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THE DETERMINATION OF TRITIUM BY
ION CURRENT MEASUREMENT

by

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SUMMARY

Tritium may be determined by measurement, with a vibrating reed electrometer, of the ion current produced in a gas within a Borkowski type ionization chamber. The effect on the ion current of the nature of the filling gas, its pressure, and the collecting voltage is discussed. Samples of gas containing from 3×10^{-10} to 0.01 curie in a volume of up to 250 cc. may be measured routinely with an accuracy of about one per cent.

INTRODUCTION

Tritium, the radioactive isotope of hydrogen, is potentially an extremely useful tracer in chemical and biological research. Its determination, however, suffers from the handicap imposed by the low energy of the beta particle emitted in its disintegration. The maximum beta energy of 18.9 Kev,⁽¹⁾ corresponding to a range⁽²⁾ of about 0.9 mg/cm², precludes the use of end window counters, and makes the counting⁽³⁾ of thick samples in windowless counters quite inefficient. Radioautography,⁽⁴⁾ although useful for many purposes, is likewise very inefficient with samples of finite thickness.

Measurement with high efficiency is more readily attained if the disintegrations take place within the active volume of the detector. Of the available methods for achieving this condition, scintillation counting of solutions^(5, 6) containing liquid scintillators offers considerable promise as a means of rapid analysis, but much development appears to be required before it can be relied upon to give accurate results in routine analyses of a wide variety of materials. More widely used, at present, are procedures in which the tritium is introduced in the form of a gas into the detector, the disintegration rate being measured by the radiation-induced ionization of the gas. Depending on the field strength employed and on the external circuitry, the disintegrations may be recorded as discrete pulses by a counting tube operating either in the Geiger^(7, 8, 9) or proportional^(3, 10, 11) region or as the total ionization collected during a given time in an ionization chamber.^(12, 13) The purpose of this report is to describe the techniques used in this Laboratory for the determination of tritium by ion current measurement and to discuss the range, reliability, and reproducibility of the method. Sufficient detail is presented to permit the evaluation of the method and its application to routine analysis.

THEORY

The chamber used for the measurement⁽¹⁴⁾ of ion current in gas samples consists of a gas-tight conducting shell having an insulated electrode and a guard ring to shield the insulator. The ions of a given sign produced by radiation in the gas contained in the chamber are collected on the electrode by applying to the shell a potential low enough so that multiplication of ions does not occur. The rate of ion collection is measured by an electroscope or an electrometer. The measured current includes not only that from the radiation in the sample, but also a "background," which must be subtracted.

The net current has a limiting value which would be obtained if all of the energy of radiation in the sample were absorbed in the gas and all of the ions so produced were collected. This value is equal to the product of the disintegration rate of the sample, the average energy per disintegration, and the number of ion pairs produced per unit of energy expended. The first two of these are fixed by the activity being measured, while the last varies with the gas. The number of ion pairs produced in various gases by tritium radiation, calculated from the data of Valentine and Curran,⁽¹⁵⁾ using 5.69 Kev. as the average energy⁽¹⁶⁾ of disintegration, is shown in Table I.

Table I

IONIZATION PRODUCED BY TRITIUM RADIATION IN SEVERAL GASES

Gas	Relative Ionization	Ion Pairs per Disintegration *
Hydrogen	0.79	150
Nitrogen	0.84	159
Air	0.86	163
Helium	0.92	175
Oxygen	0.93	177
Methane	1.00	188
Argon	1.11	211

*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.

In practice, the net current is less than the limiting value because of the loss of energy to the walls of the chamber and the loss of ions by recombination. Some loss of ions by recombination occurs in the volume of the chamber not exposed to the electric field; the fraction lost is determined by the design of the chamber. The loss of ions by recombination in the active volume is a function of the field strength and of the nature, concentration, and mean free path of the ions; at constant field strength it increases with the pressure and rate of ionization of the filling gas. The loss of energy to the walls is decreased by increasing the dimensions of the chamber, the pressure, or the number of electrons in each molecule of the gas.

The background arises from drift of the instrument as well as from extraneous radiation in the atmosphere and within the chamber. The radiation in the chamber includes that from the retention of previously measured samples and that from the materials of construction. The background resulting from penetrating radiation in the atmosphere, including cosmic rays and atmospheric contaminants, is proportional to the volume of the chamber and the pressure of the gas. Increasing the efficiency of the chamber by increasing these factors does not, therefore, necessarily increase the sensitivity of measurement.

