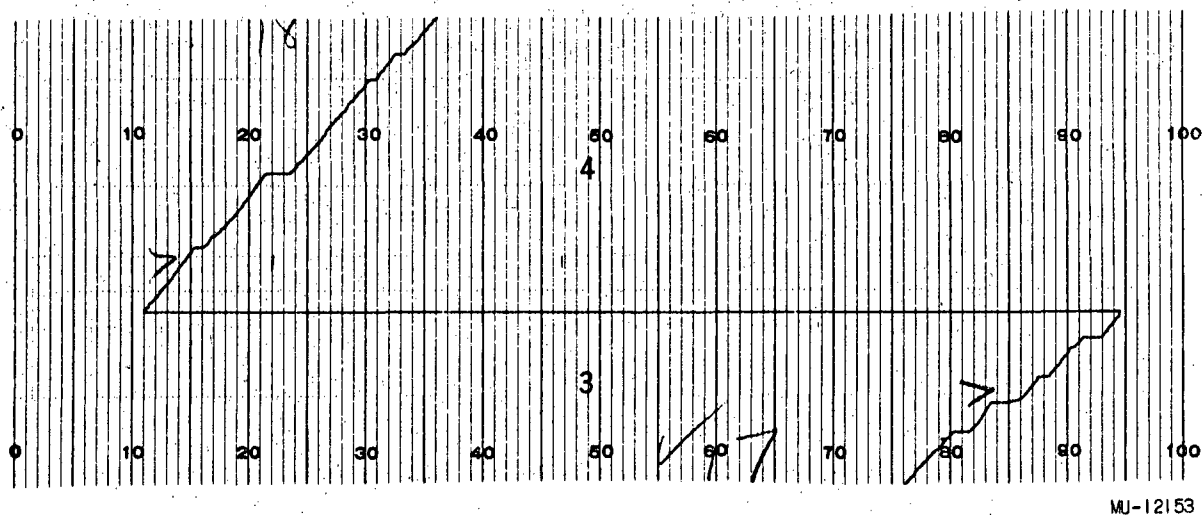
MU-12153

Fig. 9. Ionization chamber chart showing a pulses. This record
is for a 100-cc ion chamber with the electrometer set on the
100-mv scale.

ting-reed electrometers are capable of operating in the rate-of-charge method. Most inexpensive models, such as those used with pH meters, so lack stability that they can be used only with an input resistance of 10^{12} ohms or less and for the high-resistance-leak method.

The high-resistance-leak method for measuring chamber current provides, within the limits of the time constant of the electrical circuit, a continuous indication of the amount of radioactivity that is in the chamber. For flow systems, this is the only procedure that can be used. It also provides a somewhat more rapid method for measuring the chamber radioactivity than the rate-of-charge method. Satisfactory resistors are obtainable in resistances up to 10^{13} ohms;* these resistors should be carefully handled, never be touched by hand; if they ever get dirty they may be cleaned by wiping the surface with pure methanol. The higher-valued resistors (especially the 10^{13}-ohm resistor) are nonlinear and show a marked temperature coefficient; use of these should be avoided unless they are necessary. They must, of course, be well shielded. There are available special holders for this purpose, including a turret switch holder in which four resistors are changed readily by moving a lever so that a wide range of sensitivities may be used in the high-resistance-leak method for ionization chamber current measurement. (See Fig. 10.) (See also footnote, p. 33.)

The calibration of ionization chambers is usually accomplished by introducing a sample of known radioactivity into the chamber and measuring the rate of charge or equilibrium voltage. For a practical guide here are some approximate calibration figures. (In practice, each ionization chamber should be individually calibrated.)

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*   Victoreen High-Megohm Resistors. Victoreen Co., Cleveland, Ohio.
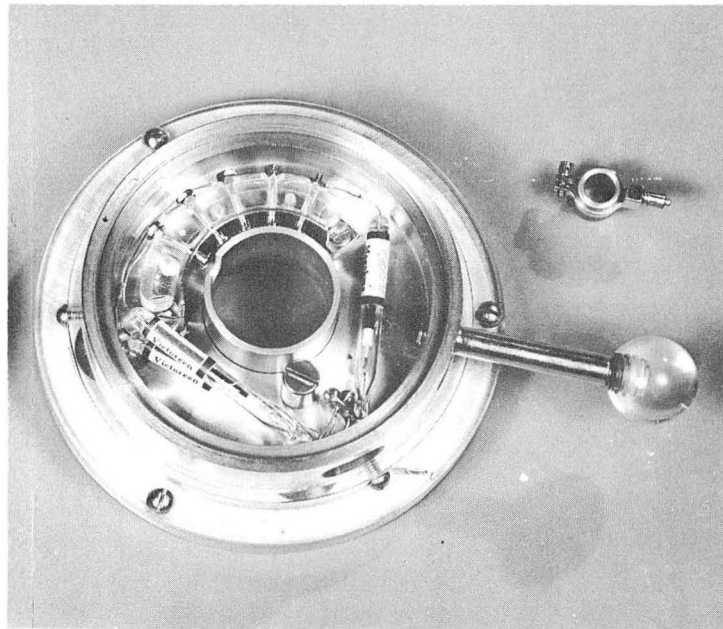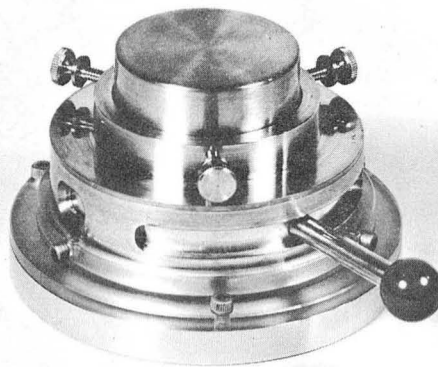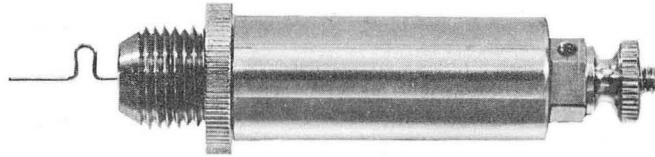
Fig. 10. Single and multiple leak-resistor holders for the vibrating-reed electrometer.

For the rate-of-charge method, the theoretical calibration factor for C^{14} in air is 2.47×10^{-5} microcurie per mv per min charge rate.* Observed drift rates with CO_2-filled experimental chambers of 100 cc capacity show values of $4.5 \pm 0.5 \times 10^{-5}$ µC per mv/min charge rate and for 250-cc chambers about 4.0×10^{-5} µC per mv/min charge rate. The amount of energy required to produce an ion pair in air or in CO_2 is comparable.

---

* Given that the electrometer head capacity is about 12 µµf, that the average $C^{14}\beta$ energy is 45 kv, that 32.5 ev are required to produce an electron pair, that $1\mu C = 2.2 \times 10^6$ dis/min and that 1 coulomb = 6.28×10^{18} electronic charges, then in an ion chamber that collects all the electrons, we have

$$1 \; \mu C \; C^{14} = \frac{\frac{45,000}{32.5}}{6.28 \times 10^{18}} \times 2.2 \times 10^6 = 4.87 \times 10^{-10} \text{ coulomb/min.}$$

In a capacitor system,

$$Q = Cv \qquad \text{where } Q = \text{coulombs,}$$
$$C = \text{capacity in farads,}$$
$$v = \text{volts.}$$

So, $\quad v/min = \dfrac{Q/min}{C} = \dfrac{4.28 \times 10^{-10}}{12 \times 10^{-12}} = 40.5$ for $1 \; \mu C \; C^{14}$.

This corresponds to a calibration constant of 2.47×10^{-5} µC/min drift rate.

For the high-resistance-leak method the theoretical calibration factor for C^{14} in air is 1.24 x 10^{-4} μC/mv potential with a 10^{12}-ohm leak resistor.* Observed values for chambers of 100 cc to 20 liters were 1.3 to 2.9 x 10^{-4} curie per mv potential with the 10^{12}-ohm resistor (see Fig. 11). The large chambers are seen to have a very excellent efficiency -- approaching that of theory. Wilzbach and Sykes have reported an ionization value for C^{14} in CO_2 for a 250-cc Borkowski-type ion chamber of 1.39 x 10^{16} coulomb/dis C^{14}. This corresponds to a calibration constant of 3.92 x 10^{-5} μC per mv/min drift rate or 1.62 x 10^{-4} μC/mv potential for a 10^{12}-ohm resistor.

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*   Given that the energy of the average $C^{14}\beta$ is 45 kv, that 32.5 ev are required to produce an electron pair in air, that 1 μC = 2.2 x 10^6 dis/min, and that an ampere-second equals 6.28 x 10^{18} electronic charges, then in an ion chamber that collects all the electrons:

$$1 \; \mu C \; C^{14} \; = \; \frac{\frac{45,000}{32.5} \times 2.2 \times 10^6}{6.28 \times 10^{18} \times 60} \; = \; 8.07 \times 10^{-12} \; \text{amp current flow.}$$

In a high-resistance-leak system with a 10^{12}-ohm leak resistor the 1 μC C^{14} then produces a voltage

$$E \; = \; IR \; = \; 8.07 \times 10^{-12} \times 10^{-12}$$

$$= \; 8.07 \; \text{volts,}$$

∴ 1 mv potential represents 1.24 x 10^{-4} μC.
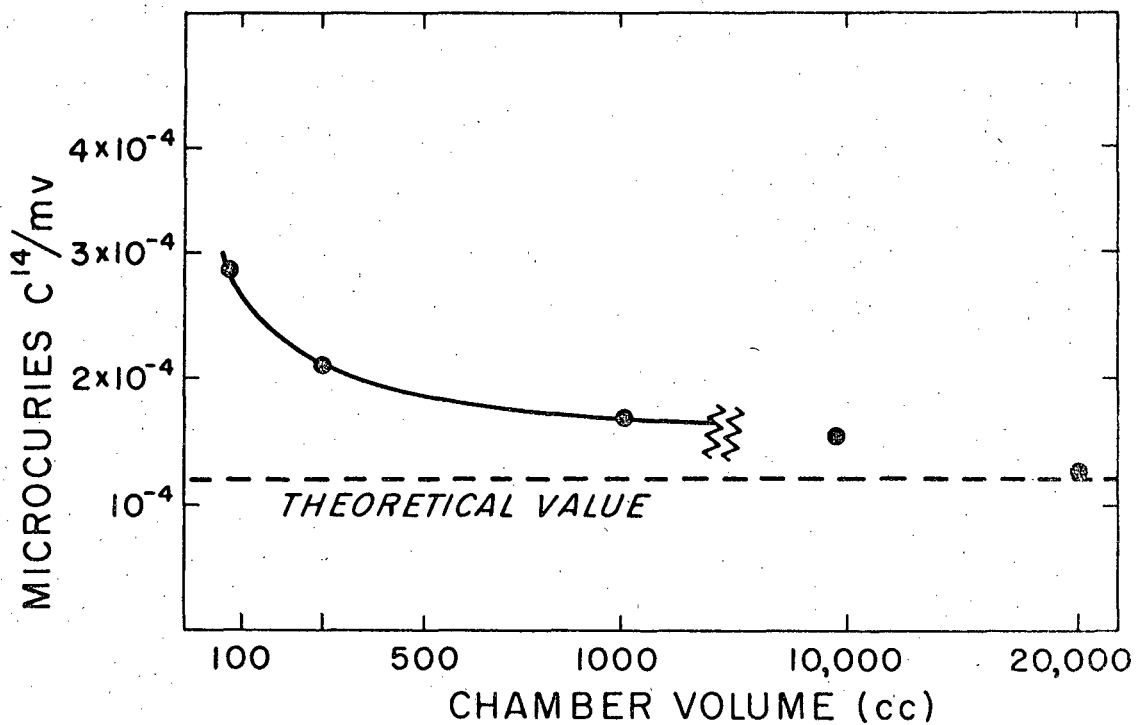
Fig. 11. Calibration constants of a series of Tolbert-Cary ion-
ization chambers. The measurements were made by using
a high-resistance-leak method and values are for μC to
produce 1 mv potential with a 10^{12}-ohm resistor.

EXPERIMENTAL PROCEDURES

We describe here six experimental procedures for measuring carbon-14 and tritium radioactivity in different types of samples. These are procedures that are in actual use by various research workers in the country, and have been proven in practice to be either very sensitive or very precise and in most cases as easy to use as is commensurate with a given sensitivity or precision.

Low-Level Carbon-14 by the Rate-of-Charge Method[29, 30]

This procedure is designed for a sample as barium carbonate, of approximately 1.2 g weight, for a vacuum system of about 50 cc volume, and for an ionization chamber of about 100 cc volume. The vacuum system used to generate the sample and transfer the CO_2 into the ionization chamber is shown in Fig. 12. The ionization chamber is a standard 100-cc ionization chamber with a good-grade insulator, preferably sapphire. This procedure is satisfactory for samples containing from 0.01 dis/min/mg barium carbonate up to about 50 dis/min/mg barium carbonate. Expressed in other units these limits are: 0.005 $\mu\mu C$/mg $BaCO_3$ to 25 $\mu\mu C$/mg $BaCO_3$ or 1 $\mu\mu C$/mmole C to 5 $m\mu C$/mmole C.