TECHNIQUES

For a determination, a sample of gas containing tritium is introduced into an evacuated ionization chamber. A stainless steel chamber with a welded shell is used to minimize corrosion by laboratory air and by the mercury frequently encountered in transferring tritium samples. A cylindrical chamber with a volume of approximately 250 cc., based on a design by C. J. Borkowski⁽¹⁷⁾ of Oak Ridge National Laboratory, has proved satisfactory. Negative ions are collected on the electrode by applying to the shell a potential negative with respect to ground. Since small fluctuations in the applied potential cause erratic readings, a constant voltage, such as may be obtained from dry cells, is required. The small ion currents normally obtained may be measured by a variety of instruments. From the standpoint of convenience and sensitivity, electronic electrometers are more satisfactory than the Lauritsen electroscope or the Lindemann electrometer, since the output of the former may be continuously recorded, permitting the subtraction of alpha pulses. The use of a dynamic condenser electrometer,⁽¹⁸⁾ rather than a direct current amplifier, is preferred because of its greater stability. With this instrument currents between 10^{-13} and 10^{-17} amp are measured by the rate of charge of an internal condenser; larger currents are measured by the voltage drop across an external resistor. The precision and accuracy of the latter method are improved by using the electrometer as a null point instrument, opposing the voltage drop with that from an external potentiometer. The readings may be converted to relative ion currents, or to absolute currents if the value of the capacitance or the resistance has been determined. It will be shown

below that the net current (the observed current minus background) is proportional to the tritium content of the sample. The calculation of the tritium content from the relative ion current requires calibration with a sample containing a known amount of tritium. The tritium content can be calculated from the absolute value of the ion current if the ion-pair yield in the gas and the efficiency of the chamber are known.

Ionization chamber - The ionization chamber designed by Borkowski⁽¹⁷⁾ was modified to permit direct attachment to the electrometer and to improve the contact of the electrode with the input terminal. The assembly of the chamber and machine drawings for the components are shown in Figure 1. The Applied Physics Corporation, Pasadena, California, can supply a chamber, Model 3095, which has the same dimensions and efficiency, but differs in the materials and details of construction.

Voltage source - For many purposes a 300 volt dry cell is satisfactory. For greater flexibility, the desired potential may be applied to the chamber conveniently from a series of dry cells connected as shown in Figure 2. The circuit includes five 90-volt dry cells, protected from accidental discharge by a megohm resistor, a condenser to minimize fluctuations in voltage, a switch to permit the selection of the desired voltage, a voltmeter to check the circuit, and a switch by means of which the voltage can be applied to the chamber with or without the voltmeter in the circuit.

Electrometer - A vibrating reed electrometer, Applied Physics Corporation, Model 30, is used for the ion current measurements. This instrument has a steady drift rate of less than 5×10^{-17} amp and a noise level of less than 5×10^{-16} coulomb. An insulating and shielding adapter, Model 3096, for mounting the resistors across which the voltage drop is measured can be supplied with the electrometer.

Resistors - Glass-covered, vacuum-sealed resistors, supplied by Victoreen Instrument Co., Cleveland, Ohio, are used. The value of the resistor required is determined by the magnitude of the current to be measured; a set of four having resistances of 10^8 to 10^{11} ohms permits the determination of quantities of tritium up to 10 millicuries.

Recorder - Satisfactory recording is achieved with a Brown "Elektronik" strip chart potentiometer, Model 153 X12, with a pen speed of $4\frac{1}{2}$ seconds for full scale travel, a chart speed of 20 inches per hour, and a full scale range of 25 mv., graduated from 0 to 100.

Potentiometer - A Rubicon potentiometer having ranges of 0 to 160 mv. and 0 to 1600 mv. is convenient.

Procedure - A simplified circuit diagram showing how the various components are connected is presented in Figure 3. For a determination of tritium, the chamber is evacuated to a pressure of 10^{-3} mm. or less, and a

6

ASSEMBLY

CHAMBER END
MATERIAL - STAINLESS STEEL - 1 REQ'D.

CHAMBER BODY
MATERIAL - STAINLESS STEEL - 1 REQ'D.