Precalibration

The volume of the ionization chamber is determined by a gasometric method, or by filling it with water and measuring the volume or weight of the water. The volume of the vacuum line between stopcocks A and D is determined by a gasometric method or by estimation. The amount of barium carbonate necessary to fill these combined volumes with CO_2 at 1 atmos pressure is calculated.
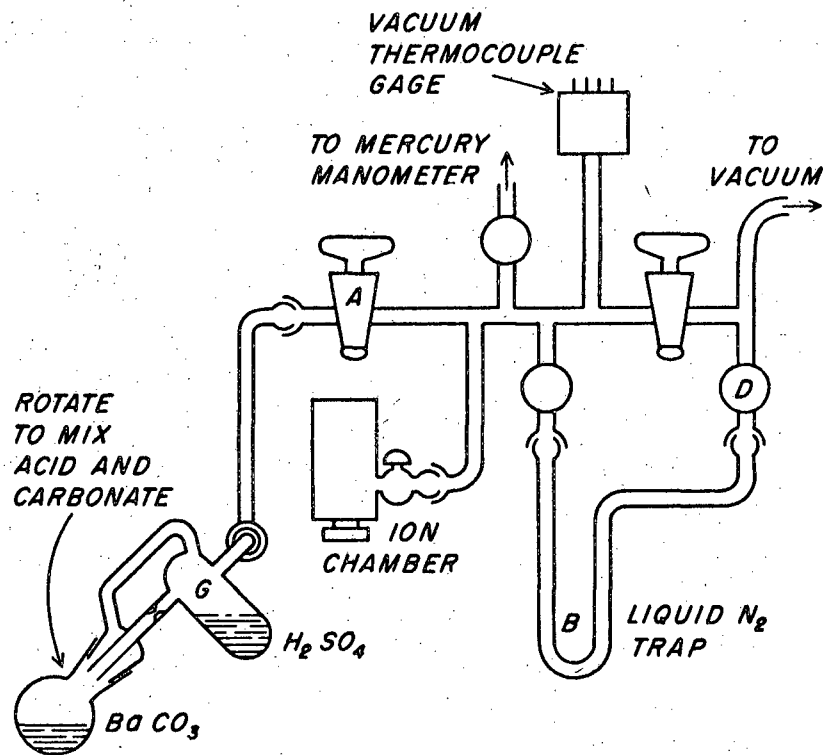
Manipulation

The calculated weight of barium carbonate is weighed out into the small generation flask F. About 20 to 25 ml of concentrated sulfuric acid is added to the generation reservoir G and the unit is assembled on the vacuum line and evacuated. Trap B is cooled in liquid nitrogen, the sulfuric acid is added slowly to the barium carbonate, and the CO_2 produced is condensed in the trap. After the generation is mostly completed, the generation flask is warmed slightly to insure complete dissolving of the barium sulfate and complete evolution of the CO_2. Stopcocks A and D are then closed and the CO_2 in the trap is allowed to warm to room temperature and expand into the ionization chamber.

Measurement of Rate-of-Charge

The ionization chamber is placed on the vibrating-reed electrometer head, connected to a collection voltage (90 volts), and allowed to sit approximately 1/2 hour. The rate of charge is then recorded for a number of full-scale chart travels or for about an hour. The 1-and 10-millivolt scales of the vibrating reed electrometer* are not particularly useful here. If the

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* Applied Physics Corp. Electrometer Model 50.

VACUUM
THERMOCOUPLE
GAGE

TO MERCURY
MANOMETER

TO
VACUUM

A

ROTATE
TO MIX
ACID AND
CARBONATE

ION
CHAMBER

D

G

$H_2 SO_4$

B   LIQUID N_2
TRAP

$Ba CO_3$

MU-12395

Fig. 12.   Minimum vacuum line for the generation of CO_2 from
$BaCO_3$ and introduction of the sample into an ionization
chamber.

sample is of very low activity the 100-millivolt scale may be used and the
alpha pulses can be seen, and if the sample has a higher activity the 1000
millivolt or higher scale must be used. The rate of charge is measured for
a number of 10-minute time intervals and is tabulated and averaged. If the
rate of charge shows a systematic variation over this period of time, this
is an indication that the insulator has not yet settled down and that more rates
of charge should be measured until the figure is constant within the accuracy
of measurement. The rate of charge is then multiplied by the calibration
constant to give the amount of radioactivity in the chamber and hence the
amount of radioactivity in the original sample.

Calibration

A sample containing a known specific activity of barium carbonate-
C^{14} is generated into the ionization chamber, using the specific vacuum
line, ionization chamber, and electrometer-recorder combination that are
to be calibrated. The rate of charge for this sample gives the calibration
factor for the entire system. Background rate of charge for the ionization
chamber must be determined and subtracted from all measurements. Two
background measurements should be made, one including the contribution
of the alpha pulses from the chamber walls and one from which these values
are subtracted. For very-low-activity samples, the alpha pulses can be
seen on the recording potentiometer tracing. If these alpha pulses are in-
dividually subtracted from the drift rate, a more precise determination of
the drift is obtained. This is because such events are so few that the sta-
tistical fluctuations in the number are great. Furthermore, a pulse con-
tributes many ion pairs per event, further accentuating their importance in
low-level activity measurements. Figure 9 shows how easily such alpha
pulses are detected in a low-level tracing. (This is one reason why a re-
cording potentiometer is advantageous in such an apparatus.) With high
activity the drift rate is so rapid that the alpha pulses cannot be distinguished.
For such samples the background that includes the alpha-particle contribu-
tion should be used.

High-Level Carbon by the Wilzbach-Sykes Method[8]

This procedure is designed for samples as organic compounds of
fair specific activity. This is because only about 10 mg of the compound
can be combusted, that is, enough to produce about 25 cc of CO_2 gas at
N.T.P. Very high sample specific activities can be handled by use of an
appropriate high-resistance leak resistor. A minimum usable specific
activity (with a 10^{12}-ohm resistor) is $3 \times 10^{-4} \mu C$ C^{14}/mg compound, or
about 600 dis/min/mg compound. Of course, by use of a rate-of-charge
procedure described above, this limit could be reduced to about 10 dis/min/
mg compound. A compound with 50 μC/mg specific activity can be meas-
ured with a 10^7-or 10^8-ohm resistor.

Combustion and Introduction of the Sample into the Ionization Chamber

Approximately 10 mg of the sample is weighed into a Pyrex 1720 tube containing 1 g of copper oxide granules. The tube should be approximately 17 cm by 11 mm inside diameter, and should be constructed with a breakable tip at one end (see Fig. 13). The tube is heated at 625°–650° C for 30 min in a furnace. The exact time and the nominal temperature will be a function of the furnace and should be experimentally determined.

The transfer of the sample into the ionization chamber is done by a combination distillation-sweep procedure (see Fig. 13). The combusted sample tube is introduced into the vacuum line as shown. The system is evacuated and trap B is cooled with liquid nitrogen. The tube holder is then rotated through 180° and back and the tube allowed to fall on its breakable tip. The CO_2 is trapped in the first U-tube, cooled in liquid nitrogen. After complete transfer is effected, the second trap is cooled in a dry-ice – acetone bath and the CO_2 is distilled from the first to the third trap, also cooled in liquid nitrogen. The vacuum-line stopcocks are then closed off, and the CO_2 is allowed to warm to room temperature and expands into the ionization chamber. Tank CO_2 is then admitted through the two-way stopcock, sweeping the remaining CO_2 into the ionization chamber. As soon as the pressure comes to one atmosphere the valve on the chamber is closed and the sample is ready for assay.

Measurement of the Ionization Chamber Current

The ionization chamber is set on the head of the vibrating-reed electrometer, the appropriate high-resistance-leak resistor connected by means of the turret switch,* and the electrometer system allowed to come to its equilibrium voltage. This value is determined and the background voltage subtracted from it, and the remaining figure is proportional to the activity in the ionization chamber.

It is also possible to measure the ionization current by means of the rate-of-charge method for high-specific-activity samples. Such a procedure has the advantage that errors due to nonlinearity, time, humidity, or temperature changes in the leak resistor are eliminated. With appreciable amounts of radioactivity the time for the condenser system to come to full charge on the 1000-millivolt electrometer scale is less than a minute. To measure such short times accurately it is necessary to use microswitches on the recording potentiometer to activate a fast clock-timing system. The approximate rate-of-charge times for 800 millivolts' change in the vibrating-reed electrometer potential is 60 to 70 sec for 0.02 μC C^{14}. The range of such an instrument can be increased by adding capacitance to the electrometer circuit.

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* The turret switch is a device for connecting several resistors, in turn, to the input circuit, or to ground, or for leaving the circuit open. It requires very high-grade and stable insulators, preferably sapphire, as it must be as stable as the electrometer. See also p. 25.
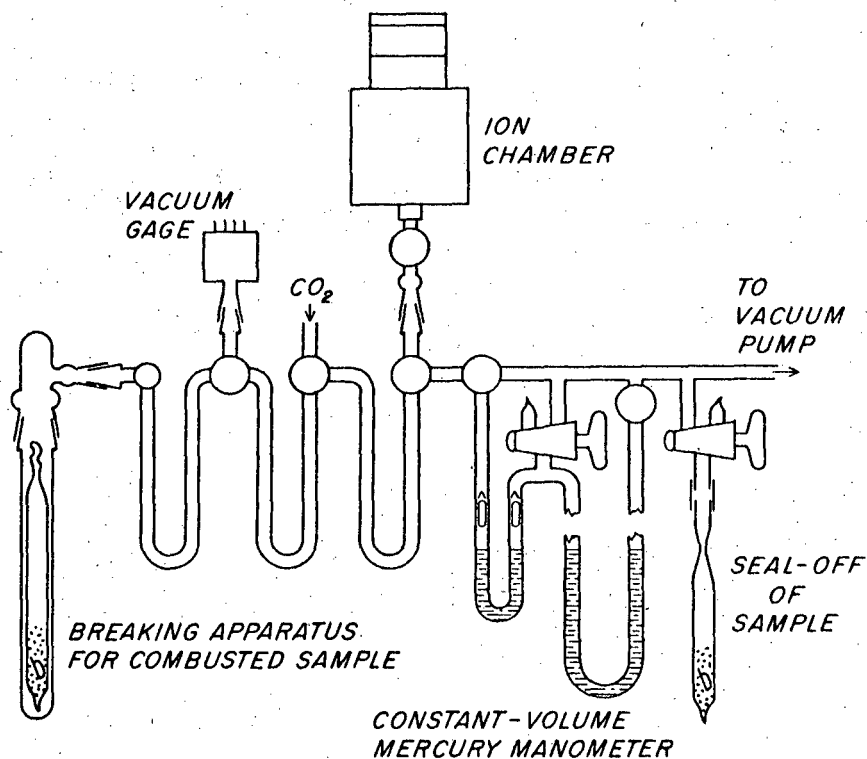
Fig. 13. Vacuum transfer line for the Wilzbach-Sykes method of C^{14} assay.

Calibration

Exact calibration of such a system is effected by introducing known amounts of radioactivity in the ionization chamber and determining the output voltage for the given electrometer-resistor combination. The values can be estimated from the data previously given. The potential is directly proportional to the leak resistor.

High-Level Carbon-14 by the Oak Ridge National Laboratory Method[11, 12]

This procedure is essentially the same as the Wilzbach-Sykes method except that the method of combusting the sample to CO_2 is different.

Equipment

Combustion and chamber-filling apparatus (Fig. 14), 250 cc ionization chamber, vibrating-reed electrometer, and recorder.

Sample Preparation

Approximately 5 to 10 mg of an organic compound is introduced into the combustion flask A. The ionization chamber is inserted on joint B and is evacuated through stopcock C. Stopcock C is then turned so that the ionization chamber is connected with the combustion flask and 10 to 15 ml of Van Slyke oxidizing mixture is added slowly to the flask. The flask is heated until the combustion of the sample is completed (5 to 10 min). Non-radioactive CO_2 is added through stopcock D, sweeping the CO_2 from the combustion flask into the ionization chamber.

Measurement of Ionization Chamber Current

This procedure is exactly the same as in Procedure B above.

Limitations of the Method

For certain types of organic compounds this combustion procedure is not complete. This is particularly true for some types of aromatic compounds which are capable of forming stable sulfonates. For materials of biological origin the procedure is usually very satisfactory.

Calibration

Same as Procedure B above.

Continuous-Recording Flow Systems for Radioactive Gases[31, 32, 33, 34]

This procedure has variously been used to measure C^{14} respiration rates in animals and humans, study photosynthesis rates in plants, and monitor atomic pile air-contamination levels. It has a wide range of applications. The animal procedure is indicated below.