CHAMBER END
MATERIAL - STAINLESS STEEL - 1 REQ'D.

INSULATOR
MATERIAL - LUCITE - 1 REQ'D.

GUARD RING
MATERIAL - STAINLESS STEEL - 1 REQ'D.

FIGURE 1.
IONIZATION CHAMBER.

9

ELECTRODE CAP

MATERIAL - STAINLESS STEEL - 1 REQ'D.

8

COLLECTING ELECTRODE

MATERIAL - STAINLESS STEEL - 1 REQ'D.

11

INSERT

MATERIAL - POLYSTYRENE - 1 REQ'D

7

ADAPTER MOUNTING

MATERIAL - STAINLESS STEEL - 1 REQ'D.

16

GASKET

MATERIAL - NEOPRENE - 1 REQ'D.

12

GASKET

MATERIAL - NEOPRENE - 1 REQ'D.

10

GASKET

MATERIAL - NEOPRENE - 1 REQ'D.

FIGURE 1. (continued)

BILL OF MATERIAL

Part	Required	Description	Material
1	1	Stopcock-10/30-straight bore	Pyrex
2	1	Chamber end	Stainless steel
3	1	Chamber body	Stainless steel
4	1	Chamber end	Stainless steel
5	1	Insulator	Lucite
6	1	Guard ring	Stainless steel
7	1	Adapter mounting	Stainless steel
8	1	Collecting electrode	Stainless steel
9	1	Electrode cap	Stainless steel
10	1	Gasket	Neoprene
11	1	Insert	Polystyrene
12	1	Gasket	Neoprene
13	1	No. 4-40NC Bristo Setscrew 1/4" L	Steel
14	1	1/8" Flat washer	Stainless steel
15	1	No. 5-40NC hex nut	Stainless steel
16	1	Gasket	Neoprene

Fig. 1 (continued)

FIGURE 2.
VOLTAGE SOURCE.

FIGURE 3.
CIRCUIT DIAGRAM.

sample of the gas to be assayed is introduced. The entire sample can be transferred to the chamber with a Toepler pump, or a known fraction of the gas can be introduced by expansion. Small amounts of a condensible gas can be introduced quantitatively by expanding from a small U-tube if diluent gas is added through the same tube. In routine measurements, the chamber is filled to a pressure slightly greater than atmospheric, adding diluent gas if necessary. A convenient system for this purpose is shown in Figure 4. The space between the stopcocks is evacuated and the filling gas, flowing at a moderate rate through the mercury bubbler, is admitted. The stopcock of the chamber is then opened until the flow of gas through the bubbler is resumed.

The chamber is mounted on the electrometer and the collecting voltage is applied, including the voltmeter in the circuit until it has been ascertained that there is no short-circuit. Currents less than 10^{-13} amp are measured by the rate of charge of the internal condenser, which has a capacitance of about 12×10^{-12} farad. The shorting switch of the electrometer is opened, and a range is selected such that the charge on the condenser, which is continuously recorded, increases at a suitable rate. The charge produced by the sample should increase uniformly; abrupt increases occasionally caused by alpha particles must be subtracted. The rate of charge may change initially while charges produced by insulator strain and by opening the shorting switch are dissipated. The shorting switch is left open until only statistical fluctuations in the rate of charge are observed or until full scale deflection is recorded. The measurement is repeated until the desired precision is obtained. The rate of charge, expressed in millivolts per minute, is proportional to the ion current.

To measure currents greater than 10^{-13} amp, an adapter is mounted on the electrometer head, and the resistor which will give the greatest voltage drop measurable on the electrometer is connected between the input terminal, H, and the feedback circuit, G. The shorting switch is opened, and the deflection is recorded. After extraneous charges have disappeared, the deflection becomes constant except for statistical fluctuations. Sufficient time is allowed to permit the determination of the average deflection with suitable precision. The voltage drop can be determined with greater accuracy if the deflection is made small by applying from the external potentiometer an opposing voltage, the value of which is added to the observed deflection. For a given resistor, the voltage drop is proportional to the ion current.

Factors for converting observed readings to relative ion currents are established by intercomparison, and are checked periodically. An intercomparison of two resistances differing by a factor of ten is best obtained from the ratio of the voltage drops produced across them by a single sample. The rate of charge produced by a suitable sample is compared with the voltage drop across the 10^{11} ohm resistor.