Equipment

(See Fig. 15.) Tank of aged compressed air, flow meters, animal cage, sulfuric acid drying bubbler, ionization chamber, together with vibrating-reed electrometer and recorder, and, if desired, a wet test gas meter. The volume of the ionization chamber and the calibration factor for the ion-
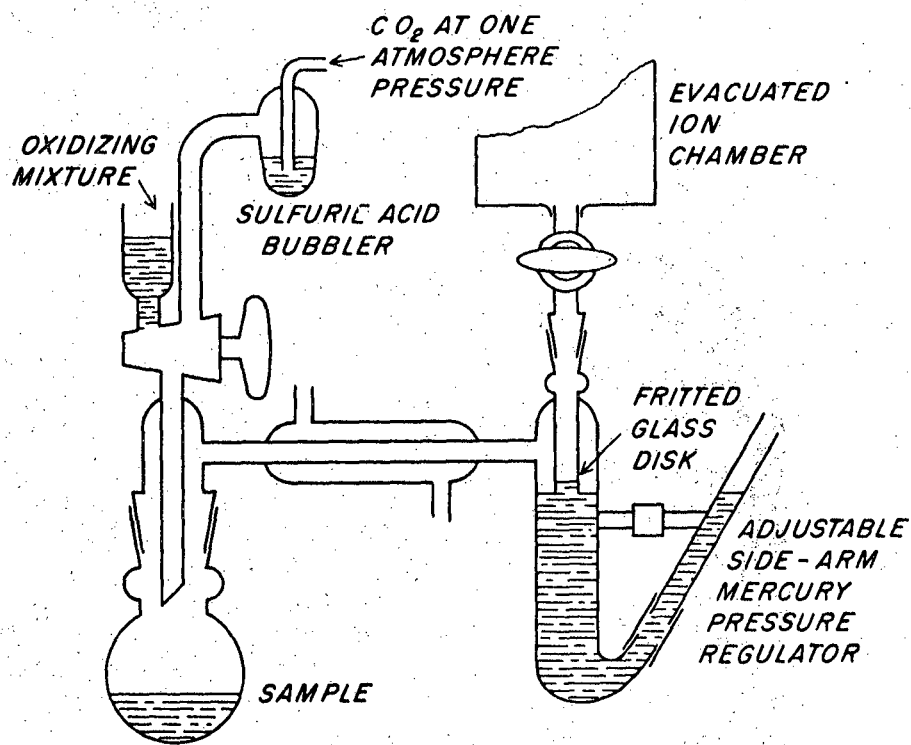
Fig. 14. Combustion and chamber-filling apparatus for $C^{14}O_2$
oxidation by the Van Slyke-Folch method.
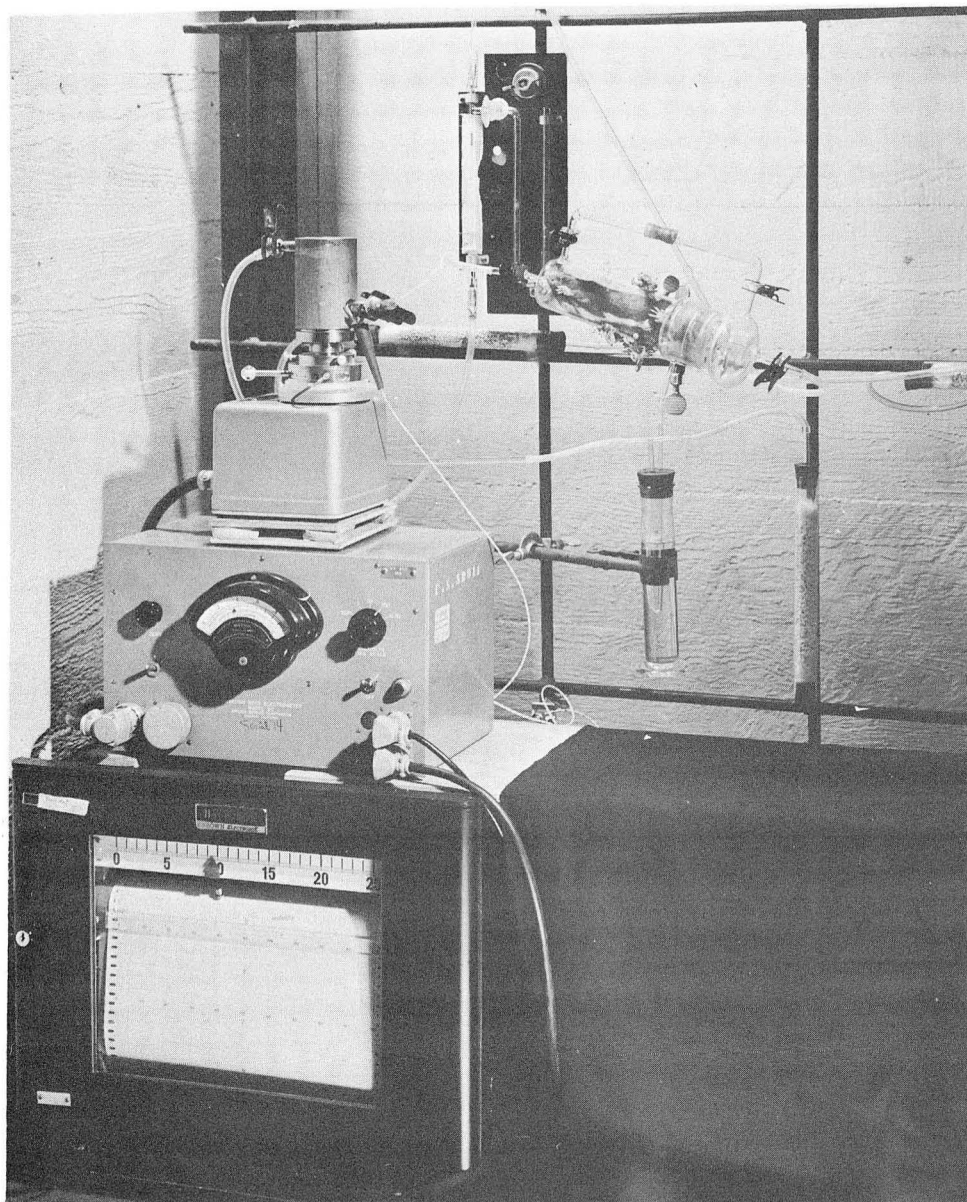
Fig. 15. Apparatus for continuous-flow recording of radioactive gases.

izonation chamber in terms of microcuries of radioactivity per millivolt potential for a given high-resistance-leak resistor should be known. The approximate calibration values may be used here.

Experimental Procedure

With the system connected as shown in Fig. 16 and with the air flowing through the system, the zero adjustment knob on the vibrating-reed electrometer is set so that the recording potentiometer reads zero. This corrects for background potential. The animal that has been given the radioactive sample is then put in the animal cage and the machine automatically thereafter gives a continuous record of his excreted breath activity. Further details of this procedure are published. [31, 32]

The time of response for such a system is a function of (a) the volume of the animal cage, the volume of the ionization chamber, and the air flow rate; and (b) of the electrical time response characteristics of the ionization chamber--vibrating-reed electrometer combination. For extremely sensitive operation the 63% response time may be several minutes long. For less sensitive operation it can be reduced to a fraction of a second. The time in seconds for 63% response of the electrometer is equal to the value in ohms of the leak resistor times the capacitance in farads of the electrometer head:

$$t = RC.$$

The time for 99% response is $t = 4.60\ RC$. Since the electrometer head capacity is about 10 μμf (10×10^{-12} f) then the 63% response time with a 10^{13}-ohm leak resistor is 100 sec, and at least 10 min are required for equilibration. For a 10^{12}-ohm resistor the 63% response time is 10 sec, and for a 10^{11}-ohm resistor it is 1 second. Smaller resistors respond so fast that this time lag is seldom a consideration.

Measurement of Tritium in Organic Compounds [14, 15]

This procedure is useful for 5 to 10 mg of sample containing 10^{-4} μC/mg T or more. The equipment required is a simple vacuum line, a furnace, ionization chamber, and vibrating-reed electrometer--recorder combination.

Reduction of the Organic Compound and Introduction into the Ion Chamber

Five to 10 mg of tritium compound, 5 to 6 mg water, 1 g zinc (Baker and Adamson, 30 mesh) and 100 mg nickelic oxide (Baker's analyzed, grey-black powder) are placed in a Pyrex 1720 tube with breakable lip (see Fig. 17). Water or liquids are introduced in small sealed ampules with bent tips, solid samples in porcelain or zinc boats. The reaction tube is constricted, evacuated, sealed off, and shaken to break the ampules and mix the contents. The samples are heated (horizontal placement) for 3 hr at $670 \pm 10°$ C. The tube is cooled and placed in the transfer vacuum line (Fig. 16). The sample is allowed to expand into the ionization chamber and then methane is flushed through stopcocks Nos. 2 and 3 to fill the chamber to 1 atmos pressure.
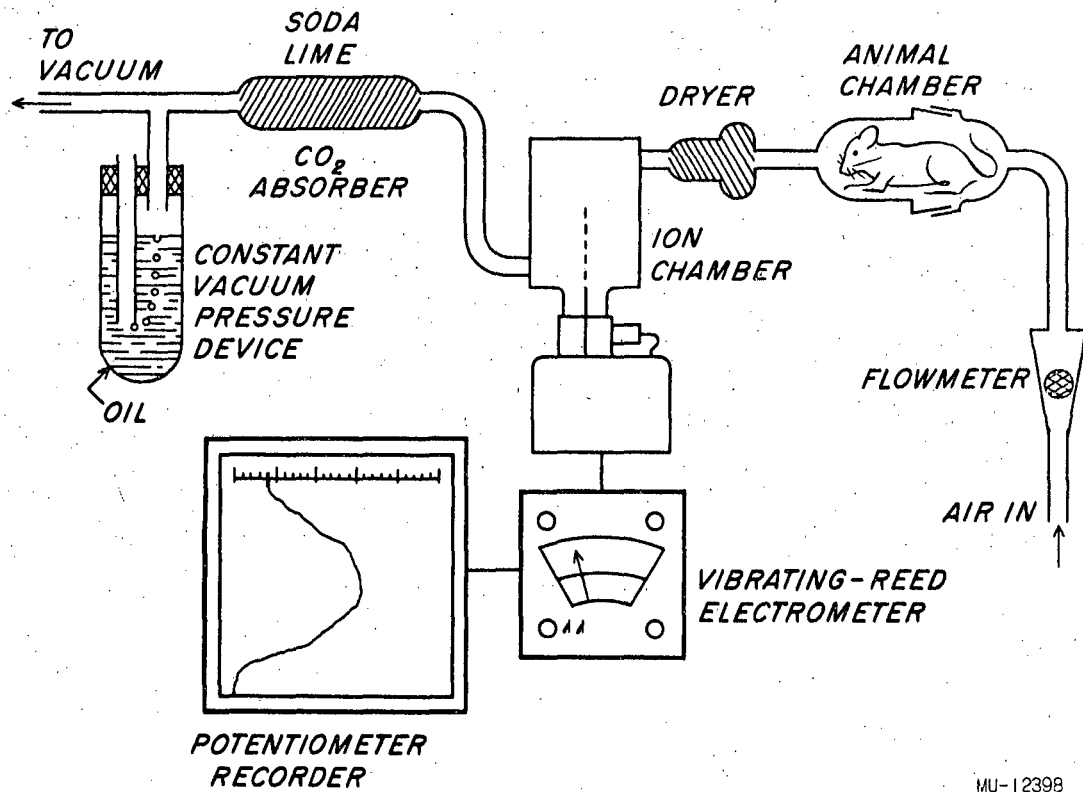
Fig. 16. Apparatus for continuous measurement of respiratory $C^{14}O_2$ from small animals.

TO
VACUUM

METHANE

Hg
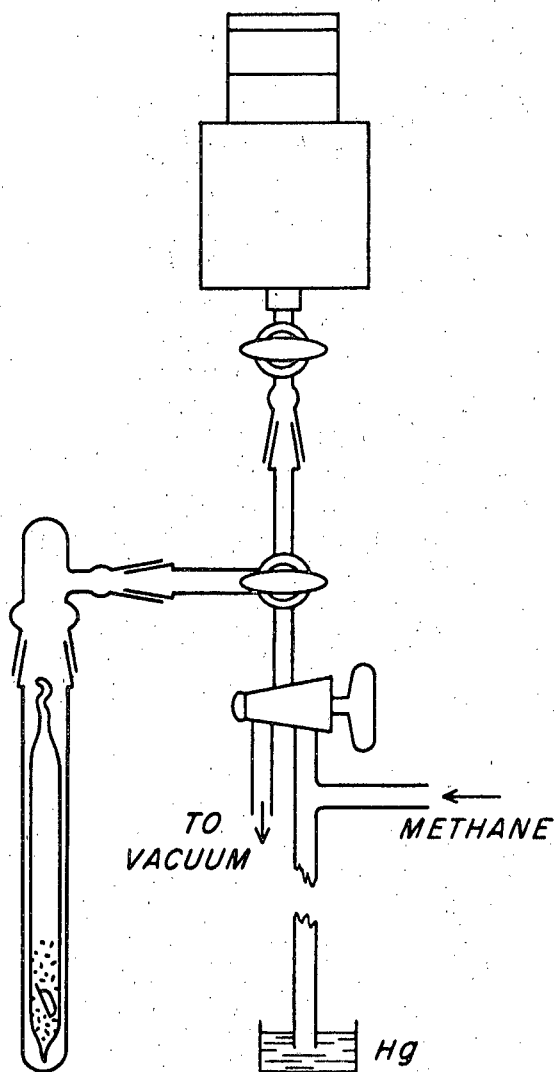
MU-12399

Fig. 17. Vacuum-line transfer system used in the measurement of tritium in organic compounds.