FIGURE 4.
FILLING SYSTEM.

RESULTS

As has previously been discussed, the ion current collected from a given quantity of tritium in an ionization chamber depends upon the nature of the filling gas, the filling pressure, and the collecting voltage. The effect of these factors has been investigated to provide information on the significance and reproducibility of ion current measurements with the described chamber under various conditions. The dependence on collecting voltage and filling pressure was studied in hydrogen, methane, and propane since convenient methods are available for converting the hydrogen in water or organic compounds to hydrogen gas^(3, 7, 8, 12, 13) or a hydrocarbon^(9, 10, 11, 19). The chamber has been calibrated with a standard tritium sample to permit the conversion of ion current measurements to absolute disintegration rates.

The ion currents collected in several gases from small amounts of a hydrogen-tritium mixture in chambers filled to atmospheric pressure were measured at saturation voltage. The ionization, relative to that in methane, is given for each gas in Table II, together with the number of ions collected per tritium disintegration. Comparison with the values in Table I indicates that except for the gases of lowest stopping power, hydrogen and helium, the efficiency of the chamber is very high.

Table II

IONIZATION COLLECTED FROM TRITIUM RADIATION IN SEVERAL GASES

Gas	Relative Ionization	Ion Pairs per Disintegration*
Hydrogen	0.685	132
Nitrogen	0.82	158
Helium	0.84	162
Carbon Dioxide	0.84	162
Methane	1.00	193
Argon	1.06	205
Propane	1.13	218

*Based on a calibration described in the text.

The variation of ion current with collecting voltage is shown in Table III for various quantities of tritium in chambers filled to atmospheric pressure with hydrogen, methane, or propane. It is seen that the loss of ions by recombination increases with the tritium content, and, at a given concentration, increases in the order: hydrogen, methane, propane. Routine measurements are made using a potential of 180 volts for hydrogen, 360 volts for methane, and 450 volts for propane. The current measured under these conditions is essentially the saturation value for quantities of tritium up to 0.1 millicurie in propane and at least one millicurie in methane and five millicuries in hydrogen.

Table III

EFFECT OF COLLECTING VOLTAGE ON ION CURRENT

Gas	Tritium Content Millicuries	Relative Ion Current*			
		V = 90	180	270	360 volts
Hydrogen	0.78	99.1	99.7	99.8	99.9
	5.30	96.4	99.4	99.8	99.9
Methane	0.01	99.2	99.8	99.9	100.0
	1.00	92.6	98.6	99.6	99.9
Propane	0.01	97.0	99.2	99.6	99.9
	0.11	85.1	95.7	98.4	99.5
	0.93	54.7	82.1	92.7	97.5

*Current collected at 450 volts defined as 100.

The current at various pressures, relative to that at atmospheric pressure, is shown in Table IV. For convenience, the chamber is filled to atmospheric pressure for routine measurement. Only in the case of hydrogen are larger currents obtained at higher pressures, but even with this gas the variation of current with pressure is small at one atmosphere.

The variation of ion current with composition has been studied for some mixtures of gases which might be introduced into the chamber deliberately, to analyze a reaction product or to permit the re-isolation of the active gas from the diluent, or accidentally, as by leakage of air. The relative currents in mixtures of hydrogen with methane and propane are shown in Figures 5 and 6, respectively. The effect of air in hydrogen and in methane

15

FIGURE 5.

ION CURRENTS IN HYDROGEN-METHANE-AIR MIXTURES.

FIGURE 6.
ION CURRENT IN HYDROGEN-PROPANE MIXTURES.

is also shown in Figure 5. Ion current measurements in both methane and propane are relatively unaffected by the presence of other gases; readings in hydrogen are considerably more sensitive to impurities.

Table IV

VARIATION IN ION CURRENT WITH FILLING PRESSURE

Gas	Relative Ion Current*			
	P = 100	400	600	700 mm. Hg.
Hydrogen	55.4	92.0	97.6	99.3
Methane	85.0	97.3	99.2	99.8
Propane	92.5	99.3	99.8	100.0

*Current with filling gas at atmospheric pressure is defined as 100.

The data presented above show that reliable ion current measurements can be obtained in all the gases studied, even under conditions which differ considerably from those routinely employed. There are, however, some advantages in the use of methane as a filling gas wherever practicable. In this gas, loss of ions by recombination is much less serious than in propane and the effect of pressure and of impurities is less than that in hydrogen.