Measurement of Ionization Current and Calibration

The measurement of the ionization current may proceed by one of the methods described in Sections A and B. For tritium calibration, constants are about one-tenth those for carbon-14. From the data of Wilzbach et al.[15] one can calculate for a 250-cc Borkowski-type chamber the following calibration factors: in hydrogen, 2.5×10^{-4} µC/mv/min drift rate or 1.28×10^{-3} µC/mv for 10^{12}-ohm resistor; in methane, 1.76×10^{-4} µC/mv/min drift rate or 8.81×10^{-4} µC/mv for 10^{12}-ohm resistor. In the fast rate-of-charge procedure approximately 60 sec charge time is required for 0.2 µCT. (Remember to correct for the tritium left in the breakable tube holder. This will be proportional to the relative volumes of the ionization chamber vs. the combined ion chamber–breakable tube holder.)

Precision calibration should be made with standard tritium-labeled water or organic compounds.

Measurement of Tritium in Tritium Water[21, 22]

This procedure is for water with a tritium specific activity of 10^{-2} µC/ml water or more. The minimum detectable specific activity is about 10^{-3} µC/ml water. Two millicuries of tritium water in a patient give adequate activity for measurement of total body water. Apparatus required includes a vacuum line, lithium aluminum hydride solution in diethyl carbitol (unfiltered saturated solution), a 100 to 250-cc ionization chamber, and a vibrating-reed electrometer–recorder combination.

Generation of Sample and Introduction into the Ionization Chamber

The ionization chamber is attached to the vacuum line as shown in Fig. 18. Six to 7 ml of solution of lithium aluminum hydride is placed in a generating flask and attached to the vacuum system. The sample, in a glass appendix, is stoppered and then frozen by dipping gradually into liquid nitrogen. The stopper is removed and the glass appendix is attached to the generating flask. Stopcock No. 1 is opened and the hydride solution is outgassed, while the sample in the appendix is kept frozen with liquid nitrogen. When the outgassing has subsided and the vacuum line has been brought to 20 microns, stopcock No. 1 is closed and the liquid nitrogen is removed from the sample and the sample thawed. When the sample is in a complete liquid state, stopcock No. 5 (to vacuum pump) and stopcock No. 3 (to vacuum gauge) are closed, then stopcock No. 1 is opened slowly. The glass appendix is then tilted to add one drop at a time of sample to the hydride solution, which is shaken as much as possible. The gas is collected in an ionization chamber and is brought to atmospheric pressure.

Measurement of Ionization Chamber Current

The measurement of the ionization chamber current for the tritium radioactivity may proceed by any of the methods described in Sections A and B above, and depends upon the total amount of racioactivity used.
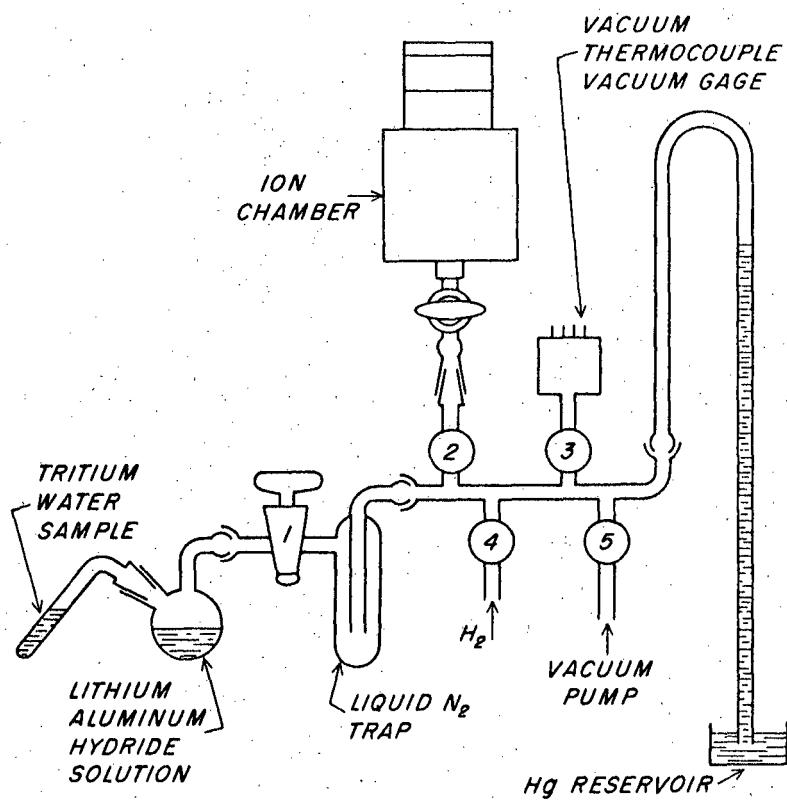
Fig. 18. Vacuum line for tritium analysis.

Calibration and Special Precautions

Calibration is achieved by use of standard samples of tritium water. There is an appreciable isotope effect in the generation of the hydrogen gas and it is suggested that the operator repeat the generation until his technique is sufficiently well established that a minimum deviation between samples is achieved. A ml or so of metallic mercury in the lithium aluminum hydride solution will help to break up the lumps of $LiAlO_2$ and $LiAl(OH)_4$, and give better results. Before a second sample may be run, an ionization chamber containing tritium gas must be evacuated for a period of half an hour. During this 30-min evacuation period, the chamber must be rinsed every 10 min with inert hydrogen. A minimum of three rinses is necessary. At the end of this pumping and flushing period the chamber should be cleared of contamination; it will then be ready for another sample.

SPECIAL PROCEDURES

Calibration of the Vibrating-Reed Electrometer and Recorder

Although the vibrating-reed electrometer and recorder are normally well calibrated, for very precise work it is desirable to check these instruments at regular intervals. The procedure is as follows: A standard potentiometer with at least 100-millivolt range (for example, Leeds and Northrup No. 8657) is connected to the center electrode of the vibrating-reed electrometer head and the feedback return line (Fig. 8). (Another very convenient place to make this connection is between Pins 5 and 6 of the recorder plug on the main amplifier. See the manufacturer's Instruction Manual for details.) With the electrometer set in the 100-millivolt scale the potentiometer output is gradually increased in 10-millivolt steps, and the recorder output voltage is noted to make sure that it increases 1/10 full scale for each step. If there is a discrepancy in the calibration of the electrometer-recorder it may be corrected by adjusting the meter resistance of the vibrating-reed electrometer output circuit. (This resistor is easily found in the manufacturer's Instruction Manual.)

### Preparation of Standard Tanks of $C^{14}O_2$

For calibrating many types of ionization chambers it is very convenient to have prepared tanks of carbon dioxide or air with small amounts of $C^{14}O_2$ radioactivity. Such tanks of gas may easily be prepared by attaching an unused gas cylinder to the vacuum line and evacuating it. $C^{14}O_2$ can then be generated from barium carbonate and drawn into the evacuated cylinder. The cylinder can then be pressured up with any desired mixture of CO_2 or CO_2-in-air to prepare a tank that may be calibrated, and once calibrated can be used over long periods of time. The only precaution in this matter is to make sure that sufficient CO_2 is present so that adsorption on the metal walls of the cylinder will not cause an appreciable error.

Collection Voltage

The collection voltage used in an ionization chamber should be sufficient to collect all the electrons, but not enough to produce secondary electrons. For a typical 250-cc cylindrical ion chamber in a static system almost all the electrons are collected by about 45 volts (Fig. 19). In a dynamic system with rapid gas flow through the chamber more voltage may be needed. In practice, one should always run such a curve for a new chamber. Choose a working voltage several times the minimum, if possible, and use good fresh 'B' batteries, as old or layer-built batteries tend to be electrically noisy.

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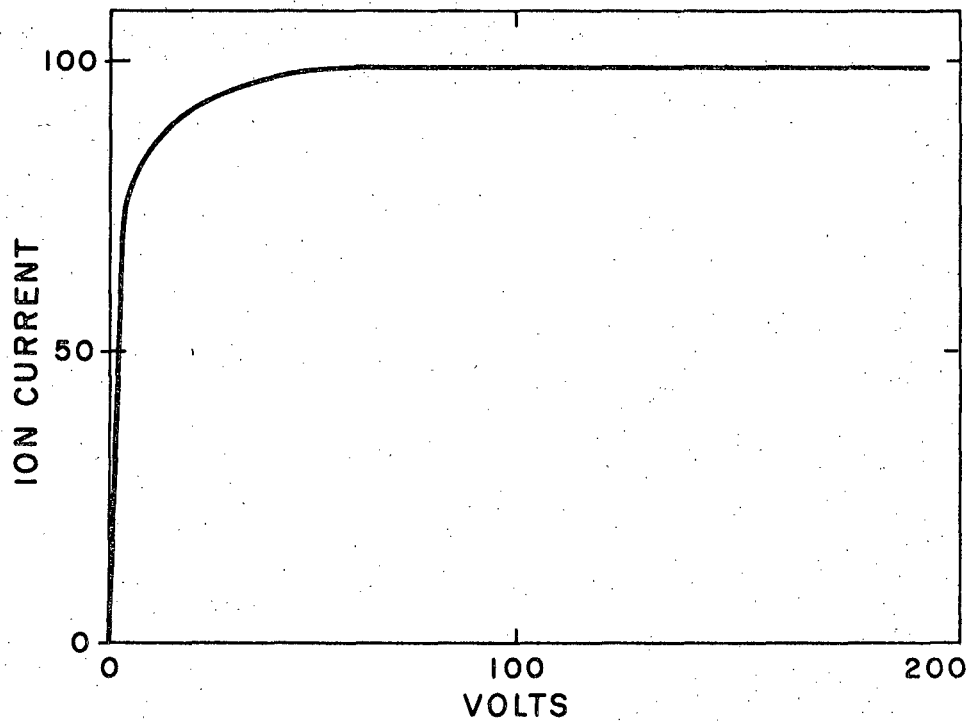
Fig. 19. Typical curve of collection voltage vs. ion current
     for a 250-cc cylindrical ionization chamber.

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REFERENCES

1. B. B. Rossi and H. H. Staub, Ionization Chambers and Counters, McGraw-Hill, New York, 1949.

2. D. H. Wilkinson, Ionization Chambers and Counters, Cambridge University Press, Cambridge, 1950.

3. G. L. Brownell and H. S. Lockhart, CO_2 Ion Chamber Techniques for Radiocarbon Measurements (a review), Nucleonics 10, No. 2, 26-32 (1952).

3a. R. F. Glascock, Isotopic Gas Analysis for Biochemists, Academic Press, New York, 1954.

4. Palevsky, Swank, and Grenchik, Rev. Sci. Instr. 18, 298-314 (1947).

5. Calvin, Heidelberger, Reid, Tolbert, and Yankwich, Isotopic Carbon, Wiley, New York, 1949.

6. Anderson, Delabarre, and Bothner-By, Anal. Chem. 24, 1298 (1952).

7. Christman, Day, Hansell, and Anderson, Anal. Chem. 27, 1935 (1955).

8. K. E. Wilzbach and W. Y. Sykes, Science 120, 494-496 (1954).

9. Van Slyke, Folch, and Plazin, J. Biol. Chem. 136, 509 (1940).

10. Calvin et al., Isotopic Carbon, pages 92-93.

11. O. K. Neville, J. Am. Chem. Soc. 70, 3499-3502 (1948).

12. A. Bonner and C. J. Collins, J. Am. Chem. Soc. 75, 3693 (1953).

13. Calvin et al., Isotopic Carbon, pages 88-92, 94-96.

14. Wilzbach, Kaplan, and Brown, Science 118, 522 (1953).

15. Wilzbach, Van Dyken, and Kaplan, Anal. Chem. 26, 880-883 (1953).

16. R. C. Thompson, Biological Applications of Tritium (a review), Nucleonics 12, No. 9, 31-35 (1954).

17. Payne, Campbell, and White, Biochem. J. 50, 500 (1952).

18. R. F. Glascock, Biochem. J. 52, 699 (1952).

19. Eidinoff, Knoll, Fukushima, and Gallagher, J. Am. Chem. Soc. 74, 5280 (1952).

20. S. Gurin and G. Delluva, J. Biol. Chem. 170, 545 (1947).

21. W. E. Siri in Advances in Medical and Biological Physics, Volume IV, edited by J. H. Lawrence and C. Tobias, Academic Press, New York, 1956.

22. Biggs, Kritchevsky, and Kirk, Anal. Chem. 24, 223 (1952).

23. C. V. Robinson, Rev. Sci. Instr. 22, 350 (1951).

24. R. C. Thompson, J. Biol. Chem. 197, 8 (1952).

25. R. K. Clark and S. S. Brar, Nucleonics 12, No. 8, 28-29 (1954).

26. M. A. Bullen, Nucleonics 11, No. 12, 15-17 (1953).

27. E. J. Wade and R. S. Stone, Nucleonics 13, No. 4, 28-30 (1955).

28. F. M. Glass, Nucleonics 10, No. 2, 36-39 (1952).

29. C. D. Janney and B. J. Moyer, Rev. Sci. Instr. 19, 667 (1948).

30. Unpublished results, B. M. Tolbert and E. M. Baker, Radiation Laboratory, University of California, Berkeley.

31. Tolbert, Hughes, Kirk, and Calvin, Arch. Biochem. Biophys. 60, 301 (1956).

32. Tolbert, Kirk, and Baker, Am. J. Physiol. (in press). See also Continuous $C^{14}O_2$ and CO_2 Excretion Studies in Experimental Animals, UCRL-2941, Aug. 1955.

33. A. T. Wilson and M. Calvin, J. Am. Chem. Soc. 77, 5948 (1955).

34. M. Calvin and P. Massini, Experientia 8, 445 (1952).