The precision of current measurements in the range of 10^{-15} to 10^{-9} amp was determined in an experiment also designed to test the proportionality of ion current to tritium content. Samples of hydrogen were generated from each of a series of dilutions of tritiated water, as well as from distilled water blanks, by reaction with zinc in a sealed tube. The samples were expanded into the chamber, diluted to atmospheric pressure with methane, and the net ion currents were determined. The results, summarized in Table V, show that, except at the lowest tritium concentration, the standard error of a single determination is one per cent or less. Over the entire range of concentrations, the factor relating ion current to disintegration rate varies by less than one per cent, with no indication of a trend.

The value of this conversion factor was determined⁽²⁰⁾ for methane using a sample with a known disintegration rate. Hydrogen gas of known tritium content was obtained by dilution of a mass-spectrometrically analyzed sample of essentially pure tritium gas. The ion currents from small samples of this gas in a chamber filled with methane were measured using resistors calibrated by the method⁽²¹⁾ of Lynch and Wesenberg. The mean values obtained in two independent experiments, based on a half-life,^(16, 22) of 12.4 years, are 3.04×10^{-17} and 3.14×10^{-17} coulomb per disintegration. From the average of these values for methane and from the relative ion currents given in Table II, the factors in Table VI have been computed.

Table V

PRECISION AND ACCURACY OF ION CURRENT MEASUREMENTS

Dilution	Relative Conc. of T	No. of Analyses	Specific* Current $\frac{\text{Amps.} \times 10^{16}}{\text{mg. H}_2\text{O}}$	Error ⁺ %	Relative Current per Disintegration	Deviation from mean %
A	1×10^6	4	1.734×10^6	0.35	1	-0.9
B	0.980×10^4	3	1.720×10^4	0.35	1.012	+0.3
C	0.949×10^2	3	1.663×10^2	1.03	1.010	+0.1
D	9.50	3	16.63	0.22	1.010	+0.1
E	1.049	2	1.824	2.61	1.003	-0.6
Weighted Mean 1.009						

* Samples of approximately 6 mg. of H_2O were analyzed; the background current was about 6×10^{-16} amp.

⁺ Standard error of a single determination.

Table VI

RELATION OF ION CURRENT TO DISINTEGRATION RATE

Gas	Coulombs/disintegration $\times 10^{17}$	Curies/ampere $\times 10^{-6}$
Hydrogen	2.12	1.275
Methane	3.09	0.874
Propane	3.49	0.775

The method of tritium assay which has been described is useful over at least a 10^8 fold range of tritium activities. The lower limit is determined by the magnitude and reproducibility of the background current, which, in our experience, is easily maintained at less than 5×10^{-16} amp. (When quantities of tritium up to one millicurie have been introduced to the chamber in the form of hydrogen, methane, or propane, backgrounds of this magnitude are obtained simply by evacuation of the chamber and refilling with non-active gas; the introduction of tritium in larger quantities or in a less volatile form may make it necessary to replace the insulator and gaskets and to wash and bake the metal parts.) The reproducibility of the background is a function of the frequency of the events that produce the current. The drift rate of the electrometer, variations in which are not readily treated statistically, is less than 5×10^{-17} amp. The remainder of the background may be regarded as

ionization produced by radiation from the atmosphere or from the chamber. The portion produced by penetrating radiation amounts to about 2×10^{-16} amp, of which about one-third can be attributed⁽²³⁾ to cosmic rays. If it is assumed* that each ionizing event within the chamber produces 300 ions it can be calculated⁽²⁴⁾ that with a background of 5×10^{-16} amp and a measuring time of one hour each for sample and background an accuracy of one per cent can be attained in the measurement of 13 disintegrations per second or 3.5×10^{-10} curie of tritium in a chamber filled with methane. This corresponds to a specific activity of 3.5×10^{-11} curie per millimole if the entire contents of the chamber consists of the active gas.

The upper limit of tritium measurement is determined by the maximum potential that can be applied to the chamber without leakage of current or multiplication of ionization. The data in Table III indicate that in hydrogen or methane saturation currents are obtained at moderate voltages for quantities of tritium up to ten millicuries.

*In methane about 200 ions are produced by a tritium disintegration and about 450 ions by an average cosmic event.

